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Tris-heteroleptic Iridium Complexes Based on Cyclometalated Ligands with Different Cores

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S Supporting Information

ABSTRACT: A series of tris-heteroleptic iridium complexes of the form $[Ir(C^N^1)(C^N^2)(acac)]$ combining 2-phenylpyridine (ppy), 2-(2,4-difluorophenyl)pyridine (dFppy), 1phenylpyrazole (ppz), and 1-(2,4-difluorophenyl)pyrazole (dFppz) as the C^N ligands have been synthesized and fully characterized by NMR, X-ray crystallography, UV-vis absorption and emission spectroscopy, and electrochemical methods. It is shown that "static properties" (e.g., absorption and emission spectra and redox potentials) are primarily dictated by the overall architecture of the complex, while "dynamic properties" (e.g., excited-state lifetime and radiative and nonradiative rate constants) are, in addition, sensitive to the specific positioning of the substituents. As a result, the two



complexes [Ir(dFppy)(ppz)(acac)] and [Ir(ppy)(dFppz)(acac)] have the same emission maxima and redox potentials, but their radiative and nonradiative rate constants differ significantly by a factor ~2. Then acetylacetonate (acac) was replaced by picolinate (pic), and two pairs of diastereoisomers were obtained. As expected, the use of pic as the ancillary ligand results in blue-shifted emission, stabilization of the oxidation potential, and improvement of the photoluminescence quantum yield, and only minor differences in the optoelectronic properties are found between the two diastereoisomers of each pair.

INTRODUCTION

Cyclometalated iridium complexes are widely studied for a range of applications including solar energy conversion,^{1–8} organic light-emitting diodes,^{9–25} light-emitting electrochemical cells,^{26–34} sensing,^{35–39} imaging,^{40–43} and synthetic methodologies.^{44,45} For more than 2 decades, these complexes have been particularly appealing because of the excellent performance of their excited states, specifically their relatively short triplet excited-state lifetimes, wide color tunability, and generally high phosphorescence quantum yield.^{46–49}

The photophysical and electrochemical properties of the complexes are crucial for the performance of the materials for a given application, and different applications may require different sets of properties. Interestingly, these properties can be precisely adjusted through engineering of the chemical structure of the complexes. However, because these properties are ultimately all linked to the same chemical structure, modifications to tune a given attribute also cause undesired variations in many others. For example, the most common strategy to blue shift the emission of cyclometalated iridium complexes is to introduce electron-withdrawing substituents, in particular fluorine, on the orthometalated phenyl group. When the highest occupied molecular orbital (HOMO) is stabilized more than the lowest unoccupied molecular orbital (LUMO), an increased HOMO–LUMO gap is obtained, which generally translates into emission at higher energy. However, stabilizing the HOMO also means an increase of the oxidation potential. As such, the complex *fac*-[Ir(ppy)₃] (ppy = 2-phenylpyridine) emits at 510 nm in dichloromethane (CH₂Cl₂) at room temperature and has an oxidation potential $E_{ox} = 0.31$ V versus ferrocene/ferrocenium (Fc⁺/Fc), while the complex *fac*-[Ir-(dFppy)₃] [dFppy = 2-(2,4-difluorophenyl)pyridine] emits at 468 nm and has $E_{ox} = 0.78$ V vs Fc⁺/Fc.⁵⁰ It is only recently that rationalization of the effect of the substituents on the HOMO and LUMO energies allows for tuning of the emission color independently of the energy of the HOMO using electron-donating groups.⁵¹

The radiative and nonradiative rate constants, respectively k_r and k_{nr} , make for another set of parameters crucial to the performance of the emissive complexes because they dictate the photoluminescence quantum yield (PLQY, Φ) and lifetime of

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Scheme 1. Chemical Structures of the Complexes Studied^a



^{*a*}Only the Λ isomers are shown, while all complexes have been isolated as a mixture of Δ and Λ isomers.

the excited state (τ). Across a series of complexes, k_r is generally rationalized based on the amount of metal character in the emitting excited state and the energy gap between the singlet and triplet states, while k_{nr} is explained by the intramolecular vibronic coupling and thermal accessibility of metal-centered (MC) states.^{52–56} A number of design strategies have been used to control the rate constants to improve the properties of the emitting state. A major drawback of these strategies is that they invariably result in the concomitant variation of the emission color and/or redox potentials of the complexes because of the intimate interplay between the chemical structure and properties.^{57–59} Therefore, distinguishing the exact effect of a structural modification on specific properties is still a major challenge.

Herein, a design approach allowing variation of the radiative and nonradiative rate constants independently of the emission maximum and redox potential is demonstrated. Our strategy is based on tris-heteroleptic complexes using cyclometalated ligands (C^N) having different cores. Compared to trishomoleptic $[Ir(C^N)_3]$ and bis-heteroleptic $[Ir(C^N)_2(La)]$ (La = ancillary ligand) complexes, tris-heteroleptic complexes $[Ir(C^N^1)(C^N^2)(C^N^3 \text{ or } La)]$ form a new family of complexes attracting increased attention.⁶⁰⁻⁷⁰ Although often challenging to synthesize and purify, they offer unparalleled opportunities for fine-tuning of the properties. However, to date, only C^N ligands with the same chemical core but different substitution patterns have been used to prepare trisheteroleptic complexes. Phenyltriazole with adamantyl and methyl substituents and phenylpyridine with, for example, fluorine, methyl, benzo, and carbonyl substituents have been reported.

We have prepared a series of $[Ir(C^{N^1})(C^{N^2})(acac)]$ complexes (acac = acetylacetonate), with C^{N^1} and C^{N^2} being ppy, dFppy, 1-phenylpyrazole (ppz), and 1-(2,4difluorophenyl)pyrazole (dFppz) making six tris-heteroleptic and four bis-heteroleptic complexes (Scheme 1). Note that the abbreviation is used for the specific ligand and the full name for the core family of ligands (e.g., "ppy" specifically represents the nonsubstituted 2-phenylpyridine ligand, while "phenylpyridine" represents any 2-phenylpyridine ligand with or without substituents).

First, different experimental conditions have been tested to evaluate the possibility of improving the yields of the reactions. Then all complexes have been isolated and characterized and their electrochemical and photophysical properties measured. Complexes 1-3 with both phenylpyridine-based ligands have been previously reported. As expected, complexes 4-6 with both phenylpyrazole-based main ligands are not emissive at room temperature. Complexes 7-10 with mixed phenylpyridine/phenylpyrazole main ligands display emission properties most similar to those of the phenylpyridine ligand used, ppy or dFppy. As such, the phenylpyrazole ligand acts as an ancillary ligand, perturbing the excited state on the phenylpyridine ligand. As a result, for complexes containing at least one chromophoric phenylpyridine ligand, the redox potentials and emission maxima are dictated by the overall number of fluorine substituents on the complexes, while k_r and k_{nr} , hence, Φ and τ , are dictated by the presence or absence of pyrazole and, for complexes with only two fluorine atoms, their position on either phenylpyridine or phenylpyrazole. In a second part, the acac ligand of complexes 3 and 9 is replaced with picolinate (pic). Contrary to acac, pic is an asymmetric ligand and two diastereoisomers are obtained for each complex, with one having the pyridine of pic trans to the phenyl of dFppy and one having the oxygen of pic trans to dFppy (Scheme 1). Isolating these diastereoisomers, we show that the properties of the two diastereoisomers are very similar, which is confirmed by theoretical calculations. Furthermore, theoretical calculations show that the increased efficiency of nonradiative deactivation processes with phenylpyrazole is mainly due to changes in the vibronic coupling, not to thermally accessible MC states.

Table 1. ¹H NMR Yields of the Reactions

entry	C^N^1	C^N^2	condition ^a	yıe [Ir(C^N	$^{1})_{2}(acac)]$	yıe [Ir(C^N	$(2^{2})_{2}(acac)]$	$(\hat{C}N^2)$	(acac)]	overall yield %
1	рру	dFppy	А	1	18	2	19	3	30	67
2			В		12		12		38	62
3			С		16		15		42	73
4	рру	ppz	Α	1	13	4	30	7	14	57
5			В		23		4		43	70
6			С		11		2		32	45
7	рру	dFppz	А	1	9	5	22	10	28	59
8			В		19		3		16	38
9			С		15		7		19	41
10	dFppy	ppz	А	2	22	4	19	9	30	71
11			В		33		4		18	55
12			С		17		2		36	55
13	dFppy	dFppz	А	2	25	5	14	8	29	68
14			В		24		5		32	61
15			С		24		5		24	53
16	ppz	dFppz	А	4	22	5	10	6	36	68
17			В		4		6		14	24
18			С		4		11		20	35

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"Condition A: $IrCl_3 xH_2O$, ethoxyethanol/water, 130 °C, 12 h. Condition B: $[Ir(COD)Cl]_2$, ethoxyethanol, 130 °C, 3 h. Condition C: $[Ir(COD)Cl]_2$, xylene, 130 °C, 3 h.

RESULTS AND DISCUSSION

Synthesis. All tris-heteroleptic acac complexes 3 and 6–10 were synthesized in two steps starting with heating of the selected ligands in the presence of an iridium source, $IrCl_3$ · xH_2O or $[Ir(COD)Cl]_2$ (COD = cyclooctadiene), to obtain a mixture of chloro-bridged dimers, followed by the reaction with sodium acetylacetonate (acacNa) in a dichloromethane/ methanol solvent mixture overnight. This results in a mixture of complexes containing the target tris-heteroleptic acac complex with the corresponding bis-heteroleptic complexes, $[Ir(ppy)_2(acac)]$ (1), $[Ir(dFppy)_2(acac)]$ (2), $[Ir(ppz)_2(acac)]$ (4) or $[Ir(dFppz)_2(acac)]$ (5).

Because the relative amount of the target tris-heteroleptic complex compared to bis-heteroleptic complexes is embedded in the mixture of chloro-bridged iridium dimers, different reaction conditions for the first step have been explored as a possible means to improve the yield of tris-heteroleptic complexes. Three sets of conditions were tested: (condition A) $IrCl_3 \cdot xH_2O$ as the iridium source with ethoxyethanol/water as the solvent and heating at 130 °C for 12 h; (condition B) $[Ir(COD)Cl]_2$ as the iridium source with ethoxyethanol as the solvent and heating at 130 °C for 3 h; (condition C) $[Ir(COD)Cl]_2$ as the iridium source with xylene as the solvent and heating at 130 °C for 3 h. Condition A is the most commonly used condition for the synthesis of chloro-bridged iridium dimers. Condition B was previously used for synthesis of the tris-heteroleptic complex 3, where the use of an iridium(I) starting material tremendously decreased the reaction time from 12 to 3 h.⁶⁰ Condition C was chosen to briefly explore the effect of the solvent and was slightly modified from a previously reported methodology.⁷

Because the reaction of the iridium chloro-bridged dimers with acacNa is quasi-quantitative in the conditions used, ¹H NMR analysis of the mixture resulting from such a reaction is a reasonable proxy for the composition of the mixture of dimers. Direct analysis of the mixture of dimers would have been an unnecessarily tedious task because of their poor solubility in most solvents and because of the high number of species generated by the reaction (seven dimers are possible). As expected, the ¹H NMR signals from the crude are a perfect combination of signals from the purified products (Figures S1–S6), which gives access to the relative amount of each complex from integration of the signals. An average molar mass was calculated from the ratio obtained, which rapidly gives access to an approximate yield for each complex without the need for purification. Isolated yields of target complexes were judged as less appropriate for this discussion because of the possible partial degradation of the complexes on acidic silica during purification.⁶⁰

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The results summarized in Table 1 allow for a qualitative discussion of the reactivity of the ligands. In terms of both the overall yields and yields of tris-heteroleptic complexes, it appears that condition A was the most generally applicable. Importantly, the tris-heteroleptic complex is the major species, except for entries 4, 8, and 11 of Table 1. Assuming a stepwise coordination of the two ligands to form the final dimer, a twostep mechanism can be hypothesized as follows: in step 1, the iridium starting material, "IrCl", reacts with a first ligand to give an intermediate "Ir(C^N)Cl" species that reacts with another ligand in step 2 to give the chloro-bridged dimer. Under condition A using an iridium(III) starting material, both steps can be considered to proceed through electrophilic substitution, while with conditions B and C using an iridium(I) starting material, the first step is ascribed to an oxidative addition, followed by an electrophilic substitution. The yield of bisphenylpyrazole complexes is always low with conditions B and C (entries 5, 6, 8, 9, 11, 12, and 14-18), suggesting that phenylpyrazole is disfavored during the oxidative addition. However, this is balanced by the higher reaction rate of the fluorinated ligands.⁷² On the other hand, in the case of electrophilic substitution, the reaction rate is disfavored by the presence of electron-withdrawing groups on the ligand,⁷² while the resulting "Ir(C^N)Cl" intermediate complex would be more reactive because of the decreased electron density on the metal. These antagonistic effects explain the absence of clear and meaningful trends, and the results will depend largely on



Figure 1. X-ray crystal structures of 3a, 3b, 9a, and 9b with ellipsoids drawn at the 50% probability level.

Table 2. Comparison between the Experimental and Theoretical Ground-State Geometries for 3a, 3b, 9a, and 9b

	bond lengths (Å)									
-	3a		3b		9a		9b			
-	DFT	X-ray	DFT	X-ray	DFT	X-ray	DFT	X-ray		
Ir–N _{pic}	2.16	2.132(4)	2.16	2.125(3)	2.16	2.137(4)	2.15	2.120(4)		
Ir–N _{C^N}	2.05	2.034(4)	2.05	2.036(3)	2.03	2.026(4)	2.03	2.028(4)		
Ir-N _{dFppy}	2.00	2.037(4)	2.04	2.033(3)	2.04	2.032(4)	2.04	2.033(4)		
Ir-O _{pic}	2.18	2.162(3)	2.04	2.152(3)	2.17	2.150(3)	2.18	2.159(3)		
Ir-C _{C^N}	2.00	2.001(4)	2.01	2.005(4)	2.01	2.008(5)	2.03	2.009(5)		
$Ir-C_{dFppy}$	2.00	1.990(3)	1.99	1.988(4)	2.00	1.979(5)	1.99	1.996(5)		
	bond angles (deg)									
			3b		9a		9b			
	DFT	X-ray	DFT	X-ray	DFT	X-ray	DFT	X-ray		
C _{dFppy} -Ir-C _{C^N}	89.53	89.6(3)	89.56	89.7(2)	89.09	88.8(2)	89.33	89.6(2)		
N _{dFppy} -Ir-N _{C^N}	175.28	175.7(2)	175.20	174.7(1)	174.71	176.0(2)	174.75	174.1(2)		
C _{C^N} -Ir-N _{C^N}	80.52	80.9(2)	80.27	80.5(2)	79.86	80.9(2)	79.49	80.3(2)		
CdFppy-Ir-NC^N	95.52	95.3(2)	97.09	95.1(2)	95.50	96.5(2)	96.84	95.2(2)		
C _{dFppy} -Ir-N _{dFppy}	80.35	80.7(2)	80.62	81.0(1)	80.44	80.7(2)	80.71	81.0(2)		
C_{dFppy} -Ir- O_{pic}	96.85	95.1(2)	173.99	174.7(1)	96.77	96.8(2)	173.24	175.7(2)		

the types of core ligands and substituents as well as the combination of ligands used. In conclusion, using an iridium(I) starting material for the synthesis of heteroleptic dimers leads to the best results in several cases (entries 2, 3, 5, 6, 12, and 14), but the use of iridium(III) is more likely to give reasonable-to-high yields of tris-heteroleptic complexes (only entry 4 shows a low yield).

The acac complexes can be purified using standard chromatography techniques with silica gel (see Figure S7 for thin-layer chromatography analyses), using triethylamine to limit the degradation induced by the acidic silica. The pic complexes were obtained by reacting **3** and **9** with BF₃ in acetonitrile to give the bis-acetonitrile complexes, followed by the reaction with picolinic acid in the presence of a base. The diastereoisomers have been purified by high-performance liquid chromatography (HPLC). All isolated complexes have been characterized by NMR (¹H, ¹³C, ¹⁹F, COESY, NOESY, and HMQC), high-resolution mass spectrometry, and Fourier transform infrared (FT-IR) spectroscopy, and their purity was evaluated with analytical HPLC and elemental analysis (Figures S8–S17).

X-ray Crystal Structures. X-ray crystal structures were obtained for all new tris-heteroleptic complexes, and they confirm the chemical structure of isomers 3a, 3b, 9a, and 9b. Single crystals have been grown by the slow diffusion of hexane into a dichloromethane solution of the complexes. The structures of **3a**, **3b**, **9a**, and **9b** are shown in Figure 1, and selected crystallographic data are provided in Tables 2 and 3. The details for all other structures are given in the Supporting Information.

As expected, all complexes have a slightly deformed octahedral coordination geometry around the iridium center with the usual cis-C,C-trans-N,N chelate configuration.

Electrochemistry. The oxidation and reduction potentials were measured by cyclic voltammetry in degassed acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆). The data are summarized in Table 4; the voltammograms are shown in Figure 2 for the acac complexes and in Figure 3 for the pic complexes.

All pyridine-containing complexes show quasi-reversible oxidation and reduction potentials. As expected, the reduction potentials of the bis-pyrazole complexes **4**–**6** are outside the limit of the system and are therefore not measurable. Because the oxidation potentials correspond to the oxidation of the iridium center, the values are primarily controlled by the overall number of fluorine substituents on the complexes with a minor effect of the presence of pyrazole, with about 30 mV per pyrazole unit replacing a pyridine unit. As such, complexes without fluorine atoms have E_{ox} values ranging from +0.42 to +0.49 V vs Fc⁺/Fc, while the addition of two fluorine substituents shifts the range to +0.58 to +0.64 V vs Fc⁺/Fc and four fluorine substituents shift the range further to +0.74 to

3a	$3b\cdot^3/_2CH_2Cl_2\cdot 0.5H_2O$	9a	$9b\cdot^3/_2$ CH ₂ Cl ₂
552222	1552223	1511802	1511803
28H18F2IrN3O2	C _{29.5} H ₂₂ Cl ₃ F ₂ IrN ₃ O _{2.5}	$C_{26}H_{17}F_2IrN_4O_2$	$C_{27.5}H_{20}Cl_3F_2IrN_4O_2$
58.65	795.05	647.63	775.02
00.01(10)	100.01(10)	99.97(10)	100.01(10)
rthorhombic	monoclinic	monoclinic	monoclinic
$na2_1$	$P2_1/c$	$P2_1/n$	P2 ₁ /c
5.0856(2)	16.7317(5)	9.2743(3)	16.3715(4)
5.3361(2)	12.3412(2)	14.7104(4)	12.2266(2)
47782(13)	15.5940(4)	16.5135(5)	15.6859(4)
0	90	90	90
)	117.541(4)	93.301(3)	118.521(3)
)	90	90	90
335.71(6)	2855.09(15)	2249.18(11)	2758.76(13)
	4	4	4
873	1.850	1.913	1.866
764	5.006	11.923	12.455
272.0	1544.0	1248.0	1500.0
$1932 \times 0.1488 \times 0.1233$	$0.2164 \times 0.1215 \times 0.0362$	$0.2106 \times 0.0601 \times 0.0459$	0.4159 × 0.1754 × 0.0943
968-54.958	5.892-50.688	8.056-136.498	6.144-144.228
4233	14404	12463	16925
197 $[R_{int} = 0.0312; R_{\sigma} = 0.0267]$	5204 $[R_{int} = 0.0269; R_{\sigma} = 0.0321]$	4103 $[R_{int} = 0.0353; R_{\sigma} = 0.0347]$	5406 [$R_{int} = 0.0310; R_{\sigma} = 0.0253$]
197/1/325	5204/0/415	4103/0/316	5406/0/397
057	1.025	1.105	1.078
1 = 0.0178; wR2 = 0.0348	R1 = 0.0258; wR2 = 0.0606	R1 = 0.0314; wR2 = 0.0803	R1 = 0.0350; wR2 = 0.0841
1 = 0.0214; wR2 = 0.0364	R1 = 0.0314; wR2 = 0.0637	R1 = 0.0361; wR2 = 0.0840	R1 = 0.0356; wR2 = 0.0845
	3a (52222) (28H ₁₈ F ₂ IrN ₃ O ₂) (8.65) (0.01(10)) (10) (10) (10) (10) (10) (10) (1	3a $3b^{-3}/_2CH_2Cl_2 \cdot 0.5H_2O$ 552222 1552223 $c_{29,3}H_{12}Cl_3F_2IrN_3O_{2.5}$ 8.65 $0.01(10)$ $100.01(10)$ thorhombicmonoclinic aa_{21} P_{21}/c $.0856(2)$ $16.7317(5)$ $.63361(2)$ $12.3412(2)$ $47782(13)$ $15.5940(4)$ 0 90 $0.35.71(6)$ $2855.09(15)$ 4 873 754 5.006 $.72.0$ 1544.0 $1932 \times 0.1488 \times 0.1233$ $0.2164 \times 0.1215 \times 0.0362$ $968-54.958$ $5.892-50.688$ 2233 14404 $97 [R_{int} = 0.0312; R_{\sigma} = 0.0321]$ 90.1025 $97/1/325$ $5204/0/415$ 0.757 1.025 $1 = 0.0178;$ wR2 = 0.0348R1 = 0.0258; wR2 = 0.0606 $1 = 0.0214;$ wR2 = 0.0364R1 = 0.0314; wR2 = 0.0637	3a $3b^3/_2CH_2Cl_2.0.5H_2O$ 9a5222215522231511802 $2_{28}H_{18}F_2IrN_3O_2$ $C_{29,5}H_{22}Cl_3F_2IrN_3O_{2.5}$ $C_{2e}H_{17}F_2IrN_4O_2$ 8.65 795.05647.63 $0.01(10)$ 100.01(10)99.97(10)thorhombicmonoclinicmonoclinic $4a^2_1$ $P_{2_1/c}$ $P_{2_1/n}$ $0.0856(2)$ 16.7317(5)9.2743(3) $6.3361(2)$ 12.3412(2)14.7104(4) $47782(13)$ 15.5940(4)16.5135(5) 0 9090 0 117.541(4)93.301(3) 0 9090 0 117.541(4)93.301(3) 0 9090 0 12855.09(15)2249.18(11) 4 4 473 1.8501.913 764 5.00611.923 72.0 1544.01248.0 $1932 \times 0.1488 \times 0.1233$ 0.2164 $\times 0.1215 \times 0.0362$ 0.2106 $\times 0.0601 \times 0.0459$ $968-54.958$ 5.892-50.6888.056-136.498 223 1440412463 97 [$R_{ipst} = 0.0312; R_{\sigma} = 0.0269; R_{\sigma} = 0.0269; R_{\sigma} = 0.0347]$ 0.0347] $97/1/325$ 5204/0/4154103/0/316 0257 1.0251.105 $1 = 0.0178; wR2 = 0.0348$ R1 = 0.0258; wR2 = 0.0606R1 = 0.0314; wR2 = 0.0803 $1 = 0.0214; wR2 = 0.0364$ R1 = 0.0314; wR2 = 0.0840

Table 4. Photophysical and Photochemical Properties of Complexes 1-10, 3a, 3b, 9a, and 9b

				(nm)			$k_{\rm r}$	$k_{\rm nr}$
	$E_{\rm ox} ({\rm V})^d$	$E_{\rm red} ({\rm V})^d$	$\lambda_{ m abs}$, nm ($arepsilon imes 10^3$, L mol $^{-1}$ cm $^{-1}$) a	RT^{b}	τ (ns), RT ^b	$\Phi_{\mathtt{PL}}{}^{b}$	(x_{10}^{-1})	(x_{10}^{-1})
1	0.43 (0.41) ^c	$-2.57 (-2.60)^{c}$	260 (39.15), 340 (9.15), 405 (4.02), 459 (2.88), 489 (1.32)	519 (520) ^c	1511 (1227) ^e	0.47 ^c	3.83 ^c	4.32 ^c
2	$0.73 (0.76)^c$	$-2.45 (-2.44)^c$	253 (45.72), 328 (11.44), 389 (4.72), 435 (2.23), 466 (0.82)	482 (484) ^c	898 (872) ^c	0.63 ^c	7.22 ^c	4.24 ^c
3	0.58 (0.57) ^c	$-2.51 (-2.52)^{c}$	256 (42.97), 334 (10.34), 398 (4.29), 449 (2.44), 479 (0.79)	503 (503) ^c	1413 (1224) ^c	0.69 ^c	5.64 ^c	2.53 ^c
4	0.49		252 (34.04), 297 (15.15), 330 (8.57), 377 (2.77), 418 (0.19)					
5	0.79		253 (31.19), 321 (8.06), 359 (2.23), 400 (0.29)					
6	0.64		251 (33.18), 269 (25.53), 294 (13.89), 325 (8.61), 370 (2.21), 408 (0.15)					
7	0.45	-2.58	256 (36.36), 295 (17.76), 335 (8.81), 374 (4.14), 405 (2.35), 456 (1.27), 487 (0.38)	519	1592	0.26	1.63	4.65
8	0.75	-2.44	253 (40.40), 289 (18.86), 325 (10.349), 361 (3.95), 385 (2.52), 430 (0.95), 461 (0.31)	483	619	0.22	3.55	12.60
9	0.61	-2.50	254 (35.00), 291 (16.91), 330 (8.85), 369 (3.63), 392 (2.21), 437 (1.01), 469 (0.37)	503	837	0.32	3.82	8.12
10	0.60	-2.52	257 (35.63), 295 (17.39), 328 (9.17), 360 (4.28), 396 (2.36), 430 (1.46), 478 (0.32)	502	1575	0.30	1.90	4.44
3a	0.73	-2.33	261 (37.55), 289 (20.99), 323 (10.15), 345 (5.81), 390 (3.87), 431 (2.33), 462 (0.27)	489, 515	1850	0.49	2.65	2.76
3b	0.72	-2.34	259 (32.69), 289 (18.54), 305 (13.67), 322 (9.37), 345 (5.39), 389 (3.66), 430 (2.14), 470 (0.23)	485, 512	1559	0.43	2.76	3.66
9a	0.76	-2.35	253 (36.20), 283 (20.92), 303 (14.62), 321 (10.91), 341 (6.86), 383 (3.28), 415 (1.65), 432 (0.93), 460 (0.24)	474, 499	1004	0.42	4.18	5.78
9b	0.73	-2.33	258 (31.18), 281 (16.35), 302 (12.57), 322 (7.66), 341 (4.18), 384 (2.34), 414 (1.42), 431 (0.84), 458 (0.19)	476sh, 498	971	0.38	3.91	6.39

^aAerated dichloromethane. ^bDegassed dichloromethane. ^cAccording to ref 60. ^aDegassed acetonitrile/TBAPF₆ (0.1 M), vs Fc⁺/Fc at 1 V s⁻¹.

+0.79 V vs Fc⁺/Fc. The effect of fluorine substituents can also be seen on the reduction potentials (no fluorine atoms, -2.57

to -2.58; two fluorine atoms, -2.50 to -2.52; four fluorine atoms, -2.44 to -2.45 V vs Fc⁺/Fc), with virtually no effect of



Figure 2. Cyclic voltammograms of complexes **1–10**: (black —) complexes with no fluorine atoms; (blue —) complexes with four fluorine atoms; (red —) complexes with two fluorine atoms.



Figure 3. Cyclic voltammograms of complexes 3a, 3b, 9a, and 9b: (black —) isomers with N-pic trans to dFppy; (red —) isomers with O-pic trans to dFppy.

replacing a pyridine with a pyrazole due to the reduction being localized on the phenylpyridine ligand.

For the complexes [Ir(dFppy)(ppz)(acac)] (9) and [Ir(ppy)(dFppz)(acac)] (10), the data are particularly interesting because they show comparable values for the oxidation and reduction potentials. This suggests that the effect of 2,4-difluorination of the phenyl ring is independent of the ligand being fluorinated. In contrast, the radiative and nonradiative

rate constants are largely influenced by the position of the 2,4difluorination (see below). In addition, these two complexes display redox potentials very similar to those of the complex [Ir(dFppy)(ppy)(acac)] (3) besides a small 20 mV shift to lower oxidation potential with 3 due to the absence of the pyrazole unit. This demonstrates that tris-heteroleptic complexes provide the possibility for different complex designs that have the same HOMO and LUMO energies and the same emission maxima (see below), while each of these designs can exhibit different values for k_r and k_{nr} .

Because the two pairs of diastereoisomers 3a, 3b, 9a, and 9b contain at least one pyridine group, they also show quasireversible oxidation and reduction potentials (Figure 3). The principal effect of replacing acac with pic is to anodically shift both oxidation and reduction potentials by ~150 mV without changing the electrochemical gap (3.06-3.11 eV compared to 3.09-3.10 eV for 3 and 9). The four complexes display very similar redox potentials, demonstrating further that these energy levels are primarily dependent on the overall structure and composition of the complexes and not on the particularities of the chemical structures. This is confirmed by theoretical calculations (see the Supporting Information), showing that the localizations of the HOMOs and LUMOs are similar for the four complexes. Furthermore, the orbitals of these complexes are similar to those of FIrpic, another well-studied iridium complex, which is not surprising considering the similarity between these molecules.⁷³⁻⁷⁸ In their ground state, **3a**, **3b**, **9a**, and 9b isomers all have HOMOs composed of significant Ir(5d) character, at around 50%. All of the occupied orbitals have some degree of Ir(5d) character and some ligand π -orbital character, with the maximum Ir(5d) contribution appearing in HOMO-1 at 61% for 3a and 3b, in HOMO-2 at 67% for 9a, and in HOMO-1 at 60% for 9b. The lower-lying unoccupied orbitals have much lower Ir(5d) character (at around 1%) and are mostly ligand-centered (LC).

Photophysical Properties. The UV-vis electronic absorption and luminescence spectra of complexes 1–10 are shown in Figure 4, and the spectra for complexes 3a, 3b, 9a, and 9b are shown in Figure 5. Data are summarized in Table 4.

As for other cyclometalated iridium complexes, the absorption spectra are dominated by strong absorption bands at 254–260 nm [$\varepsilon \sim (30-45) \times 10^3$ M⁻¹ cm⁻¹] attributed to LC ${}^{1}\pi\pi^{*}$ transitions followed by weaker transitions [$\varepsilon \sim (5-$ 20) \times 10³ M⁻¹ cm⁻¹] of charge-transfer (CT) character between 300 and 440 nm corresponding to transitions from the iridium center to the ligand (metal-to-ligand charge transfer, MLCT). The last weak transitions ($\varepsilon < 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) observed at lowest energy are attributed to the direct population of the emitting triplet state. As expected, 4-6show a blue-shifted absorption compared to the phenylpyridine complexes with onset absorptions below 430 nm, coherent with nonmeasurable reduction potentials, suggesting a high-energy LUMO. The absorption profiles in the MLCT regions of 7-10are very similar to those of their corresponding phenylpyridinebased bis-heteroleptic complex 1 or 2 with roughly halved molar extinction coefficients, due to the presence of only one phenylpyridine ligand. The higher-energy transitions between 260 and 350 nm exhibit some more phenylpyrazole-like character such as the 297 nm peak of 4 being visible on 7 (Figure 4) or the 294 and 325 nm peaks of 6 also appearing in 9 and 10 (Figure 4).

The bis-pyrazole complexes 4-6 are not emissive at room temperature. At 77 K in frozen tetrahydrofuran, they display a



Figure 4. Absorption (left) and emission (right) spectra measured at room temperature in dichloromethane (abs) and in degassed dichloromethane (em) of (top) 1, 4, and 7, (middle) 2, 5, and 8, and (bottom) 3, 6, 9, and 10.

broad emission band with emission maxima at 538, 515, and 503 nm for 4, 6, and 5, respectively (Figure S32), and, hence, are blue-shifted as the number of fluorine increases. Such bands have been previously attributed to metal–ligand-to-ligand charge transfer (³MLLCT).^{79,80} The emission profiles of the tris-heteroleptic complexes follow the trend of typical iridium complexes with phenylpyridine-based ligands, with a blue-shifted emission as the overall number of fluorine substituents is increased. Replacing a pyridine with a pyrazole induces only a minor broadening (~100 cm⁻¹) of the spectra without changing the emission maxima (1 vs 7; 2 vs 8; 3 vs 9 and 10). This is in line with the HOMO–LUMO gap also not being affected by the structural change and demonstrates that,



Figure 5. Absorption (left) and emission (right) spectra measured at room temperature in dichloromethane (abs) and in degassed dichloromethane (em) of (top) 3a and 3b and (bottom) 9a and 9b.

for these acac complexes, the difference between the electrochemical and optical gaps is fairly constant and independent of the presence or absence of a pyrazole unit. Combined with the UV-vis profiles and redox potentials, these clues strongly suggest that the excited state is localized on the phenylpyridine ligand.

As seen above, replacing a pyridine with a pyrazole in complexes 1-3 has virtually no effect on the redox potentials and emission spectra. However, such a structural modification has a significant impact on the radiative and nonradiative rate constants. The excited-state lifetimes and quantum yields have been measured (see Table 4) and used to calculate radiative (k_r) = Φ/τ) and nonradiative $[k_{nr} = (1-\Phi)/\tau]$ rate constants, assuming unitary intersystem crossing. Compared to the bisphenylpyridine complexes 1-3, the phenylpyridine/phenylpyrazole mixed complexes 7–10 display distinctly lower Φ with τ dictated by the chosen phenylpyridine. As such, 7 and 10 that contain ppy have $\tau = 1.60$ and 1.58 μ s, respectively, very close to 1.52 μ s of 1, while 8 and 9 that contain dFppy have $\tau = 0.62$ and 0.84 μ s, respectively, very close to 0.90 μ s of 2. Similar τ with lower Φ results in lower (down to about half) k_r and higher (up to 3 times) $k_{\rm nr}$ for the phenylpyridine/phenylpyrazole mixed complexes compared to the bis-phenylpyridine complexes without changing the emission spectra or the redox potentials. This is particularly striking for complexes 9 and 10, which differ only by the position of the 2,4-difluorination: their optoelectronic properties differ only in their largely different excited-state lifetimes.



Figure 6. Comparison between the experimental and computed absorption spectra. The vertical bars represent the electronic transitions calculated with LR-TDDFT, with their heights being proportional to the oscillator strengths. The dashed lines were obtained by convoluting the experimental results with a Gaussian broadening function of full width at half-maximum of 20 nm.

The reduction of k_r and increase of k_{nr} induced by the presence of a phenylpyrazole ligand can be rationalized by invoking a perturbative participation of the nonchromophoric phenylpyrazole ligand to the excited state localized on the phenylpyridine ligand. Indeed, studies of $[Ir(ppz)_3]$ and $[Ir(dFppz)_3]$ have pointed to these complexes having low k_r on the order of 10^4 s^{-1} , high k_{nr} on the order of 10^{12} s^{-1} , and an excited-state energy of about 3 eV.

When comparing the **a** and **b** diastereoisomers, no significant differences can be found: **3a** and **9a** are very similar to **3b** and **9b**, respectively. The only statement that can be made without exercising too much speculation is that isomers **a** with the pyridine of the pic trans to the dFppy ligand have a slightly higher (about 10%) absorption coefficient throughout the absorption spectra and that their excited-state properties are more favorable because of a slightly lower k_{nr} . This close similarity between the two isomers is confirmed by theoretical calculations.

The absorption spectra at the ground-state equilibrium geometry were calculated using linear-response time-dependent density functional theory (LR-TDDFT). A total of 45 (singlet) states for each complex were computed in order to cover the experimental absorption spectral range. Details of the transitions with the largest oscillator strengths are given in Table S11. The spectra obtained with the calculations are in good agreement with experiments (Figure 6). The first excited state (S_1) of both isomers has an MLCT character and a large HOMO \rightarrow LUMO contribution, which is, however, less than 50% in all four cases.

The estimates we obtained for the triplet emission peaks, with the U-DFT calculations, were 2.35 eV (527 nm) for 3a, 2.36 eV (524 nm) for 3b, 2.49 eV (498 nm) for 9a, and 2.48 eV (500 nm) for 9b. Experimental peaks are at 2.54 eV (489 nm), 2.56 (485 nm), 2.48 eV (500 nm), and 2.49 eV (498), respectively. For 3a and 3b, our results are slightly red-shifted but well within the expected error of the method.

The spin densities calculated at the U-DFT-optimized geometries in the T_1 state are shown in Figure S41. These transitions have large Ir(5d) contributions and are mostly localized on the ppy ligands for 3a and 3b and on the dFppy ligands for 9a and 9b, with minor contributions on the pic ligand, and we observe that there is very little difference

between the isomers. The same results are obtained with density differences calculated at the LR-TDDFT-optimized T_1 geometries (Figure 7). The density differences also show particularly well that the first triplet has a combination of MLCT and LC character because we can distinguish the electron (blue color) and hole (red color) contributions to the state. The similarity between the electronic structures, observed in both the spin densities and the density differences, of the two isomers excludes the possibility that it causes a difference in



Figure 7. Density differences of **3a**, **3b**, **9a**, and **9b** at the LR-TDDFToptimized T_1 geometries. The blue parts represent the positive parts of the density (the electron), while the red parts represent the negative parts (the hole).

broadness observed in the emission spectra. This suggests that this difference is very likely due to vibronic couplings. These vibronic couplings may also be responsible for the nonradiative deactivation of the excited states.^{54,81} Indeed, MC states are, in all four cases, over 2 eV higher than T₁ (see the Supporting Information). Activation energies into the MC state are therefore expected to also be relatively high, and thermal activation into these quenching states is not very efficient, although only a complete sampling of the configuration space would answer this question.^{82,83} Another deactivation pathway can be due to transitions into poorly emissive metal–ligand (ppy)-to-ligand (pic) charge-transfer states.⁸²

Because of the similarities between the isomers, we will briefly discuss the pairs in comparison to their parent acac complexes 3 and 9. Compared to 3, 3a and 3b show ~0.06 eV blue-shifted absorption and emission spectra, and 9a and 9b show ~0.06 eV blue-shifted absorption and ~0.14 eV blueshifted emission spectra compared to 9. So, while both 3 and 9 display emission maxima in green at 502 nm, 3a and 3b emit at 485-489 nm and 9a and 9b at 475 nm, both in the bluishgreen region, with 9a and 9b coming close to FIrpic (468 nm) in spite of having only two fluorine substituents.

A change of the ancillary ligand is a common strategy to tune the emission color of cyclometalated iridium complexes either because La is nonchromophoric and affects the energy of the HOMO much more than the energy of the LUMO⁵⁷ or because La is chromophoric, which can result in the ancillary ligand being the emitting ligand.^{84,85} In our case, pic is a nonchromophoric ligand; therefore, changing acac for pic was expected to result in a blue shift due to larger stabilization of the HOMO. As was just seen, the emission is indeed blueshifted in complexes 3a, 3b, 9a, and 9b compared to 3 and 9, respectively. However, this cannot be attributed to a larger stabilization of the HOMO because the electrochemical gap is constant within experimental error upon going from acac to pic (see the Electrochemistry section). Therefore, the reasons for the observed blue shift have to be attributed to the additional term differentiating the electrochemical gap with the optical gap.⁸⁰

CONCLUSION

In summary, a series of tris-heteroleptic cyclometalated iridium(III) complexes, $Ir(C^N^1)(C^N^2)(acac)$ (C^N^1 , $C^N^2 = ppy$, dFppy, ppz, dFppz), and the corresponding bis-heteroleptic complexes have been synthesized and fully characterized. In addition, the use of picolinate as the ancillary ligand with [Ir(dFppy)(ppy)] and [Ir(dFppy)(ppz)] cores provided two pairs of diastereoisomers that have been fully separated.

The exploration of various reaction conditions to obtain the chloro-bridged iridium dimer showed that both iridium(I) and iridium(III) can be used as starting materials to obtain trisheteroleptic complexes and that the most suitable conditions depend on the core and substituents of the ligands used. If the reactivity of the ligands is known, this opens up opportunities for devising an effective stepwise synthesis with the potential to greatly increase the yield of the trisheteroleptic complex.

Photophysical and electrochemical studies showed that absorption and emission wavelengths and redox properties are governed primarily by the overall structure of the complexes, while dynamic properties such as radiative and nonradiative constants are controlled by the specific placement of the substituents. As a result, it is possible to vary $k_{\rm r}$ and $k_{\rm nr}$ without significantly impacting other properties.

When pic was used as the ancillary ligand, it was found that both diastereoisomers have very similar photophysical and electrochemical properties. It may therefore be possible to use the mixture of isomers as materials for application without the need for tedious purification.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01307.

Full experimental procedures and characterization (including NMR spectra, X-ray crystallography, FT-IR spectra, and HPLC traces) and additional computational data (PDF)

Accession Codes

CCDC 1511801–1511806 and 1552222–1552224 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data_request/cif, or by emailing data_request@ccdc.cam.ac. uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The authors declare no competing financial interest.

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