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Formazanate Complexes of Bis-Cyclometalated Iridium

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ABSTRACT: In this work we describe a series of bis-cyclometalated iridium(III) formazanate complexes, expanding the coordination chemistry of the redox-active formazanate class to iridium. A total of 18 new complexes are described, varying the substituent pattern on the formazanate and the identity of the cyclometalating ligand on iridium. Eight of the new compounds are structurally characterized by single-crystal X-ray diffraction, which along with NMR spectroscopy evinces two binding modes of the formazanate. Two of the compounds are isolated in a C_2 -symmetric geometry where the formazanate is bound in a six-member chelate “closed” conformation, involving the 1- and 5-positions of the 1,2,4,5-tetraazapentadienyl formazanate core. In most of the examples, the major isomer that forms and is exclusively isolated involves the formazanate bound in a five-member chelate “open” form, coordinating through the 1- and 4-positions of the formazanate core and resulting in C_1 point-group symmetry. All complexes are characterized by UV-vis absorption spectroscopy and cyclic voltammetry, with these features depending primarily on the substitution pattern on the formazanate, and to a lesser extent on the identity of the cyclometalating ligand and formazanate binding mode.

INTRODUCTION

The coordination chemistry of formazans, which are a class of chromophoric conjugated organic molecules with a 1,2,4,5-tetraazapentadienyl core, has long been investigated with transition metals and main group metals. The nitrogen-rich redox active formazans have also been intensively studied in the fields of bioinorganic chemistry^{1,2} and catalysis^{3–5}, and a few successful applications have emerged over time in biomedical assays, textile dyes, and colorimetric indicators of cell activity.^{6–9} The monoanionic form of formazans (referred to as “formazanates”) have become a well-known *N*-chelating ligand class in recent years, structurally analogous to the ubiquitous β -diketiminato ligand class but with redox activity at much more accessible potentials and strong visible absorption, primarily because of LUMOs that are significantly stabilized relative to β -diketiminates.^{10–13} The growing interest in formazanate coordination complexes is largely due to the ligand-based redox processes, which can facilitate multielectron redox behavior,¹⁴ bond activation,¹⁵ and excited-state charge separation. In particular, the stabilized LUMOs in formazanates result in relatively stable reduced products, greatly expanding the redox chemistry of these complexes in small-molecule activation and other contexts.^{16–18}

Complexes of first-row transition metals with formazanates have been extensively reported,^{5,19} including copper complexes which mediate oxygen activation.^{20,21} The ligand-based redox chemistry of low-coordinated iron complexes^{22–24} and bis-chelated zinc complexes^{25,26} has recently been characterized. Unique magnetic properties were demonstrated in heteroleptic cobalt and bis(formazanate) iron complexes.^{27–29} Formazanate complexes of group 14 elements and ruthenium highlight the redox non-innocence of some classes of formazanate complexes.^{16,30} Furthermore, boron chelates of formazanates not only exhibit tunable redox properties but are also in many cases photoluminescent,^{31–36} finding applications as cell-imaging agents,^{33,37} electrochemiluminescence emitters,^{38,39} multifunctional polymers,^{40,41} and precursors to a wide range of BN heterocycles.^{42,43}

In spite of these numerous examples, coordination complexes of formazans with third-row transition metals remain rare. Dithizonate complexes with a formazan-like core were described where coordination of sulfur to the metal was observed.⁴⁴ Complexes of dianionic aryl formazanate ligands which involve *o*-phenoxy or *o*-benzoate donors were found to be coordinated in a tridentate fashion with a few heavy transition metals, but none of them were extensively characterized or analyzed for further studies.^{45–48} Since the strong orbital overlap between radially extended 5d orbitals and the formazanate π system could perturb the inherent redox and optical properties of the formazanates and the 5d metal center could promote formazanate-centered triplet photophysics, our group began investigating third-row transition metal complexes of formazanates. We have expanded the coordination chemistry of formazanates a series of heteroleptic platinum complexes^{49,50} and accessed homoleptic azo-imine platinum complexes⁵¹ via hydrogenative cleavage of formazans.

In this work, we describe a diverse set of cyclometalated iridium(III) formazanate complexes. Cyclometalated iridium(III) compounds have been extensively studied in a number of contexts,^{52–57} primarily due to their good thermal and photostability, relatively short phosphorescence lifetime, and high photoluminescence quantum yields. Although the synthetic chemistry of cyclometalated iridium(III) formazanates largely parallels that of our previous cyclometalated platinum(II) formazanate series,^{49,50} moving from platinum(II) to iridium(III) allows us to evaluate the effects of coordination geometry and d-electron count on the structural chemistry, redox properties, and optical properties of 5d metal formazanates. We describe 18 new cyclometalated iridium(III) formazanate complexes of the type $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{formazanate})$ ($\text{C}^{\wedge}\text{N}$ = cyclometalating ligands). These neutral complexes feature four different cyclometalating ligands and six structurally and electronically varied triaryl- and diarylformazanates. A general synthetic route is presented here, and 8 of 18 compounds are structurally characterized by single crystal X-ray diffraction.

tion, which reveals two distinct coordination modes for the formazanate. The substitution patterns on the formazanate strongly influence the observed ligand-centered redox potentials, with subtle influences from the C[^]N ligand that suggest some degree of mixing between iridium d-orbitals and formazanate π orbitals. The UV-vis absorption spectra show intense bands from the contributions of both formazanates and Ir-C[^]N fragments, and solvatochromic studies assist in the assignment of these features. This work demonstrates that alteration of the C[^]N and formazanate ligands offers two layers of control over the redox and optical properties of neutral iridium formazanate complexes.

RESULTS AND DISCUSSION

Synthesis. Scheme 1 depicts the general synthetic procedure of the series of 18 heteroleptic cyclometalated iridium formazanate complexes of the type Ir(C[^]N)₂(formazanate). Compounds are numbered based on the identity of the C[^]N ligand, with the associated letter designating the structure of the formazanate ancillary ligand. Two cyclometalating ligands, 2-phenylpyridine (ppy) and 2-(2,4-difluorophenyl)pyridine (F₂ppy), are partnered with all six formazanates studied here (**Fza**–**Fzf**), to produce products **1a**–**1f** and **2a**–**2f**, while the other two C[^]N ligands, 2-phenylbenzothiazole (bt) and 1-phenylisoquinoline (piq), are used to prepare a smaller subset of complexes (**3a**, **3b**, **3e**, **3f**, **4a**, and **4f**). The chloro-bridged dimers [Ir(C[^]N)₂(μ -Cl)]₂ are treated with a stoichiometric amount of free formazan in ethanol in the presence of excess triethylamine, by refluxing for 20–36 hours. The reaction is general and tolerates a variety of electronically modified formazans, which include different combinations of electron-donating (-CH₃, -OCH₃) and electron-withdrawing (-CN) substituents at either the azo aryl substituent (R¹) or at the central position of the backbone (R²). Reactions involving triarylformazanates (**Fza**–**d**) showed a distinct color change from purple (free formazan) to dark green or blue upon coordination of the formazanate to iridium. In contrast, in reactions involving diarylformazanates, the color of the product is almost identical to the free formazan, and these are most conveniently monitored by TLC. The isolated yields vary from 43–80% across the series.

NMR analysis of crude reaction mixtures indicates the possibility of two isomeric products. In particular, some of the complexes with electron-donating substituents on the formazanate, **1a**, **1b**, **3a**, **3b**, and **4a**, as well as **1c** (R² = *p*-C₆H₄-CN), initially showed the presence of two products in their ¹H NMR spectra, one with apparent C₂ symmetry and one with C_i symmetry. As unequivocally determined by X-ray crystallography (see below), these features are attributed to two different binding modes of the formazanate, one that involves a five-member chelate ring “open” form, binding through the 1- and 4-positions of the formazanate core, and the other a more typical six-member chelate “closed” form, binding through the 1- and 5-positions and denoted by a prime symbol (') in the compound numbering scheme. Varying the reaction solvents (dichloromethane, tetrahydrofuran) and temperature did not significantly alter the isomeric ratio, and prolonged heating of isolated mixtures of isomers did not lead to significant interconversion. Chromatographic purification was not effective as both isomers are similar in polarity. Recrystallization of the above-mentioned products was generally a good approach for purifying the mixtures, allowing **3a**, **3b**, and **4a** to be isolated as the C_i-symmetric “open” form with only trace amount of the “closed” isomer present. In contrast, in the C[^]N

= ppy series recrystallization allowed isolation of **1b'** and **1c'** exclusively as the C₂-symmetric “closed” isomer, whereas **1a/1a'** was isolated as a mixture of isomers even after repeated recrystallization attempts. The remaining triarylformazanate iridium complexes were all isolated in the five-member chelate conformation, as were all diarylformazanate complexes prepared from **Fze** and **Fzf**. To summarize, 15 of the 18 complexes were isolated in pure form as the five-member chelate “open” form, whereas only **1b'** and **1c'** were obtained in the “closed” form and **1a** was isolated as a mixture of both isomers. All of the compounds are air and moisture stable and are fully characterized by ¹H, ¹³C{¹H}, and ¹⁹F (for **2a**–**2f**) NMR spectroscopy and elemental analysis, which establish identity and bulk purity. NMR spectroscopy is especially useful for distinguishing the two isomers, with the C₂-symmetric “closed” isomer displaying chemical equivalency of the C[^]N ligands and the two R¹ substituents on the formazanate.

Scheme 1. General synthesis of complexes **1**–**4**.

X-ray Crystallography. The structures of **1c'**, **1d**, **2a**, **2c**, **2c'**, **2d**, **2e**, **3a**, and **4a** were confirmed by single-crystal X-ray diffraction, are shown in Figure 1 and Figure S1. Formazanate bond lengths and angles are summarized in Table 1 with refinement details collected in Tables S2–S4. The iridium metal center resides in the center of distorted octahedral coordination geometry with two C[^]N ligands and one formazanate. In all cases, the nitrogen atoms of C[^]N ligands are in a trans position relative to each other. The Ir–C bond distances (2.014(7)–2.033(4) Å) and Ir–N bond distances involving the C[^]N ligands (2.036(17)–2.091(8) Å) of all complexes are similar to those of the previously reported cyclometalated Ir complexes.^{52,54} Complex **1c'** crystallized with the formazanate exclusively in the six-membered chelate “closed” form, whereas in **2c** both isomers were present, modeled as a two-part disorder with 71% of the “open” form

Figure 1. X-ray crystal structure of complexes **1c'**, **2a**, **2c** ("open"), **2c'** ("closed"), **2d**, and **3a**, with ellipsoids shown at the 50% probability level and hydrogen atoms omitted. To better visualize the geometric differences between the "open" and "closed" forms, the bottom stick diagrams show bond lengths of **2d** and **1c'** in Å, with esd values in parentheses.

Table 1. Summary of crystallographic bond lengths (Å) and angles (deg).

	1c'	1d	2a^a	2c^b	2c'^b	2d	2e	3a	4a
d (Ir–N3/4) ^c	2.173(3)	2.208(8)	2.161(4)	2.210(5)	2.142(9)	2.152(2)	2.155(6)	2.1545(18)	2.192(3)
d (Ir–N6)	2.127(3)	2.119(8)	2.125(4)	2.110(3)	2.110(3)	2.135(3)	2.103(7)	2.1234(17)	2.153(3)
d (N3–N4)	1.309(4)	1.318(11)	1.313(5)	1.285(7)	1.325(12)	1.278(3)	1.263(11)	1.292(2)	1.309(5)
d (N4–C1)	1.344(5)	1.376(12)	1.383(5)	1.400(6)	1.418(10)	1.418(4)	1.397(11)	1.404(3)	1.378(5)
d (N5–C1)	1.363(5)	1.333(12)	1.328(6)	1.349(5)	1.349(5)	1.315(4)	1.314(12)	1.332(3)	1.330(6)
d (N5–N6)	1.294(4)	1.314(11)	1.313(5)	1.297(4)	1.297(4)	1.348(3)	1.304(8)	1.322(2)	1.322(5)
∠N(3/4)–Ir–N(6) ^d	82.45(11)	74.1(3)	74.53(14)	70.50(15)	94.5(3)	74.45(9)	75.6(3)	73.88(7)	73.62(13)

^a Average of two crystallographically independent molecules. ^b Both isomers disordered in the same crystal structure. ^c Formazanate Ir–N distance. Relevant distance is Ir–N3 for "closed" isomers **1c'** and **2c'**, and Ir–N4 for the rest. ^d Formazanate N–Ir–N chelate angle. Relevant angle is ∠N(3)–Ir–N(6) for "closed" isomers **1c'** and **2c'**, and ∠N(4)–Ir–N(6) for the rest.

(**2c**) and 29% of the "closed" form (**2c'**). As shown in Table 1 and Figure 1, the binding mode of the formazanate ("open" vs. "closed") has little influence on the Ir–N (formazanate) bond distances, which range between 2.103(7) and 2.210(5) Å and are significantly longer than those in other formazanate chelate complexes (1.809–2.090 Å).^{16,25,26,28,49,50,58} The different chelating modes of formazanates, however, impact the bond distances within the formazanate core critically. For both cases of **1c'** and **2c'**, which include the "closed" form of the formazanate, full π delocalization within the formazanate is indicated. The two N–N and two N–C distances are nearly equal and intermediate between single and double bonds. In contrast, for

"open form" formazanate chelating complexes, in many cases there are alternating short and long bond distances in the formazanate core, which is particularly apparent in the structures of **2d**, **2e**, **3a**, and **4a**. In these cases, the N(3)–N(4) distances exterior to the five-member chelate ring are shorter than the N(5)–N(6) distances in the chelate ring, and the N(4)–C(1) distance is significantly longer than N(5)–C(1). This pattern of bond distances is consistent with less π delocalization in the "open" form, which in the localized limit consists of alternating single and double bonds, as shown in the structure diagram in Scheme 1. Unsurprisingly, the other major structural difference between the "open" and "closed" forms is the

Figure 2. Overlaid electronic absorption spectra of (a) **2a–2f**, (b) **1f–4f**, and (c) **3a, 3b, 3e**, and **3f**. Spectra were recorded in tetrahydrofuran (THF) solution in room temperature. Data was collected in intervals of 1 nm, and symbols are included on each plot are to help distinguish the overlaid spectra.

chelate angles of formazanates, which for the “open” forms range between 74.10(3) and 74.45(9)° ($\angle N(4)–Ir–N(6)$), except **2c** which has an abnormally small chelate angle (70.50(15)°). The formazanate bite angles are larger for the C_2 -symmetric isomers, observed to be 82.45(11)° in **1c** and 94.5(3)° in **2c'**. There does not appear to be any systematic dependence of the key structural metrics on the presence of electron-withdrawing or electron-donating groups on the formazanate periphery.

The observation of both structure types (“open” and “closed”) suggests that the two structures are similar in free energy, though overall the “open” isomer seems to be favored. This observation stands in contrast to many previously described platinum(II) formazanates, where only the “closed” binding mode was observed.^{49,50} The covalent radii of platinum and iridium are quite similar,⁵⁹ so we don’t think the preference for a five-member chelate is because iridium(III) is smaller than platinum(II), nor are there any obvious electronic differences between the two isomers (see description of UV-vis and electrochemistry below). We propose that the “open” binding mode relieves steric pressure in these complexes, avoiding close approaches of the formazanate *N*-aryl substituent with the aryl rings of the cyclometalating ligand. In previously characterized bis-cyclometalated iridium β -diketiminato complexes from our group, we noted a close stacking arrangement of the *N*-aryl groups and the cyclometalated aryl groups,^{60,61} which is avoided in **1c'** (“closed” isomer) by a buckling of the formazanate backbone. In contrast, in all of the “open”-form structures presented here, except in **2c** where the two isomers are disordered, the aryl substituent at the iridium-bound N(6) is safely away from the steric congestion of the cyclometalating ligands, oriented orthogonal to the nearest cyclometalated aryl ring in a cleft between the two C^N ligands. Thus, the crystallographic evidence suggests that it is steric effects that are likely responsible for the “open” chelate conformation most of these complexes adopt.

UV-vis Absorption Spectroscopy. UV-vis absorption spectra of all cyclometalated iridium formazanate complexes were recorded, and Table 2 represents the summarized absorption data in tetrahydrofuran (THF). Figure 2 displays spectra of the complexes **2a–2f**, **1f–4f**, and **3a, 3b, 3e**, and **3f**. UV-vis absorption spectra of the remaining complexes in THF are shown in Figures S44 and S45. None of the complexes are photoluminescent in the visible region at room temperature or 77 K. All of the complexes described here are highly colored, appearing green or bluish green for the triarylformazanate complexes and greenish brown to dark red for the diarylformazanates complexes. These iridium formazanate compounds display

low-energy absorption bands between 525–677 nm with extinction coefficients between 2200–13000 M^{−1}cm^{−1} in the visible range of the spectrum, which is assigned as a formazanate ligand-centered $\pi \rightarrow \pi^*$ transition primarily involving HOMO and LUMO orbitals. As shown in Table 2 these low-energy absorption maxima are nearly identical for all of the triarylformazanate complexes **1a/1b**, **2a/2b**, **3a/3b** and **4a**, ranging from 628–639 nm for these complexes which have electron-donating substituents at both the R¹ and R² position of the formazanate scaffold (Figures 2, S44, and S45). Complex **1a** is isolated as a mixture of “open” and “closed” isomers but no significant spectral differences are observed by comparing this with the other **Fza** complexes that exist exclusively in the “open” configuration. The position of the low-energy absorption band depends strongly on the identity of the substituents at the central R² position of the formazanate backbone. Placing the electron withdrawing 4-cyanophenyl group in the R² position (**Fzc**) causes a hypsochromic shift of ~27–38 nm (715–989 cm^{−1}) in the low-energy absorption maximum for complexes **1c'** and **2c** relative to the respective **Fza** and **Fzb** complexes. In contrast, this low-energy absorption band is red-shifted for complexes **1d** (677 nm) and **2d** (655 nm), when the 4-cyanophenyl substituent is on the formazanate nitrogen atoms, i.e. R¹ = CN. As shown in Table 2, replacing the aryl group at the R² position with a cyano group in diarylformazanate (**Fze** and **Fzf**) complexes results in a significant blue-shift, with the low-energy absorption maximum occurring between 520 nm (**1f**) and 578 nm (**3e**) in this subset of complexes. This significant blue-shift in the formazanate $\pi \rightarrow \pi^*$ transition is likely a result of the decreased conjugation in the diarylformazanate analogues.

Additionally, higher-energy absorption bands are observed in the near-UV and visible regions, dependent primarily on the identity of the cyclometalated ligands, characteristic of Ir(d) $\rightarrow \pi^*$ metal-to-ligand and charge transfer (MLCT) bands and only slightly affected by the *N*-aryl substituents of the formazanate ligands. These bands typically overlap with other high-energy absorption features, likely localized $\pi \rightarrow \pi^*$ transitions, though in general F₂ppy-ligated complexes **2a–f** display MLCT bands at the shortest wavelengths, with piq complexes (**4a** and **4f**) having MLCT bands at the longest wavelength, consistent with many other cyclometalated iridium complexes.⁶² Complexes of **Fzc** (R² = 4-cyanophenyl) display a distinct absorption at ~400 nm, which is not observed in other members of the series and is likely attributed to a transition localized on the 4-cyanophenyl substituent. In many complexes, particularly in the bt (**3**, Figure 2c) and piq series (**4**, Figure S45), the high-energy absorption features overlap with low-energy formazanate-centered

bands, giving rise to panchromatic visible absorption, as observed for previously reported cyclometalated platinum formazanate compounds with C[^]N = 2-phenylquinoline (pq), an isomer of piq.⁵⁰

Table 2. Summary of UV-vis absorption data recorded in tetrahydrofuran (THF) at room temperature.

	λ / nm ($\epsilon \times 10^{-3}$ / M ⁻¹ cm ⁻¹)
1a/1a'	265 (53), 480 (6.7), 633 (13)
1b'	261 (25), 463 (3.6), 630 (3.2)
1c'	264 (71), 387 (42), 602 (8.7)
1d	270 (17), 370 ^a (6.8), 677 (4.6)
1e	260 (30), 380 ^a (8.0), 476 (5.8), 554 (6.6)
1f	258 (33), 342 (10), 401 ^a (7.9), 520 (7.5)
2a	250 (34), 347 ^a (13), 445 (3.2), 628 (8.6)
2b	252 (27), 454 (2.9), 639 (7.5)
2c	251 (52), 390 (18), 601 (10)
2d	260a (38), 313 ^a (23), 360 ^a (17), 655 (10)
2e	250 (28), 300 (14), 454 ^a (4.2), 551 (6.5)
2f	261 (15), 353 ^a (5.4), 532 (3.5)
3a	320 (43), 410 ^a (11), 630 (12)
3b	262 (36), 319 (39), 635 (10)
3e	263 (34), 319 (36), 382 ^a (18), 443 ^a (14), 578 (2.2)
3f	266 (38), 321 (36), 384 ^a (13), 443 (12), 596 (6.7)
4a	293 (51), 349 ^a (29), 435 ^a (9.0), 638 (9.4)
4f	285 (44), 343 (26), 403 (14), 443 (13), 525 ^a (10)

^a Shoulder.

UV-vis spectra were also recorded in three solvents of varying polarity (toluene, THF, and MeOH), shown in Figures S46–S48, and only slight solvatochromic shifts of <10 nm were observed for the low-energy absorption bands in all cyclometalated iridium formazanate complexes, further supporting the assignment of this band as a ligand-localized $\pi \rightarrow \pi^*$ transition with minimal charge-transfer character. Taken together, these results show that the UV-vis absorption features of the iridium formazanate complexes depend on the location and identity of the substituents on the formazan scaffold as well as the cyclometalating ligand. Changing substituents at the R¹ and R² position of the formazanate ligand allows predictive control over the formazanate-based low energy $\pi \rightarrow \pi^*$ transition, which spans a relatively broad range of 520–677 nm in this series of complexes.

Electrochemistry. The electrochemical properties of complexes **1–4** were investigated by cyclic voltammetry (CV) experiments, and the results are summarized in Table 3 with the voltammograms shown in Figures 3 and S49–S51. The compounds display both oxi-

dation and reduction features in their cyclic voltammograms. Ligand-centered reductions that occur at mild potential are generally one of the most important features of coordinated formazanate complexes, and these features are discussed here along with the Ir^{IV}/Ir^{III} oxidation waves.

Table 3. Summary of electrochemical data for complexes **1–4**.

	Ir ^{IV} / Ir ^{III} E^{ox} (V)	Fz-centered E^{red} (V)
1a/1a'	−0.02	−1.96 ^a
1b'	−0.10	−1.97 ^a
1c'	0.23	−1.95
1d	0.37	−1.41
1e	0.55	−1.61, −2.10 ^a
1f	0.86	−1.26, −1.70
2a	0.08	−1.83 ^a
2b	−0.02	−1.89 ^a
2c	0.23	−1.79 ^a
2d	0.51	−1.31, −1.78
2e	0.70	−1.50, −1.94 ^a
2f	1.15	−1.22, −1.71
3a	0.01	−1.98 ^a
3b	−0.06	−1.95 ^a
3e	0.68 ^a	−1.72
3f	0.97	−1.29, −1.74
4a	0.01	−1.96 ^a
4f	0.83 ^a	−1.27, −1.68

^a Irreversible wave. $E_{\text{p,c}}$ or $E_{\text{p,a}}$ is reported.

Overlaid CVs of complexes **2a–2f** with different formazanate substituents (top) and overlaid CVs of four diarylformazanate complexes **1f**, **2f**, **3f**, and **4f** (bottom) are shown in Figure 3. The first reduction wave for all complexes is assigned as a formazanate-centered one electron reduction which occurs in the range of −1.22 to −1.98V (all potentials referenced to the ferrocenium/ferrocene couple). The F₂ppy series (**2a–f**) provides the best insight into the effect of the formazanate structure on the redox properties, since this series includes all six formazanate ligands studied here and all of them bind exclusively in the five-member chelate “open” form in these analogues. As the data in Figure 3 and Table 1 shows, the redox potentials in **2a–c** follow the trend expected from the electron donating/withdrawing attributes of the substituents, although the effects are modest. Moving from **2a** to **2b**, where the R¹ substituent is changed from CH₃ to a more electron-donating OCH₃, results in a cathodic (negative) shift of the reduction potential by 60 mV. Similarly, comparing **2a** to **2c**, where the *p*-C₆H₄-OCH₃ R² substituent is replaced with the more electron-withdrawing *p*-cyanophenyl, we note a 40 mV anodic (positive) shift in the reduction potential. A much more dramatic change in potential occurs when electron-withdrawing cyano substituents are added to the R¹ position, with the potential in **2d** more positive than that of **2a** by over 500 mV. Similarly large effects are observed in **2e** and **2f**, where the R² aryl substituent

Figure 3. Overlaid cyclic voltammograms of complexes **2a–2f** (top), and **1f**, **2f**, **3f**, and **4f** (bottom). CVs were recorded in CH_2Cl_2 with 0.1 M NBu_4PF_6 supporting electrolyte, using a glassy carbon working electrode and a scan rate of 0.1 V/s. The arrows indicate the scan direction. Concentrations were not carefully controlled, and currents are low in some of the plots because of limited solubility in CH_2Cl_2 .

is replaced with a cyano group, resulting in comparatively mild formazanate-based reduction potentials, in particular in **2f** ($\text{R}^1 = \text{R}^2 = \text{CN}$, $E_{\text{red}} = -1.22$ V). Similar substituent effects are observed in the other members of the series with different cyclometalating ligands.

The effects of the cyclometalating ligand on the reduction potentials are modest, and in general the observed reduction potential is mainly determined by the substituent pattern on the formazanate. Fluorination of the phenylpyridine ligand causes an overall anodic shift (~ 100 mV on average) for complexes **2a–2f** (Figure 3) if we compare them with the set **1a–1f**, but complexes with $\text{C}^{\wedge}\text{N} = \text{bt}$ or piq have very similar potentials to their ppy analogues, at parity of formazanate structure. In addition, the potentials for the complexes

that were isolated as the “closed” isomer (**1b'** and **1c'**) or as a mixture of isomers (**1a**) are all very similar to the other members of the series with the same formazanate ligand, suggesting that the formazanate-centered LUMO energy and corresponding redox potential depend little on the binding mode of the formazanate.

All of the complexes here (except **3e** and **4f**) also display a formal $\text{Ir}^{\text{IV}}/\text{Ir}^{\text{III}}$ redox couple which has slight dependence on the identity of the $\text{C}^{\wedge}\text{N}$ ligand but is highly sensitive to the identity of the formazanate ligands. Electron-rich complexes **1a/1b**, **2a/2b**, **3a/3b** and **4a** oxidize at similar potentials across the series, and again the isomeric form of the complex does not appear to have a large effect on the observed potential (Table 3). The oxidation potential of these seven complexes are very near the Fc^+/Fc potential and again have a slight dependence on the formazanate substituents, with the most electron-rich **Fzb** complexes being easiest to oxidize. The addition of cyano substituents in the remaining complexes renders the complexes more difficult to oxidize, with shifts in potential that are qualitatively similar to those discussed above for the reduction potentials. The four **Fzf** complexes, where $\text{R}^1 = \text{R}^2 = \text{CN}$, have the most positive oxidation potentials (≥ 0.83 V), and the complexes where only one of the R^1 and R^2 positions includes a cyano group (**Fzc–e**) have $\text{Ir}^{\text{IV}}/\text{Ir}^{\text{III}}$ potentials intermediate between the most electron-rich and electron-poor members of the series. As with the reduction potentials, the $\text{C}^{\wedge}\text{N}$ ligands exert a modest effect on the formally $\text{Ir}^{\text{IV}}/\text{Ir}^{\text{III}}$ couple, with F_2ppy complexes being the most difficult to oxidize for a given formazanate ligand. We note that although this oxidation potential can be formally classified as $\text{Ir}^{\text{IV}}/\text{Ir}^{\text{III}}$, and in typical cyclometalated iridium complexes the HOMO does include significant Ir $d\pi$ character,⁶³ the strong dependence of this potential on the formazanate structure implies that the HOMO in the complexes described here is also primarily formazanate ligand-centered, like the LUMO. Consistent with this supposition, previously reported platinum formazanate complexes from our group,⁴⁹ as well as cyclometalated iridium complexes with structurally analogous β -diketiminato ancillary ligands,⁶¹ both have HOMOs that are almost exclusively formazanate or β -diketiminato-centered, with minor contribution from the metal.

One other noteworthy insight to come out of this work is the effect of the metal center and coordination geometry on the formazanate-centered optical transitions and redox properties. Our group has also prepared an extensive series of cyclometalated platinum formazanate complexes,⁵⁰ using many of the same cyclometalating ligands and formazanates used in this work (except for **Fzd**, and piq , which we did not use to prepare any platinum complexes). In the UV-vis absorption spectra, in every case the low-energy formazanate $\pi \rightarrow \pi^*$ transition is significantly blue-shifted in the iridium complexes, by at least 23 nm (767 cm^{-1}) and as much as 122 nm (3650 cm^{-1}) when comparing **1f** to its platinum congener. In the cyclic voltammograms, the formazanate-centered reduction potentials are substantially different as well, cathodically (negatively) shifted by at least 290 mV and as much as 500 mV in the iridium complexes. We do note that some of the reduction waves in the iridium complexes are irreversible, which makes these comparisons less quantitatively meaningful, but even in cases where both the platinum and iridium analogues have well-behaved, reversible reduction waves the iridium complex is more difficult to reduce by a substantial margin. Although electrochemical oxidation of the platinum complexes tends not to be as well-behaved and we have not investigated it as thoroughly, we

can compare some complexes and we find that the iridium complexes are in general easier to oxidize, although the oxidation potentials are not as sensitive to the identity of the metal as the reduction potentials, in all cases differing by <200 mV. Taken together, these observations indicate that, compared to cyclometalated platinum formazanate complexes, the iridium analogues have destabilized HOMO and LUMO energies and larger HOMO–LUMO gaps. The significant differences between the formazanate-centered properties in platinum and iridium complexes underscores the importance of d-orbital overlap with the formazanate in determining frontier orbital energies, an emerging theme in our work on formazanate 5d metal complexes.

Conclusion

In this work, we disclose the first examples of cyclometalated iridium formazanate complexes prepared by a general synthetic strategy and a thorough study of the electronic modification of the formazanate ligand on the electrochemical and photophysical properties is also presented. Structural elucidation of the complexes reveals two distinct binding modes for the formazanate, with the typical six-membered chelate form and an unusual five-membered “open” structure both observed. A systematic comparison of different cyclometalated and formazanate ligands reveals that the redox potentials are much more sensitive to the identity of the substituents on the formazanate backbone. The UV-vis absorption features prove some predictable control of photophysical properties by tuning the formazanate and cyclometalated ligands independently. In future works, we plan to continue our exploration of 5d metal formazanate complexes, further underscoring the effects of the metal identity, oxidation state, and coordination geometry on the formazanate-derived redox and optical properties.

EXPERIMENTAL SECTION

Materials. Reactions were carried out in a nitrogen atmosphere using standard Schlenk techniques. Solvents, starting materials, and reagents were of commercial origin and used without further purification unless stated otherwise below. Tetrahydrofuran (THF) and toluene for UV-vis spectroscopy, and acetonitrile and dichloromethane (DCM) for electrochemical measurements were dried by the method of Grubbs⁶⁴, passing through dual alumina columns on a commercial solvent purification system (SPS). The acetonitrile was further dried by storage over 3A molecular sieves. Tetrabutylammonium hexafluorophosphate (TBAPF₆) was recrystallized from hot ethanol and ferrocene was sublimed at ambient pressure before use in electrochemical experiments. CDCl₃ and CD₃CN for NMR spectroscopy were stored over potassium carbonate and molecular sieves to remove acidic impurities and moisture. The ligands 3-*p*-methoxyphenyl-1,5-di-*p*-tolylformazan (**Fza**), 1,3,5-tri-*p*-methoxyphenylformazan (**Fzb**) and 3-*p*-cyanophenyl-1,5-di-*p*-tolylformazan (**Fzc**), and 3-*p*-tolyl-1,5-di-*p*-cyanophenylformazan (**Fzd**) were prepared by the method of Hicks *et al.*⁶⁵ The ligands 3-cyano-1,5-di-*p*-tolylformazan (**Fze**) and 3-cyano-1,5-di-*p*-cyanophenylformazan (**Fzf**) were prepared by following the literature procedures.³¹ The iridium precursors [Ir(ppy)₂(μ-Cl)]₂ (ppy = 2-phenylpyridine), [Ir(F₂ppy)₂(μ-Cl)]₂ (F₂ppy = 2-(2,4-difluorophenyl)pyridine), [Ir(bt)₂(μ-Cl)]₂ (bt = 2-phenylbenzothiazole), and [Ir(piq)₂(μ-Cl)]₂ (piq = 1-phenylisoquinoline) were prepared by a modified version of the well-known Nonoyama procedure.^{66,67}

Physical Methods. NMR spectra were recorded at room temperature using a JEOL ECA-600, ECA-500, or ECA-400 NMR spectrometer. UV-vis absorption spectra were recorded in THF, toluene, and MeOH solutions in screw-capped 1 cm quartz cuvettes using an Agilent Cary 8454 UV-vis spectrophotometer. Cyclic voltammetry (CV) measurements were performed with a CH Instruments 602E potentiostat interfaced with a nitrogen glovebox via wire feedthroughs. Samples were dissolved in dichloromethane (CH₂Cl₂) with 0.1 M TBAPF₆ as a supporting electrolyte. A 3 mm diameter glassy carbon working electrode, a platinum wire counter electrode, and a silver wire pseudo-reference electrode were used. Potentials were referenced to an internal standard of ferrocene. The bulk purity for all complexes is established by elemental analysis, performed by Atlantic Microlab, Inc.

Ir(ppy)₂(Fza) (1a/1a'). [Ir(ppy)₂(μ-Cl)]₂ (101 mg, 0.0942 mmol) and **Fza** (67 mg, 0.19 mmol) were combined in ethanol (15 mL) with excess triethylamine (0.10 mL), and the mixture was deoxygenated under the protection of N₂. The mixture was refluxed for 24 h and the color changed from red to green. The reaction completion was confirmed by TLC, which showed two green products of almost identical polarity, likely the “open” and “closed” isomers. The solvent was removed using rotary evaporation, and the product was re-dissolved in ethyl acetate to filter through neutral alumina in order to remove insoluble impurities. After removing ethyl acetate, column chromatography (hexane / ethyl acetate gradient eluent, neutral alumina) was performed to purify the product but attempts to separate the isomers using chromatography was not successful. Both isomers were eluted together from the column, and the combined products were recrystallized (THF / pentane) later to get dark green solid. NMR analysis suggests a ca. 2:1 ratio of the “open” (**1a**) and “closed” (**1a'**) isomers, which results in very similar integration values for the resonances associated with each isomer. As such, a clear assignment of the peaks was not possible, and integration values for the ¹H NMR peaks are not provided. The spectrum is shown in Figure S2 with relative integration values shown. Yield: 83 mg (51%). ¹H NMR (400 MHz, CDCl₃) δ: 8.70 (d, *J* = 5.6 Hz, ArH), 8.63 (d, *J* = 5.6 Hz, ArH), 8.43 (d, *J* = 6.0 Hz, ArH), 7.93 (d, *J* = 7.8 Hz, ArH), 7.58–7.87 (m, ArH), 7.30 (d, *J* = 7.8 Hz, ArH), 7.20 (dd, *J* = 5.9 Hz, ArH), 6.94–7.11 (m, ArH), 6.86 (d, *J* = 7.8 Hz, ArH), 6.73 (t, *J* = 7.3 Hz, ArH), 6.47–6.69 (m, ArH), 6.12–6.38 (m, ArH), 5.94 (d, *J* = 7.8 Hz, ArH), 5.57 (d, *J* = 7.8 Hz, ArH), 3.80 (s, OCH₃, both isomers coincident), 2.12 (s, CH₃), 2.10 (s, CH₃), 2.04 (s, CH₃). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ: 169.3, 168.5, 167.5, 158.8, 158.6, 158.2, 156.9, 154.7, 153.7, 152.4, 152.2, 151.8, 150.1, 149.6, 149.0, 143.7, 143.5, 142.8, 136.8, 136.7, 136.5, 134.4, 134.3, 134.2, 133.8, 133.2, 131.1, 130.2, 129.6, 129.0, 128.8, 128.5, 128.3, 127.6, 127.4, 125.6, 123.8, 123.7, 123.4, 122.2, 121.9, 121.5, 121.3, 120.6, 120.1, 119.3, 119.0, 118.9, 118.7, 113.4, 55.47, 55.4, 20.94, 20.85. Anal. Calcd for C₄₄H₃₈IrN₆O: C, 61.52; H, 4.46; N, 9.78. Found: C, 61.69; H, 4.47; N, 9.76.

Ir(ppy)₂(Fzb) (1b'). The title compound was prepared by the general method described above for complex **1a/1a'**, using [Ir(ppy)₂(μ-Cl)]₂ (50 mg, 0.047 mmol) and **Fzb** (37 mg, 0.094 mmol). The product was isolated as a mixture of isomers and recrystallized later (CH₂Cl₂ / pentane) to get a dark green solid. Yield: 36 mg (43%). We were unable to obtain satisfactory elemental analysis for this compound, but the NMR spectrum in Figures S4 and S5 provide evidence for bulk purity. The minor impurity peaks in the ¹H NMR

spectrum arise from a small amount of the “open” isomer **1b** present in the isolated product. ^1H NMR (400 MHz, CDCl_3) δ : 8.70 (d, J = 5.5 Hz, 2H, ArH), 7.82 (d, J = 8.7 Hz, 2H, ArH), 7.60–7.71 (m, 4H, ArH), 7.21–7.28 (m, 2H, ArH), 6.95–7.03 (m, 2H, ArH), 6.86 (d, J = 8.7 Hz, 2H, ArH), 6.65 (t, J = 7.3 Hz, 2H, ArH), 6.51–6.61 (m, 6H, ArH), 6.18–6.32 (m, 6H, ArH), 3.80 (s, 3H, OCH_3), 3.62 (s, 6H, OCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ : 168.5, 158.3, 156.8, 154.8, 150.0, 149.0, 148.9, 143.7, 136.9, 134.3, 133.8, 130.1, 128.9, 125.6, 124.6, 123.7, 121.5, 120.7, 118.8, 113.4, 113.1, 112.2, 55.47, 55.21.

Ir(ppy)₂(Fzc) (1c'). $[\text{Ir}(\text{ppy})_2(\mu\text{-Cl})]_2$ (54 mg, 0.05 mmol) and **Fzc** (34 mg, 0.10 mmol) were combined in ethanol (10 mL) with excess triethylamine (0.1 mL), and the mixture was deoxygenated under the protection of N_2 . The mixture was refluxed for 36 h, and the color changed from red to green. The reaction completion was confirmed by TLC. Solvent was removed using rotary evaporation, and the product was re-dissolved in a minimum amount of ethyl acetate. After that column chromatography (hexane / ethyl acetate gradient eluent, neutral alumina) was performed to purify the product, which was crystallized by vapor diffusion of pentane into a concentrated CH_2Cl_2 solution. Yield: 43 mg (50%). ^1H NMR (500 MHz, CDCl_3) δ : 8.68 (d, J = 5.5 Hz, 2H, ArH), 7.98 (d, J = 8.6 Hz, 2H, ArH), 7.69–7.74 (m, 2H, ArH), 7.65 (d, J = 7.9 Hz, 2H, ArH), 7.52 (d, J = 8.6 Hz, 2H, ArH), 7.18–7.20 (m, 2H, ArH), 7.05 (ddd, J = 7.2, 5.8, 1.2 Hz, 2H, ArH), 6.61–6.65 (m, 2H, ArH), 6.57 (dd, J = 7.4, 1.1 Hz, 2H, ArH), 6.53 (d, J = 8.1 Hz, 4H, ArH), 6.44 (d, J = 8.4 Hz, 4H, ArH), 6.17 (d, J = 7.0 Hz, 2H, ArH), 2.11 (s, 6H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ : 168.5, 153.8, 153.7, 149.7, 146.8, 146.0, 143.5, 137.2, 134.9, 133.7, 131.7, 129.0, 127.6, 124.1, 123.7, 123.1, 121.8, 120.9, 120.4, 119.0, 107.6, 20.9. Anal. Calcd for $\text{C}_{44}\text{H}_{34}\text{N}_7\text{Ir}$: C, 61.95, H, 4.02, N, 11.49. Found: C, 62.04, H, 4.00, N, 11.36.

Ir(ppy)₂(Fzd) (1d). The title compound was prepared by the general method described above for complex **1c'**, using $[\text{Ir}(\text{ppy})_2(\mu\text{-Cl})]_2$ (54 mg, 0.050 mmol) and **Fzd** (37 mg, 0.10 mmol). Yield: 62 mg (72%). ^1H NMR (500 MHz, CDCl_3) δ : 8.46 (d, J = 5.7 Hz, 1H, ArH), 8.34 (d, J = 5.6 Hz, 1H, ArH), 7.83–7.88 (m, 1H, ArH), 7.82 (d, J = 7.2 Hz, 1H, ArH), 7.73 (d, J = 8.3 Hz, 2H, ArH), 7.72 (dd, J = 7.1, 1.3 Hz, 1H, ArH), 7.68 (d, J = 7.2 Hz, 1H, ArH), 7.33 (dd, J = 7.9, 1.0 Hz, 1H, ArH), 7.25 (d, J = 8.1 Hz, 1H, ArH), 7.20 (s, 2H, ArH), 7.18 (s, 2H, ArH), 7.10 (d, J = 8.9 Hz, 4H, ArH), 6.87 (d, J = 8.6 Hz, 2H, ArH), 6.79 (td, J = 7.6, 1.2 Hz, 1H, ArH), 6.68–6.74 (m, 2H, ArH), 6.40 (td, J = 7.5, 1.1 Hz, 1H, ArH), 6.35 (d, J = 8.2 Hz, 2H, ArH), 5.91 (dd, J = 7.8, 0.9 Hz, 1H, ArH), 5.63–5.67 (m, 1H, ArH), 2.37 (s, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ : 168.9, 167.4, 161.3, 160.4, 157.0, 155.9, 155.3, 151.6, 149.1, 148.3, 147.2, 143.4, 142.6, 138.3, 137.6, 137.5, 132.1, 132.0, 130.7, 130.5, 130.2, 129.7, 129.1, 128.9, 124.3, 124.2, 122.6, 122.5, 122.3, 122.2, 121.1, 120.5, 119.8, 119.5, 119.4, 108.3, 105.7, 21.5. Anal. Calcd for $\text{C}_{44}\text{H}_{31}\text{N}_8\text{Ir}$: C, 61.17, H, 3.62, N, 12.97. Found: C, 61.03, H, 3.68, N, 12.72.

Ir(ppy)₂(Fze) (1e). The title compound was prepared by the general method described above for complex **1c'**, using $[\text{Ir}(\text{ppy})_2(\mu\text{-Cl})]_2$ (54 mg, 0.050 mmol) and **Fze** (28 mg, 0.10 mmol). Yield: 47 mg (60%). ^1H NMR (500 MHz, CDCl_3) δ : 8.37 (d, J = 5.5 Hz, 1H, ArH), 8.27 (d, J = 5.4 Hz, 1H, ArH), 7.78–7.83 (m, 1H, ArH), 7.76 (d, J = 7.7 Hz, 1H, ArH), 7.68–7.72 (m, 1H, ArH), 7.65 (d, J = 7.9

Hz, 1H, ArH), 7.27 (s, 1H, ArH), 7.19 (d, J = 7.4 Hz, 1H, ArH), 7.12–7.16 (m, 1H, ArH), 7.05–7.09 (m, 1H, ArH), 6.82 (d, J = 8.5 Hz, 2H, ArH), 6.74 (td, J = 7.5, 0.8 Hz, 1H, ArH), 6.67 (d, J = 7.8 Hz, 3H, ArH), 6.59 (t, J = 7.8 Hz, 1H, ArH), 6.38 (d, J = 8.0 Hz, 2H, ArH), 6.30 (t, J = 7.8 Hz, 1H, ArH), 6.22 (d, J = 8.1 Hz, 2H, ArH), 5.89 (d, J = 7.5 Hz, 1H, ArH), 5.55 (d, J = 7.5 Hz, 1H, ArH), 2.13 (s, 3H, CH_3), 2.04 (s, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ : 168.8, 167.2, 167.2, 153.7, 151.2, 150.6, 150.4, 149.7, 148.1, 143.4, 142.6, 137.4, 136.4, 136.3, 135.2, 132.0, 130.9, 129.9, 129.4, 128.5, 128.3, 124.0, 123.9, 122.6, 122.3, 122.1, 121.9, 120.1, 120.1, 119.2, 119.2, 116.2, 21.0, 21.0. Anal. Calcd for $\text{C}_{38}\text{H}_{30}\text{N}_7\text{Ir}$: C, 58.75, H, 3.89, N, 12.62. Found: C, 58.90, H, 3.89, N, 12.42.

Ir(ppy)₂(Fzf) (1f). The title compound was prepared by the general method described above for complex **1c'**, using $[\text{Ir}(\text{ppy})_2(\mu\text{-Cl})]_2$ (54 mg, 0.050 mmol) and **Fzf** (30 mg, 0.10 mmol). Yield: 41 mg (52%). ^1H NMR (500 MHz, CD_3CN) δ : 8.40 (d, J = 5.6 Hz, 1H, ArH), 8.26 (d, J = 5.5 Hz, 1H, ArH), 7.97 (t, J = 7.1 Hz, 1H, ArH), 7.91 (d, J = 8.0 Hz, 1H, ArH), 7.85 (t, J = 7.8 Hz, 1H, ArH), 7.76 (d, J = 8.0 Hz, 1H, ArH), 7.32 (d, J = 7.7 Hz, 1H, ArH), 7.28 (dd, J = 7.6, 4.3 Hz, 2H, ArH), 7.20–7.24 (m, 1H, ArH), 7.17 (d, J = 8.7 Hz, 2H, ArH), 7.00 (d, J = 8.5 Hz, 2H, ArH), 6.98 (d, J = 8.7 Hz, 2H, ArH), 6.75 (t, J = 7.0 Hz, 1H, ArH), 6.69 (dd, J = 10.7, 4.2 Hz, 1H, ArH), 6.66 (dd, J = 11.5, 4.2 Hz, 1H, ArH), 6.49 (d, J = 8.4 Hz, 2H, ArH), 6.40 (t, J = 6.9 Hz, 1H, ArH), 5.83 (d, J = 7.6 Hz, 1H, ArH), 5.60 (d, J = 7.5 Hz, 1H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CD_3CN) δ : 167.7, 166.1, 155.3, 154.2, 152.5, 151.5, 150.5, 146.8, 144.0, 143.2, 138.8, 138.8, 137.9, 137.2, 132.2, 132.0, 130.6, 129.9, 129.4, 124.4, 124.1, 123.9, 123.5, 123.0, 122.6, 121.1, 120.6, 120.1, 119.7, 118.7, 118.64, 114.6, 110.1, 108.1. Anal. Calcd for $\text{C}_{38}\text{H}_{24}\text{N}_9\text{Ir}$: C, 57.13, H, 3.03, N, 15.78. Found: C, 57.30, H, 3.18, N, 15.56.

Ir(F₂ppy)₂(Fza) (2a). The title compound was prepared by the general method described above for complex **1c'**, using $[\text{Ir}(\text{F}_2\text{ppy})_2(\mu\text{-Cl})]_2$ (61 mg, 0.050 mmol) and **Fza** (36 mg, 0.10 mmol). Yield: 76 mg (82%). ^1H NMR (500 MHz, CD_3CN) δ : 8.57 (d, J = 4.3 Hz, 1H, ArH), 8.44 (d, J = 4.5 Hz, 1H, ArH), 8.17 (d, J = 6.9 Hz, 1H, ArH), 8.03 (d, J = 6.9 Hz, 1H, ArH), 7.92 (d, J = 8.1 Hz, 2H, ArH), 7.78–7.85 (m, 1H, ArH), 7.71 (td, J = 8.0, 1.2 Hz, 1H, ArH), 7.11 (ddd, J = 7.3, 5.9, 1.4 Hz, 1H, ArH), 7.08 (ddd, J = 7.3, 5.9, 1.4 Hz, 1H, ArH), 6.88 (dd, J = 7.0, 3.0 Hz, 4H, ArH), 6.71 (d, J = 6.7 Hz, 2H, ArH), 6.51 (d, J = 6.5 Hz, 2H, ArH), 6.27 (ddd, J = 12.3, 9.1, 2.3 Hz, 1H, ArH), 6.15 (d, J = 5.9 Hz, 2H, ArH), 6.06 (ddd, J = 12.5, 9.3, 2.3 Hz, 1H, ArH), 5.41 (dd, J = 7.0, 1.8 Hz, 1H, ArH), 5.11 (dd, J = 7.0, 1.8 Hz, 1H, ArH), 3.81 (s, 3H, OCH_3), 2.15 (s, 3H, CH_3), 2.13 (s, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_3CN) δ : 165.8 (d, J_{CF} = 5.3 Hz), 164.2 (d, J_{CF} = 5.5 Hz), 163.5 (d, J_{CF} = 10.2 Hz), 163.3, 161.7 (d, J_{CF} = 9.8 Hz), 161.0 (d, J_{CF} = 7.7 Hz), 159.8 (d, J_{CF} = 5.2 Hz), 158.8, 158.4, 154.2, 152.2, 151.8, 151.6, 149.8, 137.9, 137.7, 135.1, 133.9, 130.2, 128.6, 128.2, 127.5, 127.2, 126.9, 123.2 (d, J_{CF} = 15.9 Hz), 122.9 (d, J_{CF} = 16.4 Hz), 122.5, 122.2, 121.7, 120.4, 113.9 (d, J_{CF} = 12.5 Hz), 113.5, 113.0 (d, J_{CF} = 13.8 Hz), 97.7 (t, J_{CF} = 26.8 Hz), 95.9 (t, J_{CF} = 27.1 Hz), 55.4, 20.9, 20.6. ^{19}F NMR (470 MHz, CDCl_3) δ : -107.6 (dd, J = 19.0, 9.2 Hz, 1F), -109.4 (dd, J = 18.9, 9.4 Hz, 1F), -110.2 (t, J = 12.4 Hz, 1F), -111.1 (t, J = 11.4 Hz, 1F). Anal. Calcd for $\text{C}_{44}\text{H}_{33}\text{N}_6\text{F}_4\text{OIr}$: C, 56.83, H, 3.58, N, 9.04. Found: C, 56.76, H, 3.67, N, 8.90.

Ir(F₂ppy)₂(Fzb) (2b). The title compound was prepared by the general method described above for complex **1c'**, using

[Ir(F₂ppy)₂(μ-Cl)]₂ (61 mg, 0.050 mmol) and **Fzb** (39 mg, 0.10 mmol). Yield: 53 mg (55%). ¹H NMR (500 MHz, CD₃CN) δ: 8.58–8.62 (m, 1H, ArH), 8.46 (d, *J* = 5.5 Hz, 1H, ArH), 8.13 (d, *J* = 8.6 Hz, 1H, ArH), 7.99 (d, *J* = 8.4 Hz, 1H, ArH), 7.93–7.97 (m, 1H, ArH), 7.83 (dd, *J* = 11.7, 5.1 Hz, 1H, ArH), 7.68 (d, *J* = 9.0 Hz, 2H, ArH), 7.29 (t, *J* = 7.3 Hz, 1H, ArH), 7.24 (t, *J* = 6.6 Hz, 1H, ArH), 6.88 (d, *J* = 9.0 Hz, 2H, ArH), 6.72 (d, *J* = 9.0 Hz, 2H, ArH), 6.41 (d, *J* = 6.9 Hz, 2H, ArH), 6.38–6.42 (m, 1H, ArH), 6.30 (d, *J* = 9.1 Hz, 2H, ArH), 6.21 (d, *J* = 8.1 Hz, 2H, ArH), 6.06–6.12 (m, 1H, ArH), 5.43 (dd, *J* = 7.6, 3.5 Hz, 1H, ArH), 5.21 (dd, *J* = 8.9, 2.4 Hz, 1H, ArH), 3.77 (s, 3H, OCH₃), 3.62 (s, 3H, OCH₃), 3.60 (s, 3H, OCH₃). ¹³C {¹H} NMR (126 MHz, CD₃CN) δ: 164.9 (d, *J*_{CF} = 7.1 Hz), 163.2 (d, *J*_{CF} = 7.4 Hz), 162.4 (d, *J*_{CF} = 5.2 Hz), 161.7 (d, *J*_{CF} = 12.1 Hz), 161.6 (d, *J*_{CF} = 13.8 Hz), 161.5, 159.7 (d, *J*_{CF} = 4.7 Hz), 159.6 (d, *J*_{CF} = 3.9 Hz), 158.8, 158.4, 157.5, 156.5, 154.7 (d, *J*_{CF} = 6.3 Hz), 151.8, 150.8, 148.1, 147.6, 138.7, 138.6, 130.5, 127.7, 127.4, 123.5, 123.3 (d, *J*_{CF} = 19.9 Hz), 123.1, 123.0, 122.7 (d, *J*_{CF} = 20.4 Hz), 121.8, 114.1 (d, *J*_{CF} = 16.5 Hz), 113.1, 112.9, 112.8, 112.6, 97.31, 96.16, 55.0, 54.9, 54.8. ¹⁹F NMR (470 MHz, CD₃CN) δ: –109.5 (dd, *J* = 18.8, 9.4 Hz, 1F), –111.2 (q, *J* = 9.5 Hz, 1F), –111.7 (t, *J* = 11.8 Hz, 1F), –111.8 (t, *J* = 11.8 Hz, 1F). Anal. Calcd for C₄₄H₃₃N₈F₄O₃Ir: C, 54.94, H, 3.46, N, 8.74. Found: C, 54.76, H, 3.51, N, 8.57.

Ir(F₂ppy)₂(Fzc) (2c). The title compound was prepared by the general method described above for complex **1c'**, using [Ir(F₂ppy)₂(μ-Cl)]₂ (61 mg, 0.050 mmol) and **Fzc** (34 mg, 0.10 mmol). Yield: 67 mg (73%). ¹H NMR (500 MHz, CDCl₃) δ: 8.48 (d, *J* = 5.9 Hz, 1H, ArH), 8.40 (d, *J* = 6.5 Hz, 1H, ArH), 8.18 (d, *J* = 8.4 Hz, 3H, ArH), 8.03 (d, *J* = 9.2 Hz, 1H, ArH), 7.85 (t, *J* = 7.8 Hz, 1H, ArH), 7.74 (t, *J* = 7.8 Hz, 1H, ArH), 7.57 (d, *J* = 8.4 Hz, 2H, ArH), 7.14 (t, *J* = 6.6 Hz, 1H, ArH), 7.11 (t, *J* = 6.6 Hz, 1H, ArH), 6.80 (d, *J* = 8.4 Hz, 2H, ArH), 6.73 (d, *J* = 8.4 Hz, 2H, ArH), 6.56 (d, *J* = 8.2 Hz, 2H, ArH), 6.23–6.31 (m, 1H, ArH), 6.18 (d, *J* = 7.8 Hz, 2H, ArH), 6.06–6.12 (m, 1H, ArH), 5.37 (dd, *J* = 8.7, 2.3 Hz, 1H, ArH), 5.11 (dd, *J* = 8.6, 2.3 Hz, 1H, ArH), 2.17 (s, 3H, CH₃), 2.15 (s, 3H, CH₃). ¹³C {¹H} NMR (151 MHz, CDCl₃) δ: 165.7 (d, *J*_{CF} = 5.5 Hz), 164.1 (d, *J*_{CF} = 4.7 Hz), 163.6 (d, *J*_{CF} = 2.4 Hz), 160.6, 160.0 (d, *J*_{CF} = 4.2 Hz), 155.8, 153.0 (d, *J*_{CF} = 5.8 Hz), 151.5, 151.3, 151.1, 149.6, 138.5, 138.1, 138.0, 136.0, 134.9, 131.9, 128.7, 128.3, 128.3, 127.3, 127.2, 123.4, 123.2, 123.1, 122.7, 122.5, 121.9, 120.3, 119.7, 113.9 (d, *J*_{CF} = 13.2 Hz), 113.4, 112.9 (d, *J*_{CF} = 13.9 Hz), 109.3, 97.99 (t, *J*_{CF} = 26 Hz), 96.41, 96.24, 21.0, 20.7. ¹⁹F NMR (470 MHz, CDCl₃) δ: –107.2 (dd, *J* = 15.1, 7.4 Hz, 1F), –108.9 (dd, *J* = 15.0, 7.4 Hz, 1F), –110.0 (t, *J* = 9.2 Hz, 1F), –110.6 (t, *J* = 9.1 Hz, 1F). Anal. Calcd for C₄₄H₃₀N₇F₄Ir: C, 57.13, H, 3.27, N, 10.60. Found: C, 57.14, H, 3.42, N, 10.46.

Ir(F₂ppy)₂(Fzd) (2d). The title compound was prepared by the general method described above for complex **1c'**, using [Ir(F₂ppy)₂(μ-Cl)]₂ (61 mg, 0.050 mmol) and **Fzd** (37 mg, 0.10 mmol). Yield: 75 mg (80%). ¹H NMR (500 MHz, CDCl₃) δ: 8.41 (d, *J* = 5.8 Hz, 1H, ArH), 8.37 (d, *J* = 5.7 Hz, 1H, ArH), 8.21 (d, *J* = 8.4 Hz, 1H, ArH), 8.08 (d, *J* = 8.3 Hz, 1H, ArH), 7.93 (t, *J* = 7.9 Hz, 1H, ArH), 7.79 (t, *J* = 7.9 Hz, 1H, ArH), 7.72 (dd, *J* = 8.1, 1.6 Hz, 2H, ArH), 7.14–7.22 (m, 6H, ArH), 7.12 (dd, *J* = 8.8, 1.9 Hz, 2H, ArH), 7.03–7.06 (m, 2H, ArH), 6.35 (d, *J* = 8.8 Hz, 3H, ArH), 6.23 (dd, *J* = 12.1, 9.4 Hz, 1H, ArH), 5.35–5.40 (m, 1H, ArH), 5.15–5.19 (m, 1H, ArH), 2.37 (s, 3H, CH₃). ¹³C {¹H} NMR (151 MHz, CDCl₃) δ: 165.5 (d, *J*_{CF} = 7.0 Hz), 164.0, 163.8 (d, *J*_{CF} = 7.5 Hz), 162.0 (dd, *J*_{CF} = 17.4, 11.9 Hz), 161.7 (d, *J*_{CF} = 7.7 Hz), 161.0, 160.1, 160.0,

159.0 (d, *J*_{CF} = 6.0 Hz), 156.5, 155.6, 152.0 (d, *J*_{CF} = 6.8 Hz), 151.6, 149.2, 138.7, 138.7, 132.3, 131.5, 129.8, 129.1, 129.0, 127.4, 127.1, 123.7 (d, *J*_{CF} = 19.8 Hz), 123.4 (d, *J*_{CF} = 19.8 Hz), 123.0, 122.9, 122.0, 120.7, 119.5, 118.6, 114.2 (d, *J*_{CF} = 17.8 Hz), 112.9 (d, *J*_{CF} = 18.0 Hz), 109.0, 106.8, 98.8 (t, *J*_{CF} = 26.6 Hz), 97.6 (t, *J*_{CF} = 26.6 Hz), 21.5. ¹⁹F NMR (470 MHz, CDCl₃) δ: –105.8 (dd, *J* = 8.6, 10 Hz, 1F), –107.0 (dd, *J* = 8.6, 10 Hz, 1F), –108.7 (t, *J* = 11 Hz, 1F), –109.2 (t, *J* = 10 Hz, 1F). Anal. Calcd for C₄₄H₂₇N₈F₄Ir: C, 56.46, H, 2.91, N, 11.97. Found: C, 56.22, H, 3.13, N, 11.70.

Ir(F₂ppy)₂(Fze) (2e). The title compound was prepared by the general method described above for complex **1c'**, using [Ir(F₂ppy)₂(μ-Cl)]₂ (61 mg, 0.050 mmol) and **Fze** (28 mg, 0.10 mmol). Yield: 46 mg (54%). ¹H NMR (400 MHz, CDCl₃) δ: 8.32 (d, *J* = 5.6 Hz, 1H), 8.27 (d, *J* = 5.7 Hz, 1H, ArH), 8.16 (d, *J* = 8.7 Hz, 1H, ArH), 8.03 (d, *J* = 9.1 Hz, 1H, ArH), 7.89 (t, *J* = 7.9 Hz, 1H, ArH), 7.79 (t, *J* = 7.9 Hz, 1H, ArH), 7.20–7.24 (m, 1H, ArH), 7.13A7.19 (m, 1H, ArH), 6.72 (s, 4H, ArH), 6.56 (d, *J* = 8.0 Hz, 2H, ArH), 6.24–6.33 (m, 1H, ArH), 6.20 (d, *J* = 8.0 Hz, 2H, ArH), 6.05–6.15 (m, 1H, ArH), 5.34 (d, *J* = 6.7 Hz, 1H, ArH), 5.06 (d, *J* = 8.6 Hz, 1H, ArH), 2.17 (s, 3H, CH₃), 2.13 (s, 3H, CH₃). ¹³C {¹H} NMR (151 MHz, CDCl₃) δ: 166.3, 163.7 (d, *J*_{CF} = 6.7 Hz), 161.9 (t, *J*_{CF} = 11.7 Hz), 161.6 (d, *J*_{CF} = 12.3 Hz), 159.9, 157.7 (d, *J*_{CF} = 6.5 Hz), 151.8, 151.7 (d, *J*_{CF} = 7.2 Hz), 151.2, 150.3, 149.9, 149.8, 138.6, 137.0, 136.1, 128.7, 128.3, 127.8, 127.3, 127.0, 123.4, 123.3 (d, *J*_{CF} = 20.4 Hz), 123.1, 122.8 (d, *J*_{CF} = 39.7 Hz), 122.3, 121.9, 120.1, 115.5, 114.2 (d, *J*_{CF} = 17.0 Hz), 113.0 (d, *J*_{CF} = 16.8 Hz), 98.4 (t, *J*_{CF} = 27.0 Hz), 96.7 (t, *J*_{CF} = 25.5 Hz), 21.0, 20.8. ¹⁹F NMR (470 MHz, CDCl₃) δ: –106.7 (dd, *J* = 19.1, 9.1 Hz, 1F), –108.4 (dd, *J* = 19.1, 9.4 Hz, 1F), –109.7 (t, *J* = 11.6 Hz, 1F), –110.2 (t, *J* = 11.6 Hz, 1F). Anal. Calcd for C₃₈H₂₆N₇F₄Ir: C, 53.77, H, 3.09, N, 11.55. Found: C, 53.75, H, 3.26, N, 11.62.

Ir(F₂ppy)₂(Fzf) (2f). The title compound was prepared by the general method described above for complex **1c'**, using [Ir(F₂ppy)₂(μ-Cl)]₂ (61 mg, 0.050 mmol) and **Fzf** (30 mg, 0.10 mmol). Yield: 51 mg (58%). ¹H NMR (500 MHz, CD₃CN) δ: 8.44 (d, *J* = 5.1 Hz, 1H, ArH), 8.31 (d, *J* = 6.5 Hz, 1H, ArH), 8.14 (d, *J* = 8.4 Hz, 1H, ArH), 8.04 (t, *J* = 8.1 Hz, 1H, ArH), 8.00 (d, *J* = 8.4 Hz, 1H, ArH), 7.92 (t, *J* = 8.0 Hz, 1H, ArH), 7.35 (ddd, *J* = 7.4, 5.8, 1.4 Hz, 1H, ArH), 7.29–7.32 (m, 1H, ArH), 7.26–7.29 (m, 2H, ArH), 7.21 (d, *J* = 8.7 Hz, 2H, ArH), 6.92 (d, *J* = 6.8 Hz, 2H, ArH), 6.54 (d, *J* = 8.4 Hz, 2H, ArH), 6.42 (ddd, *J* = 12.6, 9.3, 2.3 Hz, 1H, ArH), 6.29 (ddd, *J* = 12.7, 9.4, 2.3 Hz, 1H, ArH), 5.37 (dd, *J* = 8.7, 2.4 Hz, 1H, ArH), 5.18 (dd, *J* = 8.7, 2.4 Hz, 1H, ArH). ¹³C {¹H} NMR (151 MHz, CD₃CN) δ: 163.8 (d, *J*_{CF} = 7.2 Hz), 163.3, 162.3 (d, *J*_{CF} = 6.6 Hz), 161.6 (d, *J*_{CF} = 12.5 Hz), 161.1, 159.5 (d, *J*_{CF} = 3.8 Hz), 156.7 (d, *J*_{CF} = 6.9 Hz), 154.8, 154.1, 152.1, 151.2, 150.4, 139.8 (d, *J*_{CF} = 15.9 Hz), 137.7, 132.3, 132.1, 131.7, 127.6, 124.5, 124.2, 123.8 (d, *J*_{CF} = 19.8 Hz), 123.6, 123.5 (d, *J*_{CF} = 20.1 Hz), 123.0, 121.0, 118.5, 118.2, 114.4, 114.1, 112.9, 110.6, 108.8, 98.7 (t, *J*_{CF} = 27.1 Hz), 97.4 (t, *J* = 27.2 Hz). ¹⁹F NMR (470 MHz, CD₃CN) δ: –107.8 (dd, *J* = 19.1, 9.2 Hz, 1F), –109.4 (dd, *J* = 19.0, 9.4 Hz, 1F), –110.6 (t, *J* = 11.4 Hz, 1F), –110.7 (t, *J* = 11.6 Hz, 1F). Anal. Calcd for C₃₈H₂₀N₉F₄Ir: C, 52.41, H, 2.31, N, 14.48. Found: C, 52.34, H, 2.59, N, 14.23.

Ir(bt)₂(Fza) (3a). The title compound was prepared by the general method described above for complex **1a/1a'**, using [Ir(bt)₂(μ-Cl)]₂ (51 mg, 0.039 mmol) and **Fza** (37 mg, 0.10 mmol). The dark green solid product was isolated as a mixture of isomers where the major

product was the five-member chelate with a trace amount of six-member chelate evident from ^1H NMR data (Figure S32). Yield: 35 mg (47%). ^1H NMR (500 MHz, CDCl_3) δ : 7.97–8.03 (m, 2H, ArH), 7.71–7.91 (m, 4H, ArH), 7.32–7.51 (m, 4H, ArH), 7.22 (d, J = 7.5 Hz, 1H, ArH), 7.02 (d, J = 8.0 Hz, 1H, ArH), 6.78–6.84 (m, 2H, ArH), 6.72 (t, J = 7.4 Hz, 1H, ArH), 6.53–6.67 (m, 2H, ArH), 6.32–6.52 (m, 9H, ArH), 6.19 (d, J = 8.0 Hz, 1H, ArH), 6.12 (d, J = 8.0 Hz, 1H, ArH), 3.76 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.08 (s, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 181.5, 179.8, 161.7, 150.2, 150.0, 149.2, 140.0, 139.5, 133.4, 131.5, 131.3, 131.0, 130.9, 130.0, 128.1, 128.0, 127.6, 127.4, 126.1, 125.6, 125.4, 123.6, 122.8, 122.4, 121.7, 121.1, 120.6, 119.7, 113.5, 55.36, 21.05, 20.89. Anal. Calcd for $\text{C}_{48}\text{H}_{37}\text{IrN}_6\text{O}_5\text{S}_2$: C, 59.42; H, 3.84; N, 8.66. Found: C, 59.44; H, 3.84; N, 8.58.

Ir(bt)₂(Fzb) (3b). The title compound was prepared by the general method described above for complex **1a/1a'**, using $[\text{Ir}(\text{bt})_2(\mu\text{-Cl})_2]$ (50 mg, 0.039 mmol) and **Fzb** (32 mg, 0.81 mmol). The product was isolated as a mixture of isomers after column chromatography, and recrystallization of the product from a THF/MeOH mixture afforded pure **3b** as a dark green solid. Yield: 39 mg (50%). ^1H NMR (400 MHz, CDCl_3) δ : 7.95–8.02 (m, 2H, ArH), 7.78–7.89 (m, 2H, ArH), 7.72 (d, J = 8.7 Hz, 2H, ArH), 7.34–7.52 (m, 4H, ArH), 7.22–7.29 (m, 1H, ArH), 7.11 (d, J = 7.3 Hz, 1H, ArH), 6.82 (d, J = 8.7 Hz, 2H, ArH), 6.72 (t, J = 7.3 Hz, 1H, ArH), 6.42–6.67 (m, 7H, ArH), 6.09–6.27 (m, 6H, ArH), 3.78 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ : 181.4, 179.7, 162.6, 158.5, 157.1, 156.2, 150.1, 149.8, 149.7, 149.2, 147.3, 146.5, 140.7, 140.1, 139.6, 134.2, 133.5, 131.6, 131.3, 131.0, 130.9, 130.0, 129.9, 128.2, 127.7, 126.0, 125.7, 125.5, 124.8, 123.7, 122.9, 122.4, 122.3, 121.7, 121.0, 120.5, 120.4, 113.6, 112.8, 112.6, 112.2, 55.55, 55.36, 55.12. Anal. Calcd for $\text{C}_{48}\text{H}_{37}\text{IrN}_6\text{O}_5\text{S}_2$: C, 57.53; H, 3.72; N, 8.39. Found: C, 57.22; H, 3.57; N, 7.91.

Ir(bt)₂(Fze) (3e). The title compound was prepared by the general method described above for complex **1c'**, using $[\text{Ir}(\text{bt})_2(\mu\text{-Cl})_2]$ (100 mg, 0.0771 mmol) and **Fze** (39 mg, 0.15 mmol). The product was obtained as a reddish green solid. Yield: 45 mg (33%). Elemental analysis returned high percentages for C and H and a low percentage for N, but the NMR spectra in Figures S36 and S37 indicate satisfactory bulk purity. ^1H NMR (400 MHz, CDCl_3) δ : 8.08 (d, J = 7.3 Hz, 2H, ArH), 7.80 (d, J = 7.8 Hz, 1H, ArH), 7.74 (d, J = 7.8 Hz, 1H, ArH), 7.68 (d, J = 8.2 Hz, 1H, ArH), 7.38–7.47 (m, 1H, ArH), 6.98–7.34 (m, 10H, ArH), 6.79–6.93 (m, 3H, ArH), 6.72 (d, J = 6.8 Hz, 3H, ArH), 6.49–6.54 (m, 1H, ArH), 6.44 (d, J = 7.8 Hz, 1H, ArH), 2.33 (s, 3H, CH_3), 2.24 (s, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ : 182.7, 180.0, 178.1, 171.7, 170.8, 150.9, 150.0, 149.9, 141.5, 139.9, 138.7, 138.2, 137.1, 133.0, 132.6, 131.2, 131.1, 130.8, 129.7, 128.5, 127.5, 127.4, 125.8, 125.6, 125.4, 125.3, 124.1, 122.8, 122.2, 121.9, 121.2, 120.8, 119.6, 119.4, 21.34, 21.23. Anal. Calcd for $\text{C}_{42}\text{H}_{30}\text{IrN}_7\text{S}_2$: C, 56.74; H, 3.40; N, 11.03. Found: C, 57.70; H, 3.93; N, 10.28.

Ir(bt)₂(Fzf) (3f). The title compound was prepared by the general method described above for complex **1c'**, using $[\text{Ir}(\text{bt})_2(\mu\text{-Cl})_2]$ (100 mg, 0.0771 mmol) and **Fzf** (46 mg, 0.15 mmol). The product was isolated as a greenish brown solid. Yield: 51 mg (38%). ^1H NMR (500 MHz, CDCl_3) δ : 7.92–7.99 (m, 2H, ArH), 7.64–7.71 (m, 1H, ArH), 7.41–7.61 (m, 5H, ArH), 7.23–7.30 (m, 1H, ArH), 7.13 (d, J

= 7.8 Hz, 2H, ArH), 7.01–7.08 (m, 2H, ArH), 6.95 (d, J = 8.2 Hz, 2H, ArH), 6.77–6.86 (m, 2H, ArH), 6.69–6.76 (m, 3H, ArH), 6.58–6.66 (m, 3H, ArH), 6.05 (dd, J = 7.8, 22.9 Hz, 2H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 181.6, 180.1, 155.6, 154.8, 152.7, 149.2, 148.4, 146.2, 139.7, 139.4, 139.1, 133.3, 132.0, 131.9, 131.5, 131.3, 131.1, 130.6, 129.1, 128.7, 126.7, 127.7, 126.4, 126.0, 123.7, 123.4, 123.3, 123.2, 122.2, 120.9, 119.2, 119.0, 118.9, 118.6, 114.2, 110.5, 108.7. Anal. Calcd for $\text{C}_{42}\text{H}_{24}\text{IrN}_9\text{S}_2 \cdot 0.25\text{C}_4\text{H}_8\text{O}_2$: C, 55.35; H, 2.80; N, 13.51. Found: C, 55.49; H, 2.67; N, 13.52.

Ir(piq)₂(Fza) (4a). The title compound was prepared by the general method described above for complex **1a/1a'**, using $[\text{Ir}(\text{piq})_2(\mu\text{-Cl})_2]$ (100 mg, 0.0785 mmol) and **Fza** (63 mg, 0.16 mmol). The product was isolated as a mixture of isomer and recrystallized later (CH_2Cl_2 /pentane) to get greenish blue solid. Yield: 74 mg (48%). ^1H NMR (400 MHz, CDCl_3) δ : 8.65–8.74 (m, 1H, ArH), 8.58–8.64 (m, 1H, ArH), 8.46 (d, J = 6.4 Hz, 1H, ArH), 8.32 (d, J = 6.4 Hz, 1H, ArH), 7.79–7.93 (m, 5H, ArH), 7.58–7.78 (m, 5H, ArH), 7.37 (d, J = 6.4 Hz, 1H, ArH), 7.30 (d, J = 6.4 Hz, 1H, ArH), 6.78–6.88 (m, 5H, ArH), 6.45–6.64 (m, 5H, ArH), 6.31–6.43 (m, 3H, ArH), 6.21–6.28 (m, 2H, ArH), 6.14 (d, J = 6.4 Hz, 1H, ArH), 5.79 (d, J = 8.0 Hz, 1H, ArH), 3.78 (s, 3H, OCH_3), 2.06 (s, 3H, CH_3), 2.02 (s, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ : 169.8, 169.4, 168.7, 160.6, 158.7, 158.6, 153.5, 153.3, 152.4, 152.0, 144.8, 144.6, 143.4, 142.7, 136.8, 136.6, 134.5, 134.2, 133.1, 133.0, 131.5, 130.9, 130.2, 129.8, 129.4, 129.3, 128.5, 128.4, 128.2, 127.7, 127.4, 127.2, 127.1, 126.2, 123.6, 122.0, 121.0, 120.6, 120.2, 119.6, 119.1, 113.4, 55.37, 20.87, 20.82. Anal. Calcd for $\text{C}_{52}\text{H}_{41}\text{IrN}_6\text{O}$: C, 65.18; H, 4.31; N, 8.77. Found: C, 65.15; H, 4.46; N, 8.50.

Ir(piq)₂(Fzf) (4f). The title compound was prepared by the general method described above for complex **1c'**, using $[\text{Ir}(\text{piq})_2(\mu\text{-Cl})_2]$ (75 mg, 0.0589 mmol) and **Fzf** (46 mg, 0.12 mmol). The product was isolated as a greenish brown solid. Yield: 60 mg (56%). ^1H NMR (600 MHz, CDCl_3) δ : 8.63 (dd, J = 8.3, 16.2 Hz, 2H, ArH), 8.10 (d, J = 6.2 Hz, 1H, ArH), 8.03 (d, J = 6.2 Hz, 1H, ArH), 7.93–8.00 (m, 2H, ArH), 7.77–7.91 (m, 5H, ArH), 7.71 (t, J = 7.9 Hz, 1H, ArH), 7.52 (d, J = 6.9 Hz, 1H, ArH), 7.44 (d, J = 6.2 Hz, 1H, ArH), 7.01–7.10 (m, 2H, ArH), 6.86–6.98 (m, 5H, ArH), 6.75–6.83 (m, 1H, ArH), 6.68 (t, J = 6.9 Hz, 1H, ArH), 6.42–6.52 (m, 3H, ArH), 6.04–6.10 (m, 1H, ArH), 5.82 (d, J = 8.3 Hz, 1H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ : 169.1, 168.1, 156.0, 155.2, 153.9, 149.6, 144.7, 144.3, 142.3, 141.6, 138.4, 137.0, 136.9, 133.1, 132.1, 131.9, 131.7, 131.5, 131.2, 130.3, 130.0, 129.8, 129.0, 128.9, 127.8, 127.5, 126.9, 126.8, 126.2, 126.1, 122.9, 122.6, 121.7, 121.5, 121.2, 119.1, 118.7, 114.6, 110.2, 108.5. Anal. Calcd for $\text{C}_{46}\text{H}_{28}\text{N}_9\text{Ir}$: C, 61.46; H, 3.14; N, 14.02. Found: C, 60.99; H, 3.18; N, 14.04.

X-ray Crystallography Details. Single crystals of **1c'**, **1d**, **2a**, **2c**, **2d**, **2e**, **3a**, and **4a** were grown by layering concentrated CH_2Cl_2 solutions with pentane or diffusing pentane into concentrated ethyl acetate solution. Crystals were mounted on a Bruker Apex II three-circle diffractometer using $\text{MoK}\alpha$ radiation (λ = 0.71073 Å). The data were collected at 123(2) K and was 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.⁶⁸ Hydrogen atoms were placed in calculated positions using the standard riding model and refined isotropically. All non-hydrogen atoms were refined anisotropically. Crystallographic details are summarized in Tables S1–S3.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data summary, crystal structures of **1d**, **2e**, and **4a**, NMR spectra of all new compounds, additional UV-vis spectra, summary of solvatochromism experiments, additional cyclic voltammograms.

Accession Codes

CCDC 191336–191343 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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SYNOPSIS TOC : Bis-cyclometalated iridium(III) formazanate complexes are presented. A total of 18 new compounds are described, characterized by cyclic voltammetry and UV-vis absorption spectroscopy. Structural characterization in the solid-state by X-ray crystallography and in solution by multinuclear NMR reveal two distinct binding modes of the chelating formazanate ligand.

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Supporting Information for

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Table S1. Summary of crystallographic data for **1c'**, **1d**, and **2a**.

	1c' ·0.5CH ₂ Cl ₂	1d ·CH ₂ Cl ₂	2a
CCDC	191336	191337	191338
Crystal data			
Chemical formula	C _{44.50} H ₃₅ ClIrN ₇	C ₄₅ H ₃₃ Cl ₂ IrN ₈	C ₄₄ H ₃₃ F ₄ IrN ₆ O
<i>M</i> _r	895.44	948.89	929.96
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Triclinic, <i>P</i> $\bar{1}$	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.3278 (11), 13.6396 (18), 32.927 (4)	7.800 (4), 13.666 (7), 19.338 (10)	13.819 (2), 17.291 (3), 31.180 (5)
α , β , γ (°)	90, 94.820 (2), 90	94.197 (6), 100.672 (6), 100.065 (6)	90, 99.037 (2), 90
<i>V</i> (Å ³)	3726.9 (9)	1982.6 (18)	7358 (2)
<i>Z</i>	4	2	8
μ (mm ⁻¹)	3.70	3.55	3.70
Crystal size (mm)	0.25 × 0.12 × 0.05	0.25 × 0.10 × 0.08	0.39 × 0.14 × 0.12
Data collection			
<i>T</i> _{min} , <i>T</i> _{max}	0.553, 0.746	0.602, 0.745	0.510, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	21621, 8442, 7359	22406, 7691, 7169	42064, 16616, 15080
<i>R</i> _{int}	0.020	0.036	0.019
(sin θ /λ) _{max} (Å ⁻¹)	0.649	0.617	0.649
Refinement			
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.029, 0.073, 1.06	0.062, 0.162, 1.08	0.031, 0.112, 1.20
No. of reflections	8442	7691	16616
No. of parameters	517	506	1015
No. of restraints	642	511	0
	$w = 1/[\sigma^2(F_o^2) + (0.0277P)^2 + 10.5019P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0734P)^2 + 44.1129P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0591P)^2 + 21.696P]$ where $P = (F_o^2 + 2F_c^2)/3$
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.34, -1.78	7.89, -3.90	3.07, -1.83

Table S2. Summary of crystallographic data for **2c**, **2d** and **2e**.

	2c	2d	2e
CCDC	191339	191340	191341
Crystal data			
Chemical formula	C ₄₄ H ₃₀ F ₄ IrN ₇	C ₄₄ H ₂₇ F ₄ IrN ₈	C ₃₈ H ₂₆ F ₄ IrN ₇
M_r	924.95	935.93	848.86
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$	Monoclinic, $C2/c$
a, b, c (Å)	11.8119 (12), 11.9432 (12), 14.7901 (15)	17.897 (5), 8.693 (3), 23.444 (7)	26.377 (4), 24.953 (4), 12.001 (2)
α, β, γ (°)	108.9555 (12), 91.9403 (13), 109.1664 (13)	90, 91.553 (4), 90	90, 114.140 (2), 90
V (Å ³)	1840.7 (3)	3646.1 (18)	7208 (2)
Z	2	4	8
μ (mm ⁻¹)	3.69	3.73	3.76
Crystal size (mm)	0.40 × 0.26 × 0.16	0.21 × 0.10 × 0.05	0.47 × 0.09 × 0.07
Data collection			
$T_{\min}, T_{\max}$	0.602, 0.746	0.562, 0.746	0.491, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10228, 7383, 7003	22114, 8437, 7123	22704, 8354, 6955
R_{int}	0.014	0.039	0.027
$(\sin \theta/\lambda)_{\max}$ (Å ⁻¹)	0.625	0.652	0.653
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.026, 0.063, 1.05	0.028, 0.058, 1.01	0.053, 0.139, 1.08
No. of reflections	7383	8437	8354
No. of parameters	526	515	452
No. of restraints	100	0	465
	$w = 1/[\sigma^2(F_o^2) + (0.029P)^2 + 3.7672P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0189P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2 + 83.6126P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	2.07, -0.93	0.95, -0.52	4.42, -3.37

Table S3. Summary of crystallographic data for **3a** and **4a**.

	3a ·MeOH	4a ·CH ₂ Cl ₂
CCDC	191342	191343
Crystal data		
Chemical formula	C ₄₉ H ₄₁ IrN ₆ O ₂ S ₂	C ₅₃ H ₄₃ Cl ₂ IrN ₆ O
<i>M</i> _r	1002.20	1043.03
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.1354 (5), 11.9908 (5), 16.0273 (7)	12.4439 (8), 13.9851 (9), 14.2806 (10)
α , β , γ (°)	91.100 (1), 99.67, 99.502 (1)	114.817 (1), 96.371 (1), 99.887 (1)
<i>V</i> (Å ³)	2078.23 (16)	2175.2 (3)
μ (mm ⁻¹)	3.36	3.24
Crystal size (mm)	0.30 × 0.19 × 0.12	0.38 × 0.23 × 0.20
Data collection		
<i>T</i> _{min} , <i>T</i> _{max}	0.583, 0.746	0.541, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	36357, 9379, 8811	13034, 9360, 8486
<i>R</i> _{int}	0.029	0.019
(sin θ /λ) _{max} (Å ⁻¹)	0.646	0.641
Refinement		
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.019, 0.044, 1.06	0.034, 0.091, 1.06
No. of reflections	9379	9360
No. of parameters	556	571
No. of restraints	15	0
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.93, -0.59	2.14, -1.63

Figure S1. X-ray crystal structure of **1d**, **2e**, and **4a**. Hydrogen atoms and solvate molecules are omitted for clarity. Ellipsoids are shown at the 50% probability level.

Figure S2. ^1H NMR spectrum of $\text{Ir}(\text{ppy})_2(\text{Fza})$ (**1a** and **1a'**), recorded at 400 MHz in CDCl_3 . Peak positions are shown below the horizontal axis. Signals for residual ethyl acetate (EA), pentane and H_2O are marked.

Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ir}(\text{ppy})_2(\text{Fza})$ (**1a** and **1a'**), recorded at 151 MHz in CDCl_3 . Peak positions are shown below the horizontal axis. Signals for residual ethyl acetate (EA), hexane and CH_2Cl_2 are marked.

Figure S4. ¹H NMR spectrum of Ir(ppy)₂(Fzb) (**1b'**), recorded at 400 MHz in CDCl₃. Peak positions are shown below the horizontal axis. Signal for residual H₂O is marked.

Figure S5. ¹³C{¹H} NMR spectrum of Ir(ppy)₂(Fzb) (**1b'**), recorded at 151 MHz in CDCl₃. Peak positions are shown below the horizontal axis. Signals for residual pentane are marked.

Figure S6. ¹H NMR spectrum of Ir(ppy)₂(Fzc) (**1c'**), recorded at 500 MHz in CDCl₃. Peak positions are shown below the horizontal axis. Signals for residual H₂O and CH₂Cl₂ are marked.

Figure S7. ¹³C{¹H} NMR spectrum of Ir(ppy)₂(Fzc) (**1c'**), recorded at 151 MHz in CDCl₃. Peak positions are shown below the horizontal axis.

Figure S8. ^1H NMR spectrum of $\text{Ir}(\text{ppy})_2(\text{Fzd})$ (**1d**), recorded at 500 MHz in CDCl_3 . Peak positions are shown below the horizontal axis. Signals for residual H_2O and CH_2Cl_2 are marked.

Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ir}(\text{ppy})_2(\text{Fzd})$ (**1d**), recorded at 151 MHz in CDCl_3 . Peak positions are shown below the horizontal axis.

Figure S10. ^1H NMR spectrum of $\text{Ir}(\text{ppy})_2(\text{Fze})$ (**1e**), recorded at 500 MHz in CDCl_3 . Peak positions are shown below the horizontal axis. Signals for residual H_2O and hexane are marked.

Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ir}(\text{ppy})_2(\text{Fze})$ (**1e**), recorded at 151 MHz in CDCl_3 . Peak positions are shown below the horizontal axis. Signal for residual acetone which was used to clean the NMR tube is marked.

Figure S12. ^1H NMR spectrum of $\text{Ir}(\text{ppy})_2(\text{Fzf})$ (**1f**), recorded at 500 MHz in CD_3CN . Peak positions are shown below the horizontal axis. Signal for residual H_2O is marked.

Figure S13. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ir}(\text{ppy})_2(\text{Fzf})$ (**1f**), recorded at 151 MHz in CD_3CN . Peak positions are shown below the horizontal axis.

Figure S14. ^1H NMR spectrum of $\text{Ir}(\text{F}_2\text{ppy})_2(\text{Fza})$ (**2a**), recorded at 500 MHz in CD_3CN . Peak positions are shown below the horizontal axis. Signals for residual ethyl acetate (EA) and pentane are marked.

Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ir}(\text{F}_2\text{ppy})_2(\text{Fza})$ (**2a**), recorded at 126 MHz in CD_3CN . Peak positions are shown below the horizontal axis. Signals for residual ethyl acetate (EA), CH_2Cl_2 , and acetone (used to clean NMR tube) are marked.

Figure S16. ^{19}F NMR spectrum of $\text{Ir}(\text{F}_2\text{ppy})_2(\text{Fza})$ (**2a**), recorded at 470 MHz in CD_3CN . Peak positions are shown below the horizontal axis.

Figure S17. ^1H NMR spectrum of $\text{Ir}(\text{F}_2\text{ppy})_2(\text{Fzb})$ (**2b**), recorded at 500 MHz in CD_3CN . Peak positions are shown below the horizontal axis.

Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ir}(\text{F}_2\text{ppy})_2(\text{Fzb})$ (**2b**), recorded at 126 MHz in CD_3CN . Peak positions are shown below the horizontal axis.

Figure S19. ^{19}F NMR spectrum of $\text{Ir}(\text{F}_2\text{ppy})_2(\text{Fzb})$ (**2b**), recorded at 470 MHz in CD_3CN . Peak positions are shown below the horizontal axis.

Figure S20. ^1H NMR spectrum of $\text{Ir}(\text{F}_2\text{ppy})_2(\text{Fzc})$ (**2c**), recorded at 500 MHz in CDCl_3 . Peak positions are shown below the horizontal axis. Signal for residual tetrahydrofuran (THF) and pentane is marked.

Figure S21. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ir}(\text{F}_2\text{ppy})_2(\text{Fzc})$ (**2c**), recorded at 151 MHz in CDCl_3 . Peak positions are shown below the horizontal axis. Signals for residual ethyl acetate (EA) and hexane are marked.

Figure S22. ^{19}F NMR spectrum of $\text{Ir}(\text{F}_2\text{ppy})_2(\text{Fzc})$ (**2c**), recorded at 470 MHz in CDCl_3 . Peak positions are shown below the horizontal axis.

Figure S23. ^1H NMR spectrum of $\text{Ir}(\text{F}_2\text{ppy})_2(\text{Fzd})$ (**2d**), recorded at 500 MHz in CDCl_3 . Peak positions are shown below the horizontal axis. Signal for residual H_2O is marked.

Figure S24. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ir}(\text{F}_2\text{ppy})_2(\text{Fzd})$ (**2d**), recorded at 151 MHz in CDCl_3 . Peak positions are shown below the horizontal axis.

Figure S25. ^{19}F NMR spectrum of $\text{Ir}(\text{F}_2\text{ppy})_2(\text{Fzd})$ (**2d**), recorded at 470 MHz in CDCl_3 . Peak positions are shown below the horizontal axis.

Figure S26. ^1H NMR spectrum of $\text{Ir}(\text{F}_2\text{ppy})_2(\text{Fze})$ (**2e**), recorded at 400 MHz in CDCl_3 . Peak positions are shown below the horizontal axis. Signal for residual H_2O is marked.

Figure S27. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ir}(\text{F}_2\text{ppy})_2(\text{Fze})$ (**2e**), recorded at 151 MHz in CDCl_3 . Peak positions are shown below the horizontal axis.

Figure S28. ^{19}F NMR spectrum of $\text{Ir}(\text{F}_2\text{ppy})_2(\text{Fze})$ (**2e**), recorded at 470 MHz in CDCl_3 . Peak positions are shown below the horizontal axis.

Figure S29. ^1H NMR spectrum of $\text{Ir}(\text{F}_2\text{ppy})_2(\text{Fzf})$ (**2f**), recorded at 500 MHz in CD_3CN . Peak positions are shown below the horizontal axis. Signals for residual ethyl acetate (EA) and H_2O are marked.

Figure S30. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ir}(\text{F}_2\text{ppy})_2(\text{Fzf})$ (**2f**), recorded at 151 MHz in CD_3CN . Peak positions are shown below the horizontal axis.

Figure S31. ^{19}F NMR spectrum of $\text{Ir}(\text{F}_2\text{ppy})_2(\text{Fzf})$ (**2f**), recorded at 470 MHz in CD_3CN . Peak positions are shown below the horizontal axis.

Figure S32. ^1H NMR spectrum of $\text{Ir}(\text{bt})_2(\text{Fza})$ (**3a**), recorded at 500 MHz in CDCl_3 . Peak positions are shown below the horizontal axis. Signals for residual water H_2O and pentane are marked.

Figure S33. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ir}(\text{bt})_2(\text{Fza})$ (**3a**), recorded at 101 MHz in CDCl_3 . Peak positions are shown below the horizontal axis.

Figure S34. ¹H NMR spectrum of Ir(bt)₂(Fzb) (**3b**), recorded at 400 MHz in CDCl₃. Peak positions are shown below the horizontal axis. Signals for residual water H₂O and methanol (CH₃OH) are marked. Methanol was used as a recrystallizing solvent.

Figure S35. ¹³C{¹H} NMR spectrum of Ir(bt)₂(Fzb) (**3b**), recorded at 151 MHz in CDCl₃. Peak positions are shown below the horizontal axis. Signals for hexane are marked.

Figure S36. ^1H NMR spectrum of $\text{Ir}(\text{bt})_2(\text{Fze})$ (**3e**), recorded at 400 MHz in CDCl_3 . Peak positions are shown below the horizontal axis. Signals for residual CH_2Cl_2 and hexane are marked.

Figure S37. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ir}(\text{bt})_2(\text{Fze})$ (**3e**), recorded at 151 MHz in CDCl_3 . Peak positions are shown below the horizontal axis.

Figure S38. ^1H NMR spectrum of $\text{Ir}(\text{bt})_2(\text{Fzf})$ (**3f**), recorded at 500 MHz in CDCl_3 . Peak positions are shown below the horizontal axis. Signals for residual ethyl acetate (EA), H_2O , and hexane are marked. The solvents remained even after prolonged drying.

Figure S39. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ir}(\text{bt})_2(\text{Fzf})$ (**3f**), recorded at 126 MHz in CDCl_3 . Peak positions are shown below the horizontal axis. Signals for residual pentane are marked.

Figure S40. ^1H NMR spectrum of $\text{Ir}(\text{piq})_2(\text{Fza})$ (**4a**), recorded at 400 MHz in CDCl_3 . Peak positions are shown below the horizontal axis. Signals for residual H_2O and pentane are marked.

Figure S41. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ir}(\text{piq})_2(\text{Fza})$ (**4a**), recorded at 151 MHz in CDCl_3 . Peak positions are shown below the horizontal axis.

Figure S42. ^1H NMR spectrum of $\text{Ir}(\text{piq})_2(\text{Fzf})$ (**4f**), recorded at 600 MHz in CDCl_3 . Peak positions are shown below the horizontal axis. Signal for residual water H_2O is marked.

Figure S43. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ir}(\text{piq})_2(\text{Fzf})$ (**4f**), recorded at 151 MHz in CDCl_3 . Peak positions are shown below the horizontal axis.

Figure S44. Overlaid electronic absorption spectra of **1a–1f**. Spectra were recorded in tetrahydrofuran (THF) in room temperature.

Figure S45. Overlaid electronic absorption spectra of **4a** and **4f**. Spectra were recorded in tetrahydrofuran (THF) in room temperature.

Figure S46. Electronic absorption spectra of complex **1a–f**, recorded in toluene, tetrahydrofuran (THF), and MeOH at room temperature. The spectra are normalized to the low-energy absorption maximum.

Figure S47. Electronic absorption spectra of complex **2a–f**, recorded in toluene, tetrahydrofuran (THF), and MeOH at room temperature. The spectra are normalized to the low-energy absorption maximum.

Figure S48. Electronic absorption spectra of complex **3a–b**, **3e–f**, **4a** and **4f**, recorded in toluene, tetrahydrofuran (THF), and MeOH at room temperature. The spectra are normalized to the low-energy absorption maximum.

Table S4. Summary of UV-vis absorption maxima for spectra recorded in tetrahydrofuran (THF), toluene, and MeOH.

	λ (nm)		
	THF	Toluene	MeOH
Ir(ppy) ₂ (Fza) (1a/1a')	265, 480, 633	478, 635	262, 472, 631
Ir(ppy) ₂ (Fzb) (1b')	261, 463, 630	468, 633	258, 459, 630
Ir(ppy) ₂ (Fzc) (1c')	264, 387, 602	385, 605	260, 387, 599
Ir(ppy) ₂ (Fzd) (1d)	270, 374 ^a , 673	271, 374 ^a , 677	269, 370 ^a , 674
Ir(ppy) ₂ (Fze) (1e)	260, 380 ^a , 476, 554	380 ^a , 478, 565	378 ^a , 477, 553
Ir(ppy) ₂ (Fzf) (1f)	258, 342, 401 ^a , 520	349, 402 ^a , 527	258, 341, 400 ^a , 512
Ir(F ₂ ppy) ₂ (Fza) (2a)	250, 347 ^a , 445, 628	346 ^a , 452, 632	249, 344 ^a , 453, 628
Ir(F ₂ ppy) ₂ (Fzb) (2b)	252, 454, 639	452, 651	260, 451, 646
Ir(F ₂ ppy) ₂ (Fzc) (2c)	251, 390, 601	387, 606	390, 605
Ir(F ₂ ppy) ₂ (Fzd) (2d)	260 ^a , 313 ^a , 360 ^a , 655	315 ^a , 361 ^a , 656	312 ^a , 357 ^a , 640
Ir(F ₂ ppy) ₂ (Fze) (2e)	250, 300, 454 ^a , 551	302, 455 ^a , 554	300, 454 ^a , 547
Ir(F ₂ ppy) ₂ (Fzf) (2f)	261, 353 ^a , 532	354 ^a , 545	261, 347 ^a , 524
Ir(bt) ₂ (Fza) (3a)	320, 410 ^a , 630	319, 412 ^a , 636	318, 403 ^a , 476 ^a , 639
Ir(bt) ₂ (Fzb) (3b)	262, 319, 635	320, 637	261, 307, 636
Ir(bt) ₂ (Fze) (3e)	263, 319, 382 ^a , 443 ^a , 578	321, 383 ^a , 451 ^a , 580	318, 378, 438 ^a , 572
Ir(bt) ₂ (Fzf) (3f)	266, 321, 384 ^a , 443, 596	323, 384 ^a , 450, 597	320, 378 ^a , 439, 595
Ir(piq) ₂ (Fza) (4a)	293, 349 ^a , 435 ^a , 638	293, 348 ^a , 437 ^a , 637	288, 344 ^a , 431 ^a , 637
Ir(piq) ₂ (Fzf) (4f)	285, 343, 403, 443, 525 ^a	346, 406, 446, 526 ^a	283, 343, 436, 522 ^a

^a= shoulder

Figure S49. Overlaid cyclic voltammograms of complexes **1a–1f**. CVs were recorded in CH_2Cl_2 with 0.1M NBu_4PF_6 supporting electrolyte, using a glassy carbon working electrode and a scan rate of 0.1 V/s. The arrows indicate the scan direction. Concentrations were not carefully controlled, which results in the different current values for these plots.

Figure S50. Overlaid cyclic voltammograms of complexes **3a, 3b, 3e, and 3f**. CVs were recorded in CH_2Cl_2 with 0.1M NBu_4PF_6 supporting electrolyte, using a glassy carbon working electrode and a scan rate of 0.1 V/s. The arrows indicate the scan direction. Concentrations were not carefully controlled, which results in the different current values for these plots.

Figure S51. Overlaid cyclic voltammograms of complexes **4a** and **4f**. CVs were recorded in CH₂Cl₂ with 0.1M NBu₄PF₆ supporting electrolyte, using a glassy carbon working electrode and a scan rate of 0.1 V/s. The arrows indicate the scan direction. Concentrations were not carefully controlled, which results in the different current values for these plots.

Ir C^N formazanate SI.pdf (6.86 MiB)

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