Inorganic Chemistry

Steric and Electronic Influence of Aryl Isocyanides on the Properties of Iridium(III) Cyclometalates

Ayan Maity,[†] Linh Q. Le,[†] Zhuan Zhu,[‡] Jiming Bao,[‡] and Thomas S. Teets^{*,†}

[†]Department of Chemistry and [‡]Department of Electrical and Computer Engineering, University of Houston, 112 Fleming Building, Houston, Texas 77204, United States

Supporting Information

ABSTRACT: Cyclometalated iridium complexes with efficient phosphorescence and good electrochemical stability are important candidates for optoelectronic devices. Isocyanide ligands are strong-field ligands: when attached to transition metals, they impart larger HOMO–LUMO energy gaps, engender higher oxidative stability at the metal center, and support rugged organometallic complexes. Aryl isocyanides offer more versatile steric and electronic control by selective substitution at the aryl ring periphery. Despite a few reports of alkyl isocyanide of cyclometalated iridium(III), detailed studies on analogous aryl isocyanide complexes are scant. We report the synthesis, photophysical properties, and electrochemical proper-



ties of 11 new luminescent cationic biscyclometalated bis(aryl isocyanide)iridium(III) complexes. Three different aryl isocyanides—2,6-dimethylphenyl isocyanide (CNAr^{dmp}), 2,6-diisopropylphenyl isocyanide (CNAr^{dipp}), and 2-naphthyl isocyanide (CNAr^{nap})—were combined with four cyclometalating ligands with differential π – π * energies—2-phenylpyridine (ppy), 2,4-difluorophenylpyridine (F₂ppy), 2-benzothienylpyridine (btp), and 2-phenylbenzothiazole (bt). Five of them were crystallographically characterized. All new complexes show wide redox windows, with reduction potentials falling in a narrow range of -2.02 to -2.37 V and oxidation potentials spanning a wider range of 0.97–1.48 V. Efficient structured emission spans from the blue region for [(F₂ppy)₂Ir(CNAr)₂]PF₆ to the orange region for [(btp)₂Ir(CNAr)₂]PF₆, demonstrating that isocyanide ligands can support redox-stable luminescent complexes with a range of emission colors. Emission quantum yields were generally high, reaching a maximum of 0.37 for two complexes, whereas btp-ligated complexes had quantum yields below 1%. The structure of the CNAr ligand has a minimal effect on the photophysical properties, which are shown to arise from ligand-centered excited states with very little contribution from metal-to-ligand charge transfer in most cases.

INTRODUCTION

Cyclometalated iridium(III) complexes continue to draw attention because of their superior optoelectronic properties such as long excited-state lifetimes (typically on the order of microseconds) and high phosphorescence quantum yields [e.g., *fac*-Ir(ppy)₃ (ppy = 2-phenylpyridine); $\Phi_{phos} = 0.97$].^{1,2} These heavy-metal complexes have been widely used in organic light-emitting diodes,³⁻⁶ light-emitting electrochemical cells,⁷⁻¹² oxygen sensing,^{13,14} catalytic applications,^{15,16} and biological imaging.^{17–19} Iridium(III) cyclometalates' standout photophysical properties are attributed to fast intersystem crossing brought on by the large spin—orbit coupling constant of the metal center, leading to efficient triplet-state population.^{20,21} The emissive triplet state is comprised of metal-to-ligand charge-transfer (³MLCT) and ligand-centered (³LC) states.²²

Heteroleptic cyclometalated iridium complexes such as $[Ir(C^N)_2(LL')]^{0/+}$, where C^N = cyclometalating ligand and LL' = ancillary ligand, are of particular interest because the structures of the C^N and LL' ligands control the mixing of ³LC and ³MLCT in their lowest-energy excited states.^{23,24} Recently, our group has disclosed a strategy to increase the metal-centered highest occupied molecular orbital (HOMO) energy of iridium(III) cyclometalates by systematically substituting oxygen atoms of the parent of the acetylacetonate ancillary ligand with nitrogen-containing β -ketoiminate (acNac) and β -diketiminate (NacNac) derivatives.²⁵ Hence, careful substitution of C^N and LL' ligands modulates the emission energy and tunes the excited-state character. Another consequence of using weak-field acNac and NacNac ligands is that the complexes become very potent excited-state reductants, which may be advantageous for photoinduced electron transfer but is not desirable for the design of robust lightemitting devices. Therefore, it is of considerable interest to design complexes that efficiently luminesce throughout the entire visible region but also show good excited-state redox stability.

Isocyanides (CNR, where R = alkyl or aryl) have been long heralded in coordination chemistry for their strong σ -donor and weak π -acceptor properties.^{26,27} Aryl isocyanides differ

Received: November 19, 2015 Published: February 24, 2016

significantly from their isolobal counterpart carbon monoxide (CO) because their steric and electronic properties can be varied judiciously by substitution at the aryl group. The Figueroa group has performed a comparative study on $k_{\rm CO}$ (Cotton-Kraihanzel CO force constant) and ¹³C chemical shift (δ_{13}) of a series of Cr(CNR)(CO)₅ complexes to demonstrate the effect of substitution on the σ -donor/ π -acceptor ratio.²⁸ Isocyanide ligands have also been used to support a number of complexes with interesting photophysical properties. Recently, Mann and co-workers have reported an unusually high emission lifetime from a phenanthroline-based copper(I) isocyanide.²⁹ The photophysical properties of isocyanide complexes of platinum(II),^{30,31} copper(I),³² rhenium(I),^{33–35} tungsten(0),³⁶ and ruthenium(II)^{37–39} have been well documented. With the goal of preparing complexes with efficient blue phosphorescence, alkyl isocyanide complexes of iridium(III) cyclometalates have been reported recently.⁴⁰⁻ Being strong-field ligands, alkyl isocyanides impart a greater HOMO-lowest unoccupied molecular orbital (LUMO) separation in biscyclometalated iridium complexes, and the emission shifts to the blue-green region. Systematic ligand modification to perturb the excited states of iridium cyclometalates is not forthcoming with alkyl isocyanides. Aryl isocyanides are superior in this respect because they offer a versatile platform to modulate the electronic properties of the complex by changing the functionality of the aryl group. Despite the feasibility of fine-tuning of the electronic properties using aryl isocyanides, reports of aryl isocyanide complexes of cyclometalated iridium(III) are sparse.47,48

Herein, we describe a comparative synthetic, structural, spectroscopic, and electrochemical study of phosphorescent iridium(III) aryl isocyanide complexes with 2,6-dimethylphenyl isocyanide (CNAr^{dipp}), 2,6-diisopropylphenyl isocyanide (CNAr^{dipp}), and 2-naphthyl isocyanide (CNAr^{nap}) as ancillary ligands and 2-phenylpyridine (ppy), 2,4-difluorophenylpyridine (F_2 ppy), 2-benzothienylpyridine (btp), and 2-phenylbenzothiazole (bt) as cyclometalating ligands (the superscript in the isocyanide ligand indicates the identity of its aryl group; Figure 1). The syntheses of 11 of these new complexes are described. Five of them have been crystallographically authenticated. We



Figure 1. Structures and abbreviations of cyclometalating (C^N) and isocyanide (L) ligands.

demonstrate that substituting aryl isocyanides (CNAr) in place of *tert*-butyl isocyanide (CN-*t*-Bu) can perturb both the electrochemical and photophysical properties. F_2ppy as the cyclometalating ligand creates the largest HOMO–LUMO separation and emits strong blue phosphorescence. Switching the substituted phenyl isocyanide (CNAr^{dmp} or CNAr^{dipp}) to naphthyl isocyanide (CNAr^{nap}) has a profound effect on the excited-state properties when paired with F_2ppy . Installing bt or btp as the cyclometalating ligand reduces the HOMO–LUMO energy gap and gives rise to emission in the green and yelloworange regions, respectively. We demonstrate here a suitable strategy for fine-tuning the excited-state properties of phosphorescent iridium(III) organometallics supported by robust and tunable aryl isocyanide ligands.

RESULTS AND DISCUSSION

Synthesis. Figure 1 depicts the cyclometalating (C^N) and aryl isocyanide (CNAr) ligands that have been used in this study and their abbreviations. $CNAr^{dipp}$ has been synthesized from the corresponding aniline following the literature procedure,³⁶ whereas $CNAr^{dmp}$ and $CNAr^{nap}$ are commercially available. Scheme 1 outlines the method adopted for the





synthesis of biscyclometalated iridium(III) isocyanides. In a typical reaction, 1 equiv of a chloro-bridged dimer, $[Ir_2(C^N)_4(\mu-Cl)_2]$, is treated with 4 equiv of CNAr in the presence of 2 equiv of silver hexafluorophosphate (AgPF₆). Filtration of the reaction mixture through Celite and precipitation by pentane and diethyl ether followed by washing with pentane afforded an analytically pure product. Following this general procedure, 11 new cationic complexes of biscyclometalated bis(aryl isocyanide)iridium(III), 1a-4c, were obtained in good-to-excellent yield. However, we were unable to obtain $[Ir(ppy)_2(CNAr^{nap})_2]PF_6$ following this general procedure or other related methods.

Synthesized compounds have been characterized by ¹H, ¹³C{¹H}, and ¹⁹F NMR spectroscopy. ¹H NMR spectra of **1a**– **4c** show a single set of resonances for the C^N and CNAr ligands indicating C_2 symmetry. A single set of Ar–F ¹⁹F resonances obtained in the spectra of **2a**–**2c** further validates this contention. Integration of the ¹H NMR signals indicates a 1:1 ratio between the C^N and CNAr ligands. Integration of the ¹⁹F signals arising from Ar–F and PF₆ in complexes **2a**–**2c** confirms the monocationic nature of the biscyclometalated iridium(III) isocyanides. The bulk purity of the compounds has been verified by elemental analysis. The compounds are airand moisture-stable and soluble in common polar organic solvents.



Figure 2. X-ray crystal structures of complexes. Ellipsoids are drawn at the 50% probability level, with hydrogen atoms, counteranions, and solvate molecules omitted.

	bond length (Å)							
	isocyanide		C^N		angle (deg)			
complex	Ir-C	C–N	Ir-C	Ir-N	bond angle $\angle Ir - C_{CNAr} - N_{CNAr}$	dihedral angle ∠Ar _{CNAr} –Ar _{CNAr}		
1a	2.013(3)	1.155(4)	2.048(3)	2.061(3)	173.8(3)	79.90		
	2.023(3)	1.151(4)	2.052(3)	2.061(3)	169.8(3)			
2a	2.005(3)	1.152(4)	2.054(3)	2.059(2)	174.8(3)	3.13		
	2.027(3)	1.166(4)	2.055(3)	2.066(2)	177.5(3)			
3b	1.999(6)	1.145(8)	2.070(5)	2.078(4)	175.2(5)	29.52		
	2.002(5)	1.151(7)	2.071(5)	2.065(4)	174.6(5)			
3c	1.982(7)	1.143(8)	2.073(6)	2.070(5)	168.7(6)	27.02		
	2.011(7)	1.155(8)	2.074(6)	2.077(5)	175.1(6)			
4a	2.013(4)	1.159(4)	2.064(3)	2.072(3)	172.5(3)	81.60		
	2.023(3)	1.157(5)	2.079(4)	2.086(3)	168.3(3)			

 Table 1. Crystallographic Parameters

Crystal Structures of Iridium(III) Aryl Isocyanide Complexes. The molecular structures of 1a, 2a, 3b, 3c, and 4a were determined by single-crystal X-ray diffraction and are depicted in Figure 2. Notable crystallographic parameters are shown in Table 1, and detailed crystallographic data are deposited in the Supporting Information. The geometries of the complexes are unexceptional. In all of the complexes, the iridium(III) metal center resides in the center of an $[Ir(C^N)_2(CNAr)_2]^+$ distorted octahedron. The nitrogen atoms of the C^N ligands are trans-disposed to each other. The $Ir-C_{CNAr}$ bonds are shorter (on average) and show larger variation than the Ir-C distances of the C^N ligands (Table 1). The Ir– C_{CNAr} bond distances measured here (1.982–2.027 Å) are similar to the reported Ir–C bond lengths of *tert*-butyl isocyanides $(2.004-2.018 \text{ Å})^{41,43}$ and mixed aryl isocyanide/ isocyanoborate complexes $(2.00-2.04 \text{ Å})^{48}$ of iridium(III). The Ir- C_{CNAr} - N_{CNAr} bond angles are slightly distorted from linearity, ranging from 168.3 to 177.5°. In a similar study, Ko and co-workers⁴⁸ have reported a slightly bent Ir- C_{CN} - B_{BAr3} bond angle $(166.3-177.5^{\circ})$ for the iridium isocyanoborate complexes. The aryl groups in the isocyanide ligands are slanted relative to each other, and the dihedral angle depends on the identity of the C^N ligands.

Electrochemistry. The electrochemical properties of 1a– 4c were studied by cyclic voltammetry in anaerobic acetonitrile solutions. Redox processes were found to be irreversible for all of the complexes and were referenced against Fc^+/Fc . Table 2 summarizes the electrochemical data. The identity of both the C^N and isocyanide ligands can impact the electrochemical features. All complexes show reduction waves at -2.02 to -2.37 V. Complexes 1a/1b, 3a, and 4c show oxidation waves at 0.97–1.48 V. The oxidation potentials of 2a–2c are outside of the operating electrochemical window for acetonitrile. The oxidation potential of 1a shows up at +1.27 V, while substituting the phenyl ring with two fluorine atoms (F₂ppy, 2a) makes it harder to oxidize and the oxidation potential shifts more positive than 1.6 V in the case of 2a. This trend continues for 2b and 2c. Three isocyanides of btp, 3a–3c, show the

Table 2. Redox Parameters^a

complex	C^N ^b	CNAr ^c	E^{ox} , V	$E^{\rm red}$, V	$\Delta E,^{e} V$
1a	рру	CNAr ^{dmp}	+1.27	-2.37	3.64
1b	рру	CNAr ^{dipp}	+1.28	-2.36	3.64
2a	F ₂ ppy	CNAr ^{dmp}	>1.6 ^d	-2.22	>3.82
2b	F ₂ ppy	CNAr ^{dipp}	>1.6 ^d	-2.19	>3.79
2c	F_2ppy	CNAr ^{nap}	>1.6 ^d	-2.21	>3.81
3a	btp	CNAr ^{dmp}	+1.07	-2.16	3.23
3b	btp	CNAr ^{dipp}	+1.08	-2.15	3.23
3c	btp	CNAr ^{nap}	+0.97	-2.09	3.06
4a	bt	CNAr ^{dmp}	+1.48	-2.02	3.50
4b	bt	CNAr ^{dipp}	+1.43	-2.02	3.45
4c	bt	CNAr ^{nap}	+1.41	-2.02	3.43

^{*a*}The solvent is acetonitrile. All redox processes were irreversible. Oxidation or reduction peak potentials are reported relative to Fc^+/Fc . Glassy-carbon working electrode, in the presence of 0.1 M (NBu₄)PF₆, at a scan rate of 100 mV/s. ^{*b*}Cyclometalating ligand. ^{*c*}Isocyanide ligand. ^{*d*}The oxidation wave was outside the electrochemical window of acetonitrile (>1.6 V). ^{*e*}\Delta E = E^{ox} – E^{red}.

smallest E^{ox} among all 11 compounds. The electron-releasing nature of the benzothiophene ring and its contribution to the metal aryl based HOMO energy level accounts for the btp compounds' low oxidation potentials. However, replacing $\text{CNAr}^{\text{dmp/dipp}}$ with CNAr^{nap} facilitates the oxidation by ca. 100 mV in the case of btp. The change of CNAr^{dmp} with $\text{CNAr}^{\text{dipp}}$ has almost no effect on the reduction potentials ($\Delta E = 0-30$ mV) for all four C^N ligands. However, substituting CNAr^{dmp} with CNAr^{nap} in the case of btp makes it easier to reduce by 70 mV. The structure of CNAr has no effect on the reduction potentials of the bt analogues, **4a**–**4c**, all of which are reduced at –2.02 V.

The effect of aryl isocyanides on the electrochemical properties can be assessed by a comparison to literature compounds that feature *tert*-butyl isocyanide. We note that the literature-reported E^{ox} and E^{red} values for $[\text{Ir}(\text{ppy})_2(t-\text{Bu-NC})_2]^+$ are +1.23 and -2.38, respectively.⁴² Replacing *t*-Bu-NC with stronger π -acceptor CNAr^{dmp}, as in the case of 1a, has made oxidation harder by only 40 mV and reduction easier by 10 mV. In contrast, switching *t*-BuNC with CNAr^{dmp} induced a marked 260 mV anodic shift in the reduction potentials of previously reported 2-phenylpyrazole-supported cyclometa-lates.⁴⁷ Thus, the sensitivity of the electrochemical features to the nature of the isocyanide (alkyl vs aryl) depends on the identity of the cyclometalating ligand.

Overall, the redox potentials of complexes 1a-4c presented in Table 2 indicate that oxidation is governed by the iridium aryl based HOMO, while the reduction is centered on the pyridyl-based (1-3) or thiazole-based (4) π^* orbital. All of these complexes are difficult to oxidize or reduce because they have a large redox gap ($\Delta E = E^{ox} - E^{red}$) that varies from 3.06 to 3.82 V. Because F_2 ppy is more electron-withdrawing than ppy, the HOMO of 2a-2c is stabilized, and we observe a higher oxidation potential that is out of the operating electrochemical window of acetonitrile. Replacing the phenyl fragment of ppy with the stronger donating benzothiophene (btp) increases the HOMO energy relative to F₂ppy and thereby makes it easier to oxidize. The isocyanide ligands described herein have a minimal effect on the HOMO-LUMO gap because the ΔE value is largely determined by the identity of the C^N ligand for a given family of complexes.

Electronic Absorption Spectroscopy. UV-vis absorption spectra of the complexes were collected in a dichloromethane (DCM) solution at ambient temperature. Complexes of CNAr^{dmp} and CNAr^{dipp} are nearly colorless (1a, 1b, 2a, and 2b) or light yellow (3a, 3b, 4a, and 4b), while those with CNAr^{nap} are darker colored. Figure 3 collects the overlaid absorption spectra of the complexes. Individual absorption spectra with extinction coefficients are deposited in the Supporting Information.



Figure 3. Overlaid absorption spectra of **1a**–**4c** in CH₂Cl₂. Individual absorption spectra are shown in the Supporting Information.

Their electronic absorption spectra show intense high-energy bands below 300 nm with extinction coefficients $\varepsilon = (17-60)$ × 10³ M⁻¹ cm⁻¹, which can be assigned to spin-allowed $\pi - \pi^*$ transitions centered at the C^N and aryl isocyanide ligands. At lower energy, several overlapping bands extend from 310 to 360 nm with $\varepsilon = (7-19) \times 10^3$ M⁻¹ cm⁻¹; these are assigned to (Ir–phenyl)-to-pyridyl charge-transfer (CT) transitions (Figure 3 and Table 3).⁴⁹

For a given cyclometalating ligand, the absorption spectra of CNAr^{dmp} (**a**, shown in black) and CNAr^{dipp} (**b**, shown in red) are nearly identical (Figure 3). For a particular isocyanide ligand, the onset of absorption depends on the identity of the cyclometalating ligand, and we found that it varies in the order btp (428 nm) > bt (400 nm) > ppy (377 nm) > F₂ppy (360 nm) for CNAr^{dmp} and CNAr^{dipp}. We note that substitution of the phenyl ring in the C^N ligand with electron-withdrawing fluorine atoms blue shifts the absorption by about 1250 cm⁻¹ (17 nm). Similarly, replacing ppy with btp, which has lower energy $\pi - \pi^*$, red shifts the absorption spectrum by over 3100

Table 3. Photophysical Properties

		emissio	$n^{\nu} \lambda_{max}/nm$				
complex	absorbance ^{<i>a</i>} λ , nm ($\varepsilon \times 10^3/M^{-1} \text{ cm}^{-1}$)	DCM at 293 K	DCM/toluene at 77 K	quantum yield $^{a,b}_{(\Phi_{ m em})}$	$\tau/\mu s^c$	$k_{\rm r}^{d} \underset{\rm s}{\times 10^{3/}}$	$k_{\rm nr} \frac{d}{s^{-1}} \times 10^4/$
1a	258 (60), 310 (sh, 16), 343 (9)	454, 486, 512	449, 481, 509, 549 (sh)	0.24	30	8.0	2.5
1b	260 (51), 311 (sh, 14), 344 (7)	454, 486, 513	448, 480, 506, 546 (sh)	0.37	25	15	2.6
2a	306 (20), 323 (sh, 13),	417, 447	412, 444, 467, 479	0.37	41	9.1	1.5
2b	306 (17), 323 (sh, 11),	417, 447	413, 444, 469, 478	0.28	41	6.8	1.7
2c	300 (52), 332 (sh, 16), 404 (sh, 1.6)	456, 489, 527, 569	485, 497, 524, 567	0.016	17, 0.4		
3a	317 (24), 346 (19), 383 (15), 397 (15)	576, 623	553, 602, 662	0.009	7, 1		
3b	317 (28), 347 (22), 383 (18), 398 (18)	575, 623	554, 603, 660	0.004	7, 1		
3c	287 (43), 316 (sh, 29), 346 (19), 380 (13)	581, 628	555, 603, 661	0.006	3, 0.4		
4a	315 (40), 361 (20), 376 (sh, 16)	500, 536, 576	497, 535, 580, 631	0.33	36	9.3	1.9
4b	315 (30), 361 (16), 378 (sh, 12)	504, (sh), 538, 576	497, 535, 580, 627	0.33	37	8.9	1.8
4c	301 (53), 359 (sh, 16), 378 (sh, 13)	515 (sh), 545, 581	495, 534, 578, 630	0.18	15	12.1	5.5

^{*a*}Recorded in DCM. ^{*b*} λ_{exc} = 310 nm. ^{*c*}The photoluminescence lifetimes (τ) were biexponential functions for 2c and 3a–3c. ^{*d*}The rates of radiative (k_r) and nonradiative (k_{nr}) decay were calculated using the equations $k_r = \Phi/\tau$ and $k_{nr} = (1 - \Phi)/\tau$.

 cm^{-1} (51 nm). All of these data indicate that the lowest-energy electronic absorptions of these complexes are dominated by (Ir–aryl)-to-pyridyl CT transitions.⁵⁰

Emission Spectroscopy. The emission spectra of the complexes were studied in a DCM solution at room temperature (298 K) and DCM/toluene glass (77 K). Figure 4 depicts the room temperature emission spectra of 1a-4c,



Figure 4. Normalized, overlaid emission spectra of 1a-4c in CH_2Cl_2 . Individual emission spectra are shown in the Supporting Information.

while the data are summarized in Table 3. All complexes emit at room temperature in a deoxygenated DCM solution. The vibronic structure is pronounced in each spectrum, suggesting a significant contribution from a LC state in the lowest-energy excited state.

The emission spectra of $[Ir(C^{N})_2(CNAr^{dmp})_2]^+$ and $[Ir(C^{N})_2(CNAr^{dipp})_2]^+$ are nearly identical for a given C^N ligand. Both **1a** and **1b** (C^N = ppy) exhibit strong blue phosphorescence with $\lambda_{max} = 486$ nm, with quantum yields $\Phi = 0.24$ and 0.37, respectively. The effect of switching the C^N ligand from ppy to F₂ppy depends on the identity of the isocyanide ligand. For example, a hypsochromic shift in the E_{0-0} transition of ca. 1950 cm⁻¹ (37 nm) is observed for CNAr^{dmp} (**2a**) and CNAr^{dipp} (**2b**) upon changing ppy to F₂ppy. Interestingly, in the case of CNAr^{nap} (**2c**), the E_{0-0} emission band shows a slight bathochromic shift of 97 cm⁻¹ (2 nm) with

respect to 1a and 1b. While the quantum yields of 2a ($\Phi = 0.37$) and 2b ($\Phi = 0.28$) are similar to those of the ppy variants, 1a ($\Phi = 0.24$) and 1b ($\Phi = 0.37$), there is a significant decrease in the quantum yield when CNAr^{dmp/dipp} is replaced with CNAr^{nap} ($\Phi = 0.016$ for 2c). All of these data suggest that for 2c the lowest-energy excited state is a 2-naphthyl isocyanide ³LC state, and the red-shifted and comparatively weak emission arises from that state. This is in agreement with the work of Gray and co-workers, where luminescence of a PPh₃Au^I– naphthyl complex originates from a naphthalene-based triplet state^{51,52} and is similar in the energy to emission observed in complex 2c.

Unlike ppy and F₂ppy, btp cyclometalated complexes are weakly emissive. The emission spectra of all three analogues of $[Ir(btp)_2(CNAr)_2]^+$ are almost identical with each other, emitting at λ_{max} = 623–628 nm, with quantum yields that vary in the range 0.004-0.009. The origin of this profound decrease in the emission intensity remains unclear, although the lifetime data (vide infra) suggest a larger k_{nr} value for the btp complexes, which suppresses the emission quantum yield. Isocyanide complexes with the bt cyclometalating ligand exhibit similar emission profiles, which reside in the green region of the spectrum. They feature a pronounced vibronic structure in each case but with a significant improvement in the quantum yield compared to isomeric btp complexes. The emission maxima of **4a** and **4b** reside at λ_{max} = 536–538, while the emission maxima of their 2-naphthyl analogue 4c exhibit a bathochromic shift of 308 cm⁻¹ (λ_{max} = 545 nm). The quantum yields of 4a and 4b are identical ($\Phi = 0.33$) and fall in the range of the complexes with CNAr^{dmp/dipp} ancillary ligands and ppy/F_2ppy C^N ligands $(\Phi = 0.24 - 0.37)$. Changing the CNAr group to CNAr^{nap} lowers the quantum yield to almost half (4c, Φ = 0.18). All of these emission measurements suggest that the complexes described here emit from a lowest-energy excited state that is predominantly LC. Except complex 2c, the identity of the aryl isocyanide in these complexes has a greater effect on the phosphorescence quantum yield than on the emission profile.

Complexes 1a, 1b, 2a, 2b, and 4a-4c display luminescence lifetimes (τ) from 15 to 41 μ s. This is in concurrence with the reported lifetimes (25-37 μ s) for *tert*-butyl isocyanide complexes of a variety of iridium cyclometalates.⁴² However, the photoluminescence decay of complexes 2c and 3a-3c is biexponential with short-lived ($\tau = 0.4-1 \ \mu$ s) and long-lived (τ

= $3-17 \ \mu s$) components. This suggests that more than one emission process is involved in these compounds. The observation of the biexponential decay behavior is not uncommon for cyclometalated iridium(III) complexes.^{18,53-57} The precise reason for the observation of multiple decay pathways is often unclear. In some cases, they are proposed to arise from dual-emission involving overlapped excited states,⁵⁶ while in other systems, they have been predicted to originate from disparate decay rates of the involved triplet sublevels within the same excited-state manifold.^{58–60} Our observation of a naphthyl-centered emission in 2c suggests the possibility that the biexponential lifetimes of naphthyl-containing 2c and 3c could arise from two different excited states, one C^N-centered and the other naphthyl-centered, although further experimentation would be needed to verify this proposal. The origin of the biexponential decay in the btp complexes 3a and 3b also remains unclear. These complexes were deemed pure by elemental analysis, but we cannot conclusively rule out a minor, highly luminescent impurity that interferes with the very weak luminescence of 3a and 3b and results in biexponential emission. The radiative and nonradiative rate constants were calculated from Φ and τ data.⁶¹ The k, values of the complexes vary in the range $(6.8-15) \times 10^3 \text{ s}^{-1}$ with the lowest values for the complexes with the highest emission energy (F_2 ppy). The $k_{\rm nr}$ values span a smaller range of $(1.5-5.5) \times 10^4$ s⁻¹, and the value decreases with increasing emission energy. The values of $26 \times 10^3 \text{ s}^{-1} (k_r)$ and $14 \times 10^4 \text{ s}^{-1} (k_{nr})$ were previously reported for the complex $[(F_2ppy)_2Ir(CN-t-Bu)_2]^{+41}$ When $cNAr^{dmp}$ is substituted to furnish analogue 2a, k_r and k_{nr} decrease to 9.1×10^3 and 1.5×10^4 s⁻¹, respectively. This suggests smaller MLCT character in the lowest-energy excited state for 2a, consistent with the expectation that CNAr^{dmp} is a stronger π acceptor than CN-*t*-Bu.^{41,62,63}

To gain additional insight into the nature of the excited states, rigidochromic shifts⁴¹ were measured by recording the emission spectra at 77 K in rigid glass. The results are shown in Figure 5, and the data are summarized in Table 3. All told, the 77 K emission spectra for a particular C^N ligand are rather insensitive to the identity of the CNAr ligand, except for 2c, where the low-temperature emission spectrum indicates an ca. 3600 cm^{-1} (70 nm) bathochromic shift compared to its



Figure 5. Low-temperature emission (77 K) spectra of complexes 1a–4c in DCM/toluene.

CNAr^{dmp/dipp} analogues, as is also observed at room temperature and is likely a result of a lower-energy naphthyl-centered emissive state. When the emission is recorded in frozen DCM/ toluene (77 K), all complexes show more pronounced vibronic structures. At 77 K, the 0–0 transition wavelength, λ_{0-0} , shows a small hypsochromic shift for all of the complexes relative to their 293 K spectra. The 77 K spectra of complexes 1a, 2c, 4a, and 4b show small hypsochromic shifts of $120-291 \text{ cm}^{-1}$ (3-7 nm) compared to those of their 293 K spectra, indicative of small polarity change between the ground and excited states and pointing to a LC transition. The rigidochromic behavior of the complexes with btp as the cyclometalating ligand is different from that of the others. Complexes 3a-3c show much larger hypsochromic shifts of 659-806 cm⁻¹ (21-26 nm) upon cooling to 77 K. This observation indicates an increased CT character in the lowest-energy excited state of these compounds and is consistent with the electrochemical data. The btp compounds have the smallest oxidation potentials (Table 2) by nearly 400 mV, indicating a HOMO energy that is destabilized relative to that of the other complexes. This gives rise to smaller $\Delta E (E_{ox} - E_{red})$ values for 3a - 3c and produces a lower-energy CT state, which mixes more efficiently with the btp-centered LC state. This difference in the excited-state character for 3a-3c may be the cause of their shorter lifetimes and smaller quantum yields, although ultimately additional studies on more structurally and electronically diverse cyclometalated iridium isocyanide complexes will help to reveal whether the difference in the emission efficiency is of electronic origin. A similar rigidochromic behavior is observed in the case of [Ir- $(bt)_2(CNAr^{nap})_2]PF_6$ (4c), where the observed hypsochromic shift is 20 nm upon cooling to 77 K. The origin of the effect in this example is not as clear because the electrochemical data for 4c are only marginally different from those of 4a/4b. It is possible that the rigidochromic shift in 4c is thermal in nature, arising from the differential population of bt- and naphthylcentered excited states as the temperature is altered.

CONCLUSION

We have reported the synthesis of 11 new iridium(III) complexes with three different aryl isocyanide ancillary ligands and four different cyclometalating ligands. The structures of five of them (1a, 2a, 3b, 3c, and 4a) have been crystallographically authenticated. The complexes are stable over a wide potential window, with reduction potentials that are similar to those of other Ir-C^N complexes and oxidation potentials that are anodically shifted by virtue of the strong-field isocyanide ligands. In all cases, this enhanced redox stability is coupled with the luminescent properties. In general, the emission energies and excited-state dynamics depend little on the structure of the isocyanide. Variable-temperature emission spectra and lifetime measurements indicate that most of these compounds emit efficiently from a LC triplet state with minimal contribution from the MLCT state. In one case (complex 2c), the low-energy triplet excited state is localized on the aryl isocyanide, CNAr^{nap}, and when the C^N ligand is btp, considerable CT character is evident, which diminishes the emission intensity. The complexes described here are promising candidates for optoelectronic applications, and continued work in our laboratory is targeting more structurally and electronically diverse combinations of cyclometallating ligands and aryl isocyanides, which can give rise to complexes with enhanced properties.

EXPERIMENTAL SECTION

General Procedures. All experiments involving aryl isocyanides were conducted under nitrogen using standard Schlenk-line techniques or inside a nitrogen-filled glovebox operating at <1 ppm of O_2 and <1 ppm of H₂O. Anhydrous solvents were used for all experiments unless mentioned otherwise. Anhydrous solvents for reactions and optical measurements were obtained by passing through dual alumina columns on a commercial solvent purification system and stored over 3 Å molecular sieves. NMR experiments were performed on JEOL NMR spectrometers. Chemical shifts are reported in parts per million (δ) with integration and multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, and m = multiplet), measured from tetramethylsilane (0 ppm), and are referenced to the solvent CDCl₃ (7.26 ppm) or CD₂Cl₂ (5.32 ppm). UV-vis data were recorded using an Agilent Carey 60 or Cary 8454 UV-vis spectrophotometer. Luminescence data were collected using a Horiba FluoroMax-4 spectrofluorometer. 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 electron paramagnetic resonance tube with a high-vacuum valve and immersed in liquid nitrogen using a finger dewar. Emission quantum yields were determined relative to a standard of quinine sulfate in 0.05 M H₂SO₄, which has a reported fluorescence quantum yield $(\Phi_{\rm F})$ of $0.53.^{64^{\prime\prime}}$ Cyclic voltammetry 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 the supporting electrolyte. A 3-mmdiameter glassy-carbon working electrode, a platinum wire counter electrode, and a silver wire pseudoreference electrode were used. Potentials were referenced to an internal standard of ferrocene. IR spectra were recorded on solid samples using a Nicolet iS10 spectrometer with an attenuated total reflectance accessory. Elemental analyses were carried out by Atlantic Microlab, Inc. (Norcross, GA) and Midwest Microlab, LLC (Indianapolis, IN).

Chemicals from commercial sources were used as received. Cyclometalated iridium(III) μ -chloro-bridged dimers, $(C^{N})_2 Ir(\mu$ -Cl)_2Ir(C^N)_2, were synthesized via the method reported by Nonoyama;⁶⁵ IrCl₃·3H₂O was refluxed with 2–2.5 equiv of a cyclometalating ligand in a 2:1 mixture of 2-ethoxyethanol and water. The isocyanide CNAr^{dipp} was prepared as described previously.³⁶ Samples for elemental analysis were recrystallized from CH₂Cl₂/pentane and often contained solvate molecules even after drying in vacuo overnight. Except solvents of crystallization, these samples were spectroscopically identical with the initially isolated powders.

Photoluminescence Lifetime Measurement. Samples were excited with a pulsed nitrogen laser (Laser Science VSL 337i; 337 nm wavelength, 4 ns fwhm pulse duration, 10 Hz) without focusing, spectrally filtered using long-pass optical filters, and detected with a Hamamatsu photomultiplier tube (photosensor H10721-20). A Tektronix oscilloscope (TDS 3052) was used to record the timing data.

Synthesis of Isocyanide Complexes. [Ir(ppy)₂(CNAr^{dmp})₂]PF₆ (1a). In the glovebox, $[Ir(ppy)_2Cl]_2$ (100 mg, 0.093 mmol) was dissolved in 15 mL of DCM to give a bright-yellow solution. To the reaction mixture were added AgPF₆ (47.1 mg, 0.186 mmol) and 2,6dimethylphenylisocyanide (55.3 mg, 0.373 mmol), resulting in a palevellow reaction mixture that was allowed to stir at 45 °C for 6 h under nitrogen. After this time period, the reaction mixture was cooled to room temperature and filtered through Celite to remove any precipitate. Solvent was removed under vacuum, rendering an offwhite precipitate that was redissolved in a minimum amount of DCM. Adding excess diethyl ether precipitated the pale-yellow product. The precipitate was collected and washed with 5 mL of pentane. Drying under vacuum for 6 h gave the product. Yield: 91%. A suitable crystal for X-ray crystallography was grown using a trifluoromethanesulfonate (OTf) salt of 1a. ¹H NMR (600 MHz, CDCl₃): δ 9.14 (d, J = 6.2 Hz, 2H, ArH), 8.09 (t, J = 6.2 Hz, 4H, ArH), 7.75 (d, J = 7.6 Hz, 2H,

ArH), 7.38–7.36 (m, 2H, ArH), 7.21 (t, *J* = 7.6 Hz, 2H, ArH), 7.09–7.06 (m, 6H, ArH), 6.97 (t, *J* = 7.2 Hz, 2H, ArH), 6.30 (d, *J* = 7.6 Hz, 2H, ArH), 2.09 (s, 12H, CH₃). ¹³C{¹H} NMR (151 MHz, CD₂Cl₂): δ 167.7, 153.3, 152.4, 144.0, 139.4, 136.4, 135.5, 131.0, 130.6, 130.1, 128.2, 126.2, 125.1, 124.7, 124.2, 121.1, 18.1. IR (ν /cm⁻¹): 2144, 2174 (C \equiv N stretching). UV–vis [DCM; λ /nm ($\varepsilon \times 10^{-3}$ /M⁻¹ cm⁻¹]: 258 (60), 310 (sh, 16), 343 (9). Anal. Calcd for C₄₀H₃₄F₆IrN₄P·0.5C₅H₁₂: C, 54.08; H, 4.27; N, 5.94. Found: C, 54.21; H, 4.21; N, 5.88.

[*lr(ppy)*₂(*CNAr^{dipp})*₂]*PF*₆ (**1b**). This compound was synthesized according to a procedure similar to that **1a**, substituting 2,6-diisopropylphenylisocyanide (70.2 mg, 0.373 mmol). A pale-yellow product was isolated. Yield: 133 mg (70%). ¹H NMR (600 MHz, CDCl₃): δ 9.14 (d, *J* = 5.5 Hz, 2H, ArH), 8.14–8.09 (m, 2H, ArH), 8.07 (d, *J* = 8.2 Hz, 2H, ArH), 7.71 (d, *J* = 8.2 Hz, 2H, ArH), 7.42 (s, 2H, ArH), 7.05 (d, *J* = 6.9 Hz, 2H, ArH), 6.97 (d, *J* = 7.6 Hz, 2H, ArH), 6.25 (d, *J* = 7.6 Hz, 2H, ArH), 2.78 (m, 4H, (CH₃)₂CH), 1.10–0.99 (m, 24H). ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 167.8, 153.2, 152.2, 145.6, 143.9, 139.8, 136.6, 131.2, 130.8, 130.6, 125.1, 124.8, 124.3, 123.8, 123.7, 121.1, 30.1, 22.5, 22.4. IR (*ν*/cm⁻¹): 2143, 2178 (C≡N stretching). UV–vis [DCM; *λ*/nm (*ε* × 10⁻³/M⁻¹ cm⁻¹)]: 260 (51), 311 (sh, 14), 344 (7). Anal. Calcd for C₄₈H₅₀F₆IrN₄P: C, 56.51; H, 4.94; N, 5.49. Found: C, 56.38; H, 5.04; N, 5.43.

 $[Ir(F_2ppy)_2(CNAr^{dmp})_2]PF_6$ (2a). This compound was synthesized according to the procedure for 1a, using $[Ir(F_2ppy)_2Cl]_2$ (100 mg, 0.082 mmol), AgPF₆ (41.5 mg, 0.164 mmol), and 2,6-dimethylphenylisocyanide (43.1 mg, 0.329 mmol). An off-white product was isolated. Yield: 154 mg (96%). ¹H NMR (600 MHz, CDCl₃): δ 9.25 (s, 2H, ArH), 8.41 (d, J = 6.9 Hz, 2H, ArH), 8.08 (t, J = 7.6, 2H, ArH), 7.52 (s, 2H, ArH), 7.22-7.12 (m, 2H, ArH), 7.06 (d, J = 6.9 Hz, 4H, ArH), 6.55 (t, J = 9.6 Hz, 2H, ArH), 5.69 (d, J = 6.2 Hz, 2H, ArH), 2.15 (s, 12H, CH₃). ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 163.9, 163.8 (dd, *J* = 270.7 and 11.8 Hz), 161.6 (dd, *J* = 251.5 and 11.8 Hz), 156.1, 154.2, 140.1, 135.8, 133.6, 130.4, 128.3, 127.9, 125.8, 125.5, 124.5 (d, J = 22.2 Hz), 113.0 (d, J = 16.3 Hz), 100.6 (t, J = 26.6 Hz), 18.3. ¹⁹F NMR (565 MHz, CDCl₃): δ -72.42 (s, 3F, PF₆), -73.68 (s, $3F, PF_6$, -104.67 (d, J = 8.9 Hz, 2F), -107.66 (t, J = 11.3 Hz, 2F). IR (ν/cm^{-1}) : 2155, 2181 (C \equiv N stretching). UV–vis [DCM; λ /nm ($\varepsilon \times$ $10^{-3}/M^{-1}$ cm⁻¹)]: 306 (20), 323 (sh, 13). Anal. Calcd for C40H30F10IrN4P: C, 49.03; H, 3.09; N, 5.72. Found: C, 49.33; H, 3.02; N, 5.57.

 $[Ir(F_2ppy)_2(CNAr^{dipp})_2]PF_6$ (2b). This compound was synthesized according to the procedure for 1a, using $[Ir(F_2ppy)_2Cl]_2$ (100 mg, 0.082 mmol), AgPF₆ (41.5 mg, 0.164 mmol), and 2,6-diisopropylphenylisocyanide (61.6 mg, 0.329 mmol). An off-white product was isolated. Yield: 151 mg (84%). ¹H NMR (600 MHz, CDCl₃): δ 9.25 (d, J = 5.0 Hz, 2H, ArH), 8.43 (d, J = 10.1 Hz, 2H, ArH), 8.12 (t, J = 7.6 Hz, 2H, ArH), 7.60–7.47 (m, 2H, ArH), 7.35 (t, J = 8.0 Hz, 2H, ArH), 7.14 (d, J = 7.8 Hz, 4H, ArH), 6.58 (ddd, J = 12.5, 9.0, and 2.4 Hz, 2H, ArH), 5.71 (dd, J = 7.8 and 2.3 Hz, 2H, ArH), 2.92-2.75 (m, 4H, $(CH_3)_2CH$, 1.19–1.01 (m, 24H, $(CH_3)_2CH$). ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 164.0 (d, J = 6.1 Hz), 163.9 (dd, J = 261.8 and 11.9 Hz), 161.7 (dd, J = 261.9 and 11.9 Hz), 155.8, 154.0, 145.7, 140.5, 133.9, 131.2, 127.9, 125.5, 124.8 (d, J = 11.1 Hz), 123.9, 123.4, 113.2 (d, J = 17.8 Hz), 100.7 (t, J = 26.6 Hz), 30.2, 22.6. ¹⁹F NMR $(565 \text{ MHz}, \text{CDCl}_3): \delta - 72.42 \text{ (s, 3F)}, -73.68 \text{ (s, 3F)}, -104.67 \text{ (d, } J =$ 8.9 Hz, 2F), -107.66 (t, J = 11.3 Hz, 2F). IR (ν/cm^{-1}): 2158, 2180 (C=N stretching). UV-vis [DCM; λ/nm ($\varepsilon \times 10^{-3}/\text{M}^{-1}$ cm⁻¹)]: 306 (17), 323 (sh, 11). Anal. Calcd for C₄₈H₄₆F₁₀IrN₄P: C, 52.79; H, 4.25; N, 5.13. Found: C, 52.91; H, 4.28; N, 5.12.

[*Ir*(*F*₂*ppy*)₂(*CNAr*^{nap})₂]*PF*₆ (**2c**). This compound was synthesized according to the procedure for **1a**, using [Ir(F₂*ppy*)₂Cl]₂ (100 mg, 0.082 mmol), AgPF₆ (41.5 mg, 0.164 mmol), and 2-naphthylisocyanide (50.4 mg, 0.329 mmol). A dark-colored product was isolated. Yield: 112 mg (67%). ¹H NMR (600 MHz, CDCl₃): δ 9.40 (d, *J* = 5.5 Hz, 2H), 8.42 (d, *J* = 9.6 Hz, 2H), 8.24 (s, 2H), 8.06 (t, *J* = 7.9 Hz, 2H), 7.94 (t, *J* = 4.5 Hz, 2H), 7.87–7.70 (m, 4H), 7.61–7.45 (m, 6H), 7.39 (d, *J* = 8.2 Hz, 2H), 6.55 (t, *J* = 9.6 Hz, 2H), 5.68 (dd, *J* = 7.4 and 2.2 Hz, 2H). ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 163.9 (d, *J* = 7.8 Hz), 163.7 (dd, *J* = 258.9 and 11.8 Hz), 161.5 (dd, *J* = 261.8 and 11.9

Hz), 156.6, 154.8, 139.8, 133.4, 132.6, 129.8, 128.7, 128.4, 127.9, 127.8, 127.6, 125.3, 124.4 (d, *J* = 20.7 Hz), 123.2, 123.1, 113.0 (d, *J* = 17.6 Hz), 100.5 (t, *J* = 26.6 Hz). ¹⁹F NMR (565 MHz, CDCl₃): δ –71.49 (d, *J* = 714.7 Hz, 6F), -105.11 (q, *J* = 9.6 Hz, 2F), -107.85 (t, *J* = 11.3 Hz, 2F). IR (ν/cm^{-1}): 2160, 2198 (C=N stretching). UV–vis [DCM; λ/nm ($\varepsilon \times 10^{-3}/\text{M}^{-1}$ cm⁻¹)]: 300 (52), 332 (sh, 16), 404 (sh, 1.6). Anal. Calcd for C₄₄H₂₆F₁₀IrN₄P·CH₂Cl₂·H₂O: C, 47.97; H, 2.68; N, 4.97. Found: C, 47.41; H, 2.58; N, 4.91.

 $[Ir(btp)_2(CNAr^{dmp})_2]PF_6$ (3a). This compound was synthesized according to the procedure for 1a, using [Ir(btp)₂Cl]₂ (100 mg, 0.077 mmol), AgPF₆ (39.0 mg, 0.154 mmol), and 2,6-dimethylphenylisocyanide (40.5 mg, 0.308 mmol). A pale-yellow product was isolated. Yield: 128 mg (81%). ¹H NMR (600 MHz, CDCl₃): δ 9.36 (d, J = 5.5 Hz, 2H, ArH), 8.10 (t, J = 7.9 Hz, 2H, ArH), 7.72 (dd, J = 13.1 and 8.2 Hz, 4H, ArH), 7.41 (t, J = 6.9 Hz, 2H, ArH), 7.20-7.09 (m, 4H, ArH), 7.00 (d, J = 7.6 Hz, 4H, ArH), 6.89 (t, J = 7.6 Hz, 2H)ArH), 5.99 (d, J = 8.2 Hz, 2H, ArH), 2.03 (s, 12H, CH₃). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 164.3, 154.5, 149.8, 145.1, 142.8, 140.7, 139.1, 135.8, 131.8, 130.3, 128.3, 125.9, 125.8, 124.7, 124.5, 123.2 (two overlapped signals), 120.8, 18.1. IR (ν/cm^{-1}) : 2152, 2184 (C \equiv N stretching). UV–vis [DCM; λ /nm ($\epsilon \times 10^{-3}/M^{-1} \text{ cm}^{-1}$)]: 317 (24), 346 (19), 383 (15), 397 (15). Anal. Calcd for C₄₄H₃₄F₆IrN₄PS₂· 0.2CH2Cl2: C, 51.19; H, 3.34; N, 5.40. Found: C, 51.29; H, 3.25; N, 5.46.

 $[Ir(btp)_2(CNAr^{dipp})_2]PF_6$ (3b). This compound was synthesized according to the procedure for 1a, using [Ir(btp)₂Cl]₂ (100 mg, 0.077 mmol), AgPF₆ (39.0 mg, 0.154 mmol), and 2,6-diisopropylphenylisocyanide (57.7 mg, 0.308 mmol). Yield: 154 mg (88%). ¹H NMR (400 MHz, CDCl₃): δ 9.38 (d, J = 6.0 Hz, 2H, ArH), 8.19–8.08 (m, 2H, ArH), 7.75 (t, J = 7.6 Hz, 4H, ArH), 7.43-7.36 (m, 2H, ArH), 7.32 (t, J = 7.8 Hz, 2H, ArH), 7.21 (t, J = 7.1 Hz, 2H, ArH), 7.09 (d, J = 7.8 Hz, 4H, ArH), 6.93 (t, J = 7.3 Hz, 2H, ArH), 6.00 (d, J = 8.2 Hz, 2H, ArH), 2.77 (t, J = 6.9 Hz, 4H, (CH₃)₂CH), 0.93 (t, J = 6.4 Hz, 24H, (CH₃)₂CH). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 164.3, 155.5, 150.0, 145.2, 142.9, 140.1, 138.9, 133.3, 132.6, 129.7, 128.7, 128.3, 127.9, 127.7, 127.6, 125.7, 124.6, 124.5, 123.3, 123.2, 123.1, 122.9, 120.5. IR (ν/cm^{-1}) : 2149, 2177 (C=N stretching). UV-vis [DCM; $\lambda/\text{nm} \ (\varepsilon \times 10^{-3}/\text{M}^{-1} \text{ cm}^{-1})$]: 317 (28), 347 (22), 383 (18), 398 (18). Anal. Calcd for C₅₂H₅₀F₆IrN₄PS₂·2CH₂Cl₂: C, 49.81; H, 4.18; N, 4.30. Found: C, 50.15; H, 4.03; N, 4.38.

 $[lr(btp)_2(CNAr^{nap})_2]PF_6$ (3c). This compound was synthesized according to the procedure for 1a, using $[Ir(btp)_2Cl]_2$ (100 mg, 0.077 mmol), AgPF₆ (39.0 mg, 0.154 mmol), and 2-naphthylisocyanide (47.3 mg, 0.308 mmol). A light-yellow product was isolated. Yield: 121 mg (74%). ¹H NMR (500 MHz, $CDCl_3$): δ 9.54 (d, J = 5.7Hz, 2H, ArH), 8.16 (d, J = 1.7 Hz, 2H, ArH), 8.06 (td, J = 7.7 and 1.5 Hz, 2H, ArH), 7.90 (t, J = 4.9 Hz, 2H, ArH), 7.79–7.65 (m, 8H, ArH), 7.54-7.44 (m, 4H, ArH), 7.40 (td, J = 6.7 and 1.5 Hz, 2H, ArH), 7.32–7.22 (m, 2H, ArH), 7.19 (t, J = 7.2 Hz, 2H, ArH), 6.91 (t, J = 7.5 Hz, 2H, ArH), 6.02 (d, J = 8.6 Hz, 2H, ArH). ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 164.3, 155.5, 150.0, 145.2, 142.9, 140.1, 138.9, 133.3, 132.6, 129.7, 128.7, 128.3, 127.9, 127.7, 127.6, 125.7, 124.6, 124.5, 123.3, 123.2, 123.1, 122.9, 120.5. IR (ν/cm^{-1}) : 2155, 2187 (C \equiv N stretching). UV–vis [DCM; λ /nm ($\epsilon \times 10^{-3}/M^{-1} \text{ cm}^{-1}$)]: 287 (43), 316 (sh, 29), 346 (19), 380 (13). Anal. Calcd for C₄₈H₃₀F₆IrN₄PS₂: C, 54.18; H, 2.84; N, 5.27. Found: C, 53.90; H, 2.99; N, 5.21.

[*Ir*(*bt*)₂(*CNAr*^{*dmp*})₂]*PF*₆ (**4a**). This compound was synthesized according to the procedure for **1a**, using [Ir(bt)₂Cl]₂ (100 mg, 0.077 mmol), AgPF₆ (39.0 mg, 0.154 mmol), and 2,6-dimethylphenylisocyanide (40.5 mg, 0.308 mmol). A pale-yellow product was isolated. Yield: 137 mg (87%). ¹H NMR (500 MHz, CDCl₃): δ 8.40 (d, *J* = 7.6 Hz, 2H, ArH), 8.15–8.11 (m, 2H, ArH), 7.78 (d, *J* = 7.6 Hz, 2H, ArH), 8.15–8.11 (m, 2H, ArH), 7.18 (t, *J* = 7.6 Hz, 2H, ArH), 7.010–7.03 (m, 6H, ArH), 6.95 (d, *J* = 7.6 Hz, 2H, ArH), 6.33 (d, *J* = 7.6 Hz, 2H, ArH), 2.02 (s, 12H). ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 183.9, 154.5, 151.2, 141.9, 137.5, 134.5, 133.6, 133.1, 132.2, 130.4, 130.2, 129.1, 128.4, 126.7, 125.9, 122.4, 19.9. IR (*ν*/ cm⁻¹): 2146, 2180 (C≡N stretching). UV–vis [DCM; *λ*/nm (*ε* × 10⁻³/M⁻¹ cm⁻¹)]: 315 (40), 361 (20), 376 (sh, 16). Anal. Calcd for

 $C_{44}H_{34}F_6IrN_4PS_2\cdot CH_2Cl_2$: C, 48.91; H, 3.28; N, 5.07. Found: C, 48.73; H, 3.11; N, 4.91.

 $[lr(bt)_2(CNAr^{dipp})_2]PF_6$ (4b). This compound was synthesized according to the procedure for 1a, using [Ir(bt)₂Cl]₂ (100 mg, 0.077 mmol), AgPF₆ (39.0 mg, 0.154 mmol), and 2,6-diisopropylphenylisocyanide (57.7 mg, 0.308 mmol). A light-yellow product was isolated. Yield 131 mg (75%). ¹H NMR (600 MHz, CDCl₃): δ 8.36 (d, J = 7.2 Hz, 2H, ArH), 8.15 (d, J = 6.9 Hz, 2H, ArH), 7.79 (d, J = 7.6Hz, 2H, ArH), 7.72–7.64 (m, 4H, ArH), 7.33 (t, J = 7.9 Hz, 2H, ArH), 7.10 (dd, J = 12.0 and 7.9 Hz, 6H, ArH), 6.97 (t, J = 6.9 Hz, 2H, ArH), 6.32 (d, J = 7.6 Hz, 2H, ArH), 2.74 (t, J = 6.9 Hz, 4H, (CH₃)₂CH), 0.90 (dd, J = 29.6 and 6.9 Hz, 24H, (CH₃)₂CH). ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 182.2, 152.2, 149.3, 145.8, 139.8, 132.8, 131.6, 131.2, 128.6, 127.5, 126.6, 125.0, 124.5, 123.9, 123.3, 120.0. 30.1, 22.7, 22.6. IR (ν /cm⁻¹): 2142, 2177 (C \equiv N stretching). UV-vis [DCM; λ /nm $(\varepsilon \times 10^{-3}/M^{-1}c m^{-1})$]: 315 (30), 361 (16), 378 (sh, 12). Anal. Calcd for C₅₂H₅₀F₆IrN₄PS₂: C, 55.16; H, 4.45; N, 4.95. Found: C, 55.66; H, 4.56; N. 4.93.

 $[Ir(bt)_2(CNAr^{nap})_2]PF_6$ (4c). This compound was synthesized according to a procedure similar to that for 1a, using [Ir(bt)₂Cl]₂ (100 mg, 0.077 mmol), AgPF₆ (39.0 mg, 0.154 mmol), and 2naphthylisocyanide (47.3 mg, 0.308 mmol). A pale-yellow product was precipitated. Yield: 98 mg (60%). ¹H NMR (600 MHz, CDCl₃): δ 8.55 (d, J = 8.2 Hz, 2H, ArH), 8.03 (d, J = 8.2 Hz, 4H, ArH), 7.94-7.87 (m, 2H, ArH), 7.85-7.73 (m, 8H, ArH), 7.62 (t, J = 7.6 Hz, 2H, ArH), 7.51 (t, J = 4.5 Hz, 4H, ArH), 7.24-7.22 (m, 2H, ArH), 7.09 (t, J = 7.6 Hz, 2H, ArH), 6.96 (t, J = 7.6 Hz, 2H, ArH), 6.31 (d, J = 7.6 Hz, 2H, ArH).). ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 181.6, 153.3, 149.5, 140.0, 133.3, 132.6, 132.5, 131.5, 130.8, 130.2, 129.3, 129.0, 128.5, 128.4, 127.9, 127.8, 127.3, 127.0, 126.4, 124.7, 123.7, 123.3, 123.0, 120.8. IR (ν/cm^{-1}): 2154, 2186 (C=N stretching). UV-vis $[DCM; \lambda/nm (\varepsilon \times 10^{-3}/M^{-1} cm^{-1})]: 301 (53), 359 (sh, 16), 378 (sh, 16), 378$ 13). Anal. Calcd for C48H30F6IrN4PS2: C, 54.18; H, 2.84; N, 5.27. Found: C, 53.98; H, 3.05; N, 5.19.

X-ray Crystallography Procedures. Single crystals were grown by vapor diffusion of pentane into concentrated CHCl₃ or CH₂Cl₂ solutions. Crystals were mounted on a Bruker Apex II three-circle diffractometer using Mo K α radiation (λ = 0.71073 Å). The data were collected at 123(2) K and processed and refined within the APEXII software. Structures were solved by direct methods in SHELXS and refined by standard difference Fourier techniques in the program SHELXL.⁵⁶ Hydrogen atoms were placed in calculated positions using the standard riding model and refined isotropically; all non-hydrogen atoms were refined anisotropically. The structure of 1a, determined as a triflate salt, was disordered in the counterion, whereas the structure of 3c contained three chloroform solvate molecules, two of which were disordered. Distance restraints (SADI) were used for all 1,2 and 1,3 distances within the disordered parts, and the rigid-bond restraints SIMU and DELU were employed for the thermal displacement parameters. Crystallographic details are summarized in Tables S1 and S2.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02691.

X-ray crystallography data for 1a·CH₂Cl₂, 2a·CHCl₃, 3b· 2CHCl₃, 3c·3CHCl₃, and 4a in CIF format, crystallographic summary tables, UV–vis absorption and emission spectra, cyclic voltammograms, and NMR spectra of all new compounds (PDF)

X-ray crystallographic data in CIF format (CIF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: tteets@uh.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the University of Houston, the Welch Foundation (Grant E-1887), and the ACS Petroleum Research Fund (Grant 54907-DNI3) for funding this research. J.B. acknowledges support from the Robert A Welch Foundation (E-1728) and the National Science Foundation (Career Award ECCS-1240510). Prof. Loi Do is acknowledged for access to the UV–vis spectrophotometer.

REFERENCES

- (1) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. J. Am. Chem. Soc. **1984**, 106, 6647–6653.
- (2) Sajoto, T.; Djurovich, P. I.; Tamayo, A. B.; Oxgaard, J.; Goddard, W. A.; Thompson, M. E. J. Am. Chem. Soc. 2009, 131, 9813-9822.
- (3) Yang, X.; Zhou, G.; Wong, W.-Y. Chem. Soc. Rev. 2015, 44, 8484–8575.
- (4) Yang, X.; Xu, X.; Zhou, G. J. Mater. Chem. C 2015, 3, 913–944.
 (5) Fan, C.; Zhu, L.; Liu, T.; Jiang, B.; Ma, D.; Qin, J.; Yang, C.
- Angew. Chem. 2014, 126, 2179–2183.
 (6) Yersin, H. E. Highly Efficient OLEDs with Phosphorescent
- Materials; Wiley-VCH: Berlin, 2008. (7) Mydlak, M.; Bizzarri, C.; Hartmann, D.; Sarfert, W.; Schmid, G.;
- De Cola, L. Adv. Funct. Mater. 2010, 20, 1812–1820. (8) Sun, L.; Galan, A.; Ladouceur, S.; Slinker, J. D.; Zysman-Colman,
- (8) Sun, L.; Gatan, A.; Ladouceur, S.; Sinker, J. D.; Zysman-Conna
 E. J. Mater. Chem. 2011, 21, 18083–18088.
- (9) Hu, T.; He, L.; Duan, L.; Qiu, Y. J. Mater. Chem. 2012, 22, 4206–4215.
- (10) Yang, C.-H.; Beltran, J.; Lemaur, V.; Cornil, J.; Hartmann, D.; Sarfert, W.; Fröhlich, R.; Bizzarri, C.; De Cola, L. *Inorg. Chem.* **2010**, 49, 9891–9901.
- (11) Graber, S.; Doyle, K.; Neuburger, M.; Housecroft, C. E.; Constable, E. C.; Costa, R. D.; Ortí, E.; Repetto, D.; Bolink, H. J. J. *Am. Chem. Soc.* **2008**, *130*, 14944–14945.
- (12) Zysman-Colman, E.; Slinker, J. D.; Parker, J. B.; Malliaras, G. G.; Bernhard, S. *Chem. Mater.* **2008**, *20*, 388–396.
- (13) Yoshihara, T.; Yamaguchi, Y.; Hosaka, M.; Takeuchi, T.; Tobita, S. Angew. Chem., Int. Ed. **2012**, *51*, 4148–4151.
- (14) Yoshihara, T.; Hosaka, M.; Terata, M.; Ichikawa, K.; Murayama, S.; Tanaka, A.; Mori, M.; Itabashi, H.; Takeuchi, T.; Tobita, S. *Anal. Chem.* **2015**, *87*, 2710–2717.
- (15) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Chem. Rev. 2013, 113, 5322-5363.
- (16) Yoon, T. P.; Ischay, M. A.; Du, J. Nat. Chem. 2010, 2, 527-532.
- (17) Zhao, Q.; Huang, C.; Li, F. Chem. Soc. Rev. 2011, 40, 2508–2524.
- (18) Zhang, G.; Zhang, H.; Gao, Y.; Tao, R.; Xin, L.; Yi, J.; Li, F.; Liu, W.; Qiao, J. Organometallics **2014**, 33, 61–68.
- (19) Maity, A.; Choi, J.-S.; Teets, T. S.; Deligonul, N.; Berdis, A. J.; Gray, T. G. Chem. Eur. J. **2013**, *19*, 15924–15932.
- (20) Tamayo, A. B.; Alleyne, B. D.; Djurovich, P. I.; Lamansky, S.; Tsyba, I.; Ho, N. N.; Bau, R.; Thompson, M. E. J. Am. Chem. Soc. 2003, 125, 7377–7387.
- (21) Thompson, P. I. D. In *Highly Efficient OLEDs with Phosphorescent Materials*; Yersin, H., Ed.; Wiley-VCH: Weinheim, Germany, 2008; pp 131–161.
- (22) Vlček, A., Jr.; Záliš, S. Coord. Chem. Rev. 2007, 251, 258–287.
- (23) Lowry, M. S.; Bernhard, S. *Chem. Eur. J.* **2006**, *12*, 7970–7977. (24) Nazeeruddin, M. K.; Humphry-Baker, R.; Berner, D.; Rivier, S.;
- Zuppiroli, L.; Graetzel, M. J. Am. Chem. Soc. 2003, 125, 8790-8797. (25) Radwan, Y. K.; Maity, A.; Teets, T. S. Inorg. Chem. 2015, 54,
- 7122–7131. (2() Milit in L. P. if F. L. if C. if (T. if)
- (26) Malatesta, L.; Bonati, F. Isocyanide Complexes of Transition Metals; Wiley: New York, 1969.
- (27) Yamamoto, Y. Coord. Chem. Rev. 1980, 32, 193-233.

- (28) Carpenter, A. E.; Mokhtarzadeh, C. C.; Ripatti, D. S.; Havrylyuk, I.; Kamezawa, R.; Moore, C. E.; Rheingold, A. L.; Figueroa, J. S. *Inorg. Chem.* **2015**, *54*, 2936–2944.
- (29) Smith, C. S.; Mann, K. R. J. Am. Chem. Soc. 2012, 134, 8786–8789.
- (30) Lai, S.-W.; Lam, H.-W.; Lu, W.; Cheung, K.-K.; Che, C.-M. Organometallics 2002, 21, 226–234.
- (31) Baya, M.; Belío, Ú.; Forniés, J.; Martín, A.; Perálvarez, M.; Sicilia, V. Inorg. Chim. Acta **2015**, 424, 136–149.
- (32) Melekhova, A. a.; Novikov, A. S.; Luzyanin, K. V.; Bokach, N. a.; Starova, G. L.; Gurzhiy, V. V.; Kukushkin, V. Y. *Inorg. Chim. Acta* 2015, 434, 31–36.
- (33) Sacksteder, L.; Lee, M.; Demas, J. N.; DeGraff, B. A. J. Am. Chem. Soc. 1993, 115, 8230-8238.
- (34) Villegas, J. M.; Stoyanov, S. R.; Huang, W.; Rillema, D. P. *Inorg. Chem.* **2005**, *44*, 2297–2309.
- (35) Ko, C.-C.; Siu, J. W.-K.; Cheung, A. W.-Y.; Yiu, S.-M. Organometallics **2011**, 30, 2701–2711.
- (36) Sattler, W.; Henling, L. M.; Winkler, J. R.; Gray, H. B. J. Am. Chem. Soc. 2015, 137, 1198–1205.
- (37) Connor, J. A.; Meyer, T. J.; Sullivan, B. P. Inorg. Chem. 1979, 18, 1388–1391.
- (38) Indelli, M. T.; Bignozzi, C. A.; Marconi, A.; Scandola, F. J. Am. Chem. Soc. 1988, 110, 7381–7386.
- (39) Leung, C.-F.; Ng, S.-M.; Xiang, J.; Wong, W.-Y.; Lam, M. H.-W.; Ko, C.-C.; Lau, T.-C. Organometallics **2009**, 28, 5709–5714.
- (40) Wu, C.; Chen, H.-F.; Wong, K.-T.; Thompson, M. E. J. Am. Chem. Soc. 2010, 132, 3133-3139.
- (41) Li, J.; Djurovich, P. I.; Alleyne, B. D.; Yousufuddin, M.; Ho, N. N.; Thomas, J. C.; Peters, J. C.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2005**, *44*, 1713–1727.
- (42) Shavaleev, N. M.; Monti, F.; Costa, R. D.; Scopelliti, R.; Bolink, H. J.; Ortí, E.; Accorsi, G.; Armaroli, N.; Baranoff, E.; Grätzel, M.;
- Nazeeruddin, M. K. Inorg. Chem. 2012, 51, 2263–2271. (43) Shavaleev, N. M.; Monti, F.; Scopelliti, R.; Armaroli, N.; Grätzel,
- M.; Nazeeruddin, M. K. Organometallics **2012**, 31, 6288–6296.
- (44) Abdel-Shafi, A. A.; Bourdelande, J. L.; Ali, S. S. Dalton Trans. 2007, 2510–2516.
- (45) Wang, X.; Li, J.; Thompson, M. E.; Zink, J. I. J. Phys. Chem. A 2007, 111, 3256-3262.
- (46) Habibagahi, A.; Mébarki, Y.; Sultan, Y.; Yap, G. P. A.; Crutchley, R. J. ACS Appl. Mater. Interfaces **2009**, *1*, 1785–1792.
- (47) Shavaleev, N. M.; Monti, F.; Scopelliti, R.; Baschieri, A.; Sambri, L.; Armaroli, N.; Grätzel, M.; Nazeeruddin, M. K. *Organometallics* **2013**, *32*, 460–467.
- (48) Chan, K.-C.; Chu, W.-K.; Yiu, S.-M.; Ko, C.-C. Dalton Trans 2015, 44, 15135-15144.
- (49) Colombo, M. G.; Guedel, H. U. Inorg. Chem. 1993, 32, 3081-3087.
- (50) Dedeian, K.; Shi, J.; Forsythe, E.; Morton, D. C.; Zavalij, P. Y. Inorg. Chem. 2007, 46, 1603-1611.
- (51) Vogt, R. A.; Gray, T. G.; Crespo-Hernández, C. E. J. Am. Chem. Soc. 2012, 134, 14808–14817.
- (52) Gao, L.; Peay, M. A.; Partyka, D. V.; Updegraff, J. B.; Teets, T. S.; Esswein, A. J.; Zeller, M.; Hunter, A. D.; Gray, T. G. Organometallics **2009**, *28*, 5669–5681.
- (53) Lo, K. K.-W.; Ng, D. C.-M.; Chung, C.-K. Organometallics 2001, 20, 4999–5001.
- (54) Dolan, C.; Moriarty, R. D.; Lestini, E.; Devocelle, M.; Forster, R. J.; Keyes, T. E. J. Inorg. Biochem. **2013**, 119, 65–74.
- (55) Waern, J. B.; Desmarets, C.; Chamoreau, L.-M.; Amouri, H.; Barbieri, A.; Sabatini, C.; Ventura, B.; Barigelletti, F. *Inorg. Chem.* **2008**, 47, 3340–3348.
- (56) Wilde, A. P.; King, K. A.; Watts, R. J. J. Phys. Chem. 1991, 95, 629-634.
- (57) Wilde, A. P.; Watts, R. J. J. Phys. Chem. 1991, 95, 622-629.
- (58) Kobayashi, T.; Ide, N.; Matsusue, N.; Naito, H. Jpn. J. Appl. Phys. 2005, 44, 1966–1969.

(59) Finkenzeller, W. J.; Yersin, H. Chem. Phys. Lett. 2003, 377, 299–305.

(60) Yersin, H.; Rausch, A. F.; Czerwieniec, R.; Hofbeck, T.; Fischer, T. Coord. Chem. Rev. 2011, 255, 2622–2652.

(61) The equations of $k_r = \Phi/\tau$ and $k_{\rm nr} = (1 - \Phi)/\tau$ were used to calculate the rates of radiative and nonradiative decay, where Φ is the quantum efficiency and τ is the luminescence lifetime of the sample at room temperature.

(62) Caspar, J. V.; Meyer, T. J. Inorg. Chem. 1983, 22, 2444-2453.

(63) Caspar, J. V.; Westmoreland, T. D.; Allen, G. H.; Bradley, P. G.; Meyer, T. J.; Woodruff, W. H. J. Am. Chem. Soc. **1984**, 106, 3492– 3500.

(64) Adams, M. J.; Highfield, J. G.; Kirkbright, G. F. Anal. Chem. 1977, 49, 1850–1852.

(65) Nonoyama, M. Bull. Chem. Soc. Jpn. 1974, 47, 767-768.

(66) Sheldrick, G. M. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112–122.