

Substituent-Dependent Azide Addition to Isocyanides Generates Strongly Luminescent Iridium Complexes

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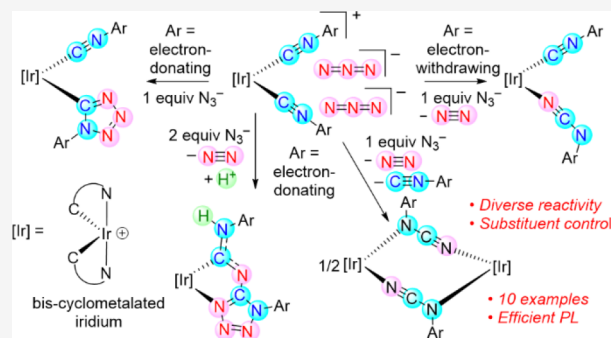


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ABSTRACT: Ligand-centered functionalization reactions offer diverse strategies to prepare luminescent organometallic compounds. These compounds can have unique structures that are not accessible via traditional coordination chemistry and can possess enhanced or unusual photophysical properties. Here we show that bis-cyclometalated iridium bis-isocyanide complexes (**1**) react with azide (N_3^-) to form novel luminescent structures. The fate of the reaction with azide is determined primarily by the substituent on the aryl isocyanide. Those with electron-withdrawing substituents (CF_3 or NO_2) react with 1 equiv of azide followed by N_2 extrusion, forming aryl cyanamido products (**2**). With electron-donating groups on the aryl isocyanide the reactivity is more diverse, and three outcomes are possible. In two cases, the isocyanide and azide undergo a $[3 + 2]$ cycloaddition to form a C-bound tetrazolato structure (**3**). In three other cases, 2 equiv of azide are involved in the formation of a previously unobserved structure, where a tetrazolato and aryl cyanamido couple and rearrange to form a chelating ligand comprised of an N-bound tetrazolato and an acyclic diaminocarbene (**4**). Finally, a bimetallic aryl cyanamido complex (**5**) is isolated in one case. All compounds are luminescent, some with exceptional photoluminescence quantum yields as high as 0.81 in solution for sky-blue emission, and 0.87 for yellow emission and 0.65 for orange-red emission in polymer films.



INTRODUCTION

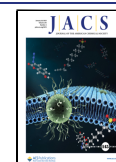
Organometallic compounds can undergo a diverse range of photophysical and photochemical processes from their low-lying triplet excited states.¹ Phosphorescence from these triplet states is critical for the performance of electroluminescent devices and other optoelectronics,^{2,3} and in the design of luminescent cellular imaging agents^{4,5} or sensors for a variety of analytes.^{6–9} Moreover, these triplet excited states can undergo energy transfer or electron transfer processes that are important elementary steps in photovoltaic devices^{10,11} and photoredox catalysis for solar fuels and organic synthesis applications.^{12–18} The performance of an organometallic compound in any of these applications depends on several factors, which include the energy, lifetime, dynamics, and redox potentials of the triplet excited state. Since the triplet excited states in organometallic compounds usually involve significant charge transfer between the metal and the ligands, both the identity of the metal and its supporting ligands play large roles in determining these key characteristics.

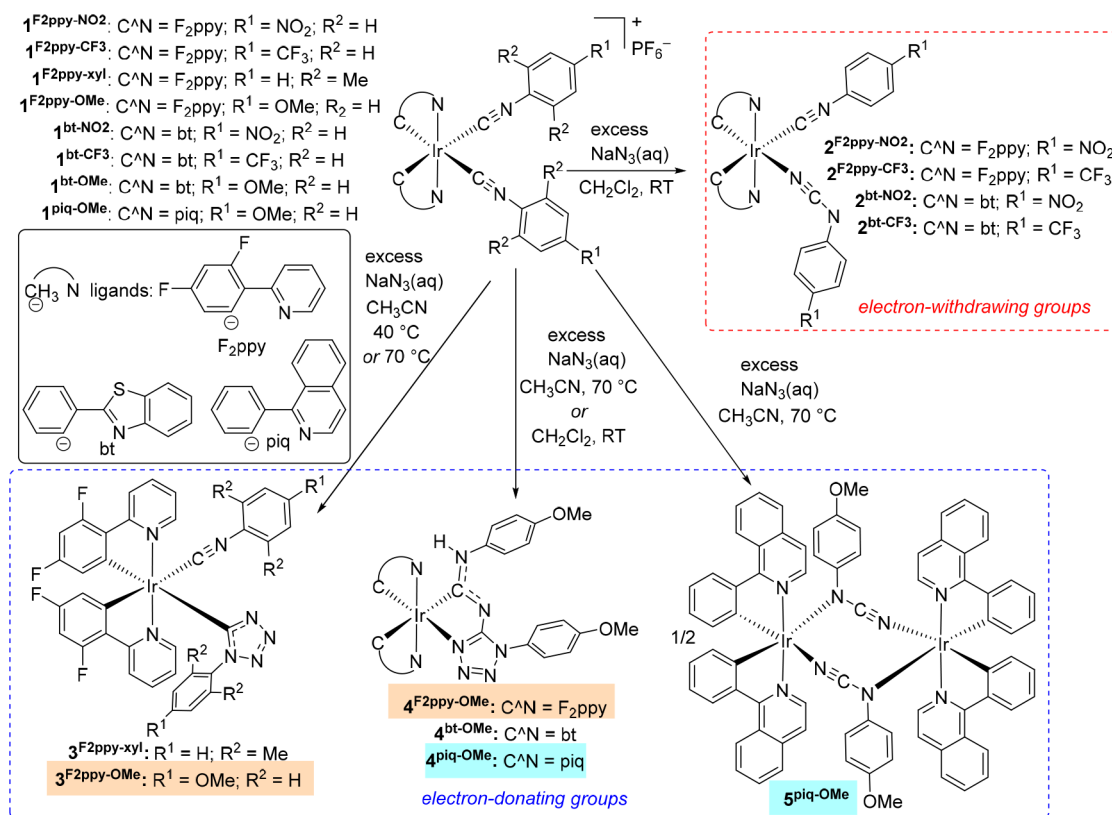
Iridium(III) organometallics, in particular those with one or more cyclometalating ligands featuring iridium-aryl bonds,¹⁹ have become standout performers in applications involving both triplet-state luminescence and redox chemistry.²⁰ Iridium(III) is particularly desirable in the design of photoactive metal

complexes. The large spin–orbit coupling constant of iridium²¹ facilitates rapid intersystem crossing to the triplet state and radiative decay back to the ground state, the octahedral geometry prevents aggregation that may be deleterious to certain applications, and the installation of cyclometalating ligands onto iridium is straightforward synthetically and highly beneficial to the attributes of the triplet excited state.²² Most cyclometalated iridium complexes have a bis-cyclometalated structure, meaning there are two bidentate cyclometalating ligands that largely control the energy of the triplet excited state, with two additional coordination sites occupied by one bidentate or two monodentate ancillary ligands, which can be a critical determinant of the excited-state dynamics.²³ Moreover, ancillary ligands in cyclometalated iridium complexes are able to tune the ground-state and excited-state redox properties, important thermodynamic parameters in photo-

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Scheme 1. Reactivity of Bis-isocyanide Complexes **1** with Sodium Azide^a

^aProducts highlighted in light orange or sky blue were produced in the same reaction as one another.

redox catalysis.²⁴ The ancillary ligands are normally installed by traditional metathesis or ligand-substitution approaches, starting with a suitable bis-cyclometalated iridium precursor. As versatile as these approaches are, they limit the choice of ligands to those that can be isolated as stable free ligands or proligands.

An emerging strategy in the design of cyclometalated iridium complexes and other classes of organometallic phosphors is to use ligand-based functionalization strategies to install supporting ligands not able to be accessed by traditional means. The best-developed example of this approach involves addition of a nitrogen-based nucleophile to a coordinated isocyanide, which forms an acyclic diaminocarbene (ADC).^{25,26} Our group has used this method to install ADCs onto luminescent iridium^{27,28} or platinum^{29,30} complexes and showed the strong σ -donor ADCs are particularly effective at supporting efficient deep-blue phosphorescence,^{29,31} and related approaches have been used to good effect by a few other groups in the design of iridium,^{7,32} rhenium,³³ or platinum^{34,35} phosphors supported by ADCs.

These previous works exclusively used amine or hydrazine nucleophiles to install ADCs, and in this work, we leverage the diverse reactivity of isocyanides with azide (N₃[−]) to prepare new structural classes of cyclometalated iridium complexes. Two important insights emerge from this study: (1) From the standpoint of fundamental reactivity and organometallic synthesis, we show that the outcome of the azide functionalization reaction depends on the electronic nature of the isocyanide. It has previously been shown, almost exclusively on square-planar *d*⁸ metal complexes, that azides and isocyanides can react to form either tetrazolato or

cyanamido products.^{36–40} The work presented here is the first to show that this reactivity can be controlled by varying substituents on the isocyanide. Moreover, we also introduce a new ligand structure type that emerges when both *cis*-oriented isocyanides react with an equivalent of azide and couple. (2) Some of the complexes thus formed by isocyanide/azide reactions are exceptionally luminescent, with high quantum yields for photoluminescence in the sky blue, yellow, or orange-red regions. These outcomes show that this azide-addition approach can lead to the formation of compounds with standout photophysical properties. In total, the reactions of eight bis-cyclometalated iridium bis-isocyanide precursors with azide are presented, which form 10 new products that have been isolated and fully characterized. The molecular structures of these compounds are described, along with their electrochemical behavior and phosphorescence properties in solution and in transparent polymer film.

RESULTS AND DISCUSSION

Azide Reactivity. Summarized in Scheme 1, the reactivity of eight different bis-cyclometalated iridium bis-isocyanide complexes [Ir(C^N)₂(CNAr)₂][PF₆] (**1**)^{41,42} with sodium azide was characterized. All compounds in this study are denoted by the identity of the cyclometalating ligand (C^N), which is 2-(2,4-difluorophenyl)pyridine (F₂ppy), 2-phenylbenzothiazole (bt), or 1-phenylisoquinoline (piq), and the aryl substituent on the isocyanide, which is 4-nitrophenyl (NO₂), 4-trifluoromethylphenyl (CF₃), 2,6-xylyl (xyl), or 4-methoxyphenyl (OMe). Reactions with aqueous sodium azide were carried out in a biphasic solvent system, using either CH₂Cl₂ (room temperature) or CH₃CN (with mild heating) as the

organic layer. All new compounds prepared in this study, which include the three bis-isocyanide precursors with 4-methoxyphenyl isocyanide and 10 azide-addition products, were characterized by a combination of NMR spectroscopy (Figures S1–S20 of the Supporting Information), IR spectroscopy (Figures S21–S32), high-resolution mass spectrometry, and, in some cases, single-crystal X-ray diffraction.

The outcome of the reaction of **1** with N_3^- depends on the electronic characteristics of the isocyanide. In all cases, ^{19}F and/or ^1H NMR spectroscopy indicate that the C_2 symmetry of the bis-isocyanide precursor descends to C_1 following reaction with N_3^- , but closer spectroscopic investigation, high-resolution mass spectrometry, and X-ray crystallography reveal four distinct products that can be cleanly isolated. When the aryl isocyanide is substituted with an electron-withdrawing group, the preferred product is of the general formula $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{CNAr})(\text{NCNAr})]$ (**2**), where one of the isocyanides has undergone formal nitrogen atom insertion to form an aryl cyanamido. Three of the four aryl cyanamido products were characterized by single-crystal X-ray diffraction, and their molecular structures are shown in Figure 1 with

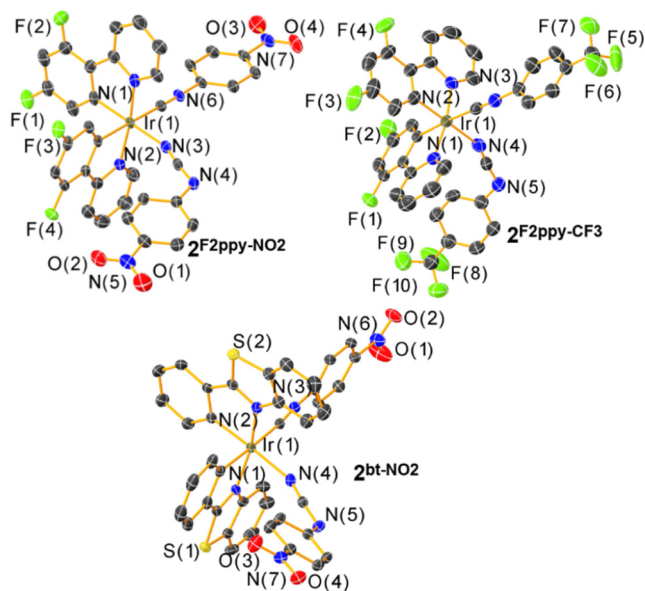


Figure 1. Molecular structures of **2F2ppy-NO₂**, **2F2ppy-CF₃**, and **2bt-NO₂**, determined by single-crystal X-ray diffraction. Thermal ellipsoids are drawn at 50% probability level, with hydrogen atoms and solvent molecules omitted for clarity.

refinement data summarized in Table S1 of the Supporting Information. Individual enlarged depictions of these structures are collected in Figures S33–S35. In all cases, the aryl cyanamido functionality is nearly linear, with $\text{N}-\text{C}-\text{N}$ angles that range between $171.4(5)^\circ$ and $175.2(5)^\circ$. The disparate short and long $\text{N}-\text{C}$ bonds proximal (1.13–1.15 Å) and distal (1.29–1.30 Å) to the iridium center indicate that the cyanamido resonance structure ($\text{N}\equiv\text{C}-\text{N}-\text{Ar}$), and not the carbodiimido ($\text{N}=\text{C}=\text{N}-\text{Ar}$), is dominant.

For bis-isocyanide precursors with electron-donating substituents on the isocyanides, there are three possible outcomes during the reaction with azide. The compounds **1F2ppy-xylyl** and **1F2ppy-OMe** undergo a $[3 + 2]$ cycloaddition with azide, which converts one of the isocyanides to a C-bound tetrazolato in products **3F2ppy-xylyl** and **3F2ppy-OMe**. The NMR spectra of

complexes **3** again indicate C_1 symmetry, with the ^1H NMR spectrum of **3F2ppy-xylyl** indicating hindered rotation of one of the two xylyl rings. HRMS analysis of these products gave m/z values ca. 28 units larger than the corresponding aryl cyanamido product, suggesting that N_2 was not extruded during the reaction. Single-crystal X-ray diffraction unambiguously confirmed the structures of both versions of **3**, shown in Figure 2 and reproduced in larger format in Figures S36 and

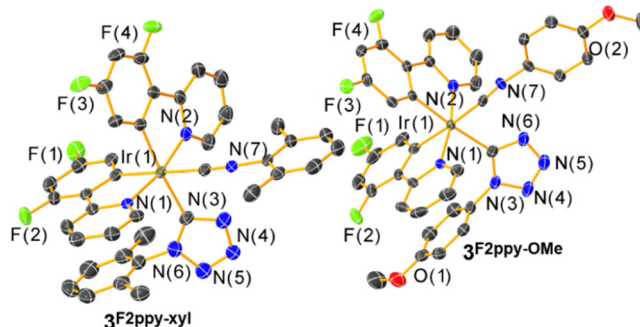


Figure 2. Molecular structures of **3F2ppy-xylyl** and **3F2ppy-OMe**, determined by single-crystal X-ray diffraction. Thermal ellipsoids are drawn at 50% probability level, with hydrogen atoms and solvent molecules omitted for clarity.

S37. Refinement data for these two compounds are summarized in Table S2. The crystal structures clearly show the five-membered π -conjugated tetrazolato bound through carbon, with the aryl ring on the tetrazolato directed toward one of the cyclometalating ligands. We presume that, for the aryl cyanamido products described above (Scheme 1 and Figure 1), the corresponding tetrazolato is formed as an intermediate, which then expels N_2 as described in other related chemistry.³⁶ When electron-donating groups are present, the tetrazolato is apparently more stable, and even prolonged heating of tetrazolato products **3F2ppy-xylyl** and **3F2ppy-OMe** in ambient atmosphere does not lead to formation of aryl cyanamido complexes. We also note that, despite using a large excess of sodium azide and long reaction times, we never observed products where both isocyanides were converted to cyanamidos, tetrazolatos, or a combination of the two.

The bis-isocyanide precursors with electron-donating groups react more sluggishly with azide than the more electron-poor analogues, on account of the reduced electrophilicity of the isocyanides, so we also screened the reaction between **1F2ppy-xylyl** and tetrabutylammonium azide, which can be executed in MeCN and does not require biphasic conditions. Because of the homogeneous nature of this reaction, we can achieve clean and quantitative conversion to **3F2ppy-xylyl** using only a slight excess of $(\text{NBu}_4)(\text{N}_3)$ under milder conditions (room temperature, overnight reaction time). However, separation of the desired product from the $(\text{NBu}_4)(\text{PF}_6)$ byproduct proved challenging via chromatography or crystallization, so this alternate route did not emerge as the preferred synthetic pathway.

In the reaction of bis-isocyanide **1F2ppy-OMe** with azide a second product was isolated, and analogous structures were also formed from **1bt-OMe** and **1piq-OMe** with different $\text{C}^{\wedge}\text{N}$ ligands. ^1H NMR spectra of these products (Figures S16, S18, and S19) do not indicate loss of any of the aromatic protons or OCH_3 protons from the isocyanide, but IR spectra (Figures

S29–S31) are completely transparent in the $\text{C}\equiv\text{N}$ stretching region, indicating functionalization of both isocyanides in these products and the absence of a cyanamido moiety. HRMS results differ from the bis-isocyanide precursor cations by ca. 56 m/z units, indicating net addition of four nitrogen atoms during the reaction, and single-crystal X-ray diffraction of one of the products, $\mathbf{4}^{\text{bt-OMe}}$, is shown in Figures 3 and S38 and

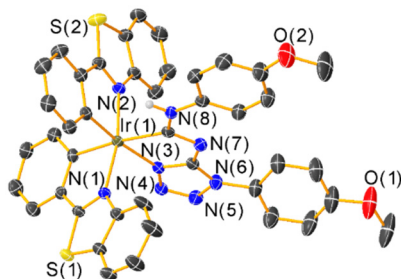


Figure 3. Molecular structure of $\mathbf{4}^{\text{bt-OMe}}$, determined by single-crystal X-ray diffraction. Thermal ellipsoids are drawn at 50% probability level, with carbon-bound hydrogen atoms omitted for clarity.

unambiguously identifies the structure. Refinement data for this structure are summarized in Table S2. This product includes a previously unobserved chelating ligand structure that combines an *N*-bound tetrazolato with an acyclic diamino carbene (ADC). This chelate presumably forms via conversion of one isocyanide to a tetrazolato and the other to an aryl cyanamido, followed by coupling of the two via *N*–C bond formation and rearrangement. Although the mechanism of this coupling and rearrangement was not studied in detail, it likely involves migratory insertion of the initially formed tetrazolato to the aryl cyanamido. The $\text{C}^{\wedge}\text{N} = \text{F}_2\text{ppy}$ and *piq* analogues of **4** were not obtained as single crystals, but their polarity is similar to that of $\mathbf{4}^{\text{bt-OMe}}$ during chromatographic purification, and their HRMS, NMR, and IR spectra are all fully consistent with the same structure type being formed.

In the azide addition reaction with $\mathbf{1}^{\text{piq-OMe}}$ described above, the chelated product $\mathbf{4}^{\text{piq-OMe}}$ was isolated as a minor product in modest yield (22%). A second, more abundant species was observed, which was separated chromatographically, isolated in 49% yield, and fully characterized. The ^1H NMR spectrum of this product only showed resonances for one 4-methoxyphenyl group per $[\text{Ir}(\text{piq})_2]^+$ center, indicating loss of one of the isocyanides during the reaction. The molecular structure of this product was determined by single-crystal X-ray diffraction and is shown in Figure 4 and reproduced in Figure S39, with refinement data summarized in Table S3. Crystallographic characterization reveals that the structure is dimeric and charge-neutral, with two aryl cyanamidos adopting a $\mu\text{-N,N'}$ bridging mode between the two $[\text{Ir}(\text{piq})_2]^+$ fragments. The core of this doubly bridged dimer is nearly rectangular in shape, owing to the *N*–Ir–*N* angles that are close to 90° and the nearly linear cyanamido $\text{N}\equiv\text{C}\text{--N}$ angles. This type of bridging motif has been observed previously, the best-characterized examples being dicopper(I) complexes.^{43–45}

From the standpoint of organometallic synthesis, the results described above are significant. While both tetrazolato and cyanamido products have been previously observed upon reaction of azides and isocyanides,^{36–40} in some cases with the tetrazolato converting to the cyanamido by thermolysis, this is the first study to show that the preference for tetrazolato or cyanamido can be controlled by the electronic nature of the

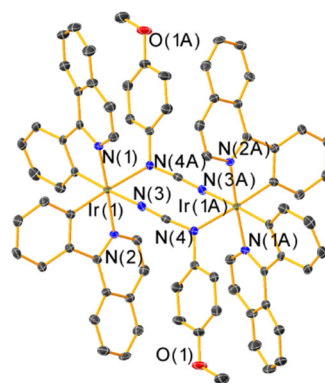


Figure 4. Molecular structure of $\mathbf{5}^{\text{piq-OMe}}$, determined by single-crystal X-ray diffraction. Thermal ellipsoids are drawn at 50% probability level, with hydrogen atoms omitted for clarity.

isocyanide. All reactions involving isocyanides with electron-withdrawing groups formed aryl cyanamido products, whereas tetrazolato complexes are usually observed with electron-donating groups. Moreover, the novel chelating ligand found in complexes **4**, which involves azide addition to both isocyanides followed by coupling of a tetrazolato and aryl cyanamido, had not been previously observed before. This chelate is an attractive carbene-containing ligand that may require metal templating to form and thus not be accessible by traditional coordination chemistry.

Electrochemistry. To evaluate the electronic effects of azide addition, the electrochemical properties of all complexes were studied by cyclic voltammetry in anaerobic acetonitrile solutions, except for $\mathbf{5}^{\text{piq-OMe}}$ where the solvent was THF. Oxidation or reduction peak potentials are reported relative to the ferrocene couple, Fc^+/Fc . Figures S40–S44 and Table S4 of the Supporting Information show the voltammograms and summarize the electrochemical data. Reduction waves depend primarily on the $\text{C}^{\wedge}\text{N}$ ligand, shifting progressively positive moving from F_2ppy to *bt* to *piq*. These shifts in reduction potential signify stabilization of the LUMO, reducing the HOMO–LUMO gap, which as described below manifests in the emission color depending primarily on the $\text{C}^{\wedge}\text{N}$ ligand. In complexes $\mathbf{2}^{\text{F}_2\text{ppy-NO}_2}$ and $\mathbf{2}^{\text{bt-NO}_2}$ the two reversible reduction waves are anodically shifted (more positive) by at least 700 mV compared to other complexes with the same $\text{C}^{\wedge}\text{N}$ ligands, and can be assigned as being centered on the 4-nitrophenyl rings. As found in many other cyclometalated iridium isocyanide complexes^{41,42} and compounds derived from them,^{27,28} the compounds reported here are unstable upon oxidation and one or more irreversible oxidation waves are observed. In general, the azide-addition products are easier to oxidize than their respective isocyanide precursor, although the complex, irreversible nature of the oxidation waves makes decisive, quantitative conclusions difficult. As described below, the effects of azide addition on the HOMO energy and associated oxidation potential result in only mild red shifts of the photoluminescence in comparison to the isocyanide precursors.

Photophysical Properties. We have previously published a few detailed studies on the photophysical properties of bis-cyclometalated iridium bis-isocyanide complexes of the type used as precursors in this study (**1**).^{41,42,46} The three complexes with 4-methoxyphenylisocyanide have not been previously reported, and their photophysical data are

summarized in Figures S45–S47 of the Supporting Information and Table 1 below. Their excitation spectra, overlaid with

Table 1. Summary of Photoluminescence Data, Recorded at Room Temperature

Complex	CH ₂ Cl ₂			2 wt % in PMMA	
	λ /nm ^a	Φ_{PL}	τ /μs	λ /nm ^a	Φ_{PL}
1 ^{F2ppy-OMe}	438, 468*	0.18	19	438, 468*	0.52
1 ^{bt-OMe}	500, 536*, 576	0.56	29	501, 537*, 578	0.75
1 ^{piq-OMe}	615	0.12	15	613	0.27
2 ^{F2ppy-NO₂}	N.D. ^b	N.D. ^b	N.D. ^b	579	0.01
2 ^{F2ppy-CF₃}	449, 476*	0.02	0.40	449, 476*	0.36
2 ^{bt-NO₂}	556	0.01	6.8	558	0.08
2 ^{bt-CF₃}	522, 555*	0.45	6.4	520, 553*	0.76
3 ^{F2ppy-xyI}	448, 476*	0.81	10	448, 475*	0.35
3 ^{F2ppy-OMe}	447, 475*	0.23	8.2	447, 475*	0.11
4 ^{F2ppy-OMe}	455, 481*	0.03	17	457, 482*	0.39
4 ^{bt-OMe}	528, 569*	0.62	1.8	528, 569*	0.87
4 ^{piq-OMe}	596, 639*	0.28	2.5	592, 631*	0.65
5 ^{piq-OMe}	624	0.54	1.5	618	0.49

^aVibronic shoulders omitted for brevity. The absolute maximum is marked with an asterisk (*). ^bThis compound is not luminescent in solution at room temperature.

UV–vis absorption spectra, are in Figures S48–S50. Complexes **1**^{F2ppy-OMe} and **1**^{bt-OMe} largely mirror the photophysical aspects of other bis-isocyanide complexes with the same C[^]N ligands, absorbing almost exclusively in the UV region, and luminescing in the sky-blue (**1**^{F2ppy-OMe}) or yellow-green (**1**^{bt-OMe}) regions with sharp vibronic structure and long lifetimes (19 and 29 μs, respectively). We have not previously

described bis-isocyanide complexes with C[^]N = piq, and the photoluminescence of **1**^{piq-OMe} occurs in the orange-red region, as expected for C[^]N = piq, with Φ_{PL} = 0.12 and τ = 15 μs (Figure S47 and Table 1).

The photophysical consequences of azide addition are of greater interest to this study, and overlaid UV–vis absorption spectra and photoluminescence spectra of the series of the azide-addition products are shown in Figure 5. In the UV–vis absorption spectra, the low-energy charge-transfer absorption bands are red-shifted in the azide-addition products relative to the isocyanide precursors, mirroring the electrochemical trends described above and again suggesting smaller HOMO–LUMO gaps upon azide addition.

Table 1 below summarizes the photoluminescence data, and excitation spectra are shown in Figures S51–S59. The nitro substituent is well-known to quench photoluminescence in most cases,⁴⁷ and accordingly, the photoluminescence of aryl cyanamido complexes **2**^{F2ppy-NO₂} and **2**^{bt-NO₂} is modest, both in solution and in PMMA film (Table 1). In **2**^{F2ppy-NO₂} there is no emission in solution at room temperature, and the PMMA emission is featureless and occurs at 579 nm, in stark contrast to the usual vibronically structured sky-blue emission that normally results when C[^]N = F₂ppy. Thus, it seems in this compound the lowest-energy excited state is a charge-transfer state involving one or both 4-nitrophenyl groups, which gives rise to weak photoluminescence.

The remaining compounds besides **2**^{F2ppy-NO₂} are luminescent both in solution and in PMMA film, with nearly identical profiles in both media (Figure 5). The photoluminescence color and wavelengths are predictably determined by the C[^]N ligand, with subtler influences of the ancillary ligand(s). To better visualize the effects of the different ancillary ligands

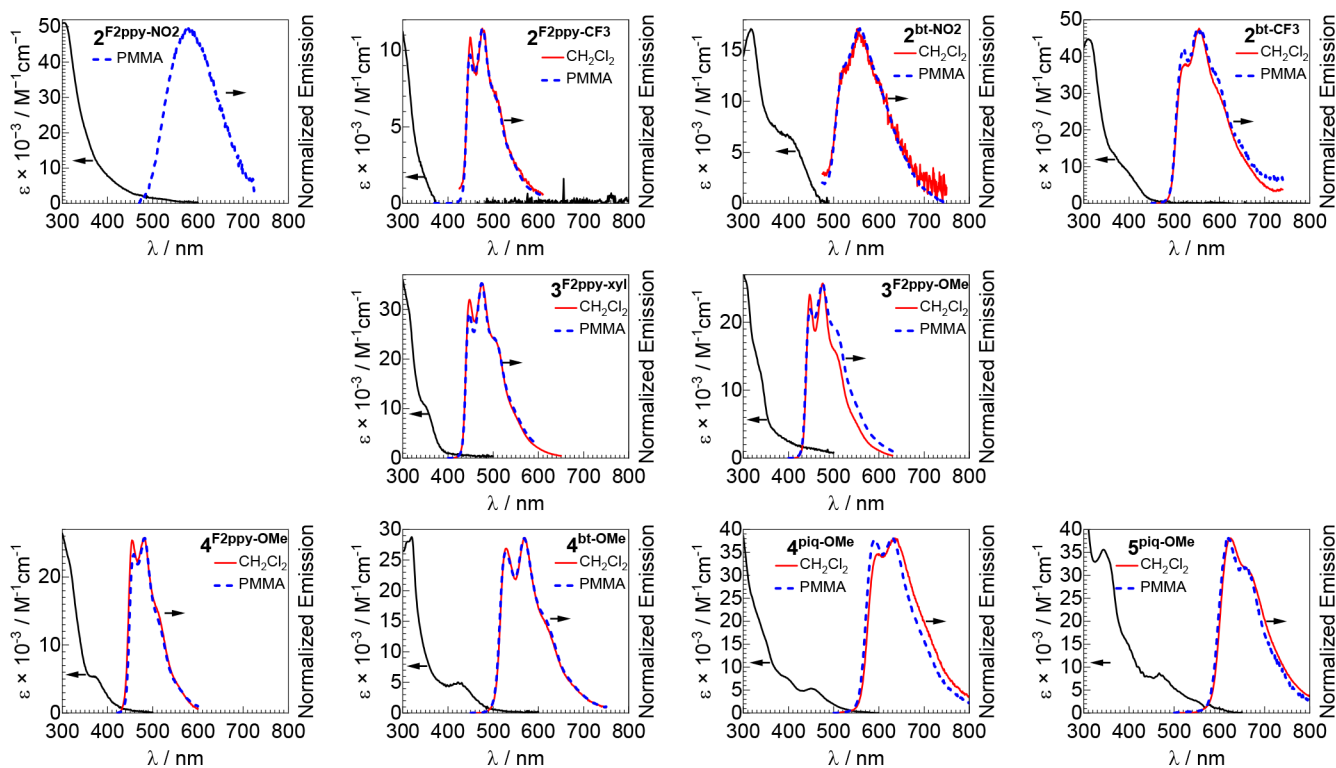


Figure 5. UV–vis absorption and photoluminescence spectra of all azide-addition products, recorded at room temperature. UV–vis absorption spectra were recorded in CH₂Cl₂ (black solid line), and photoluminescence spectra were recorded in CH₂Cl₂ (red solid line) and as a 2 wt % transparent PMMA film (blue dashed line). The complex **2**^{F2ppy-NO₂} is not luminescent in solution at room temperature.

formed by azide addition, Figure 6 overlays photoluminescence spectra organized by C^N ligand, with photoluminescence in

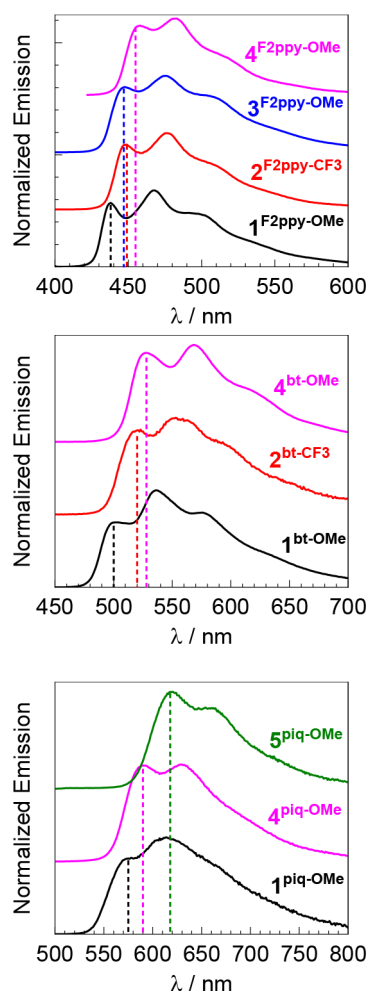


Figure 6. Overlaid photoluminescence spectra of complexes from each class, arranged by C^N ligand. Spectra were recorded in 2 wt % PMMA at room temperature. The dashed vertical lines indicate the λ_{0-0} values for better comparison.

PMMA films shown. In all cases, azide addition results in a red shift in photoluminescence, which we attribute to a reduction in π -acidity as one or both isocyanides are converted, which reduces the HOMO–LUMO and T_1 energy slightly. In the F₂ppy series, the photoluminescence wavelengths increase in the order $1 < 2 \approx 3 < 4$. Addition of a single equivalent of azide to form either an aryl cyanamido (2) or tetrazolato (3) product results in nearly identical photoluminescence profiles, and the addition of 2 equiv to form 4 enables a larger red shift. The same trend is observed with the three C^N = bt complexes shown in Figure 6, with even more pronounced shifts in these yellow-emitting complexes. The λ_{0-0} wavelength in 2^{bt-CF₃} shifts by ca. 22 nm (843 cm^{−1}) relative to the bis-isocyanide precursor, and in 4^{bt-OMe} with the chelating *N*-tetrazolato-ADC ligand an additional 6 nm (218 cm^{−1}) shift is observed. In the piq series there is likewise a measurable red shift of λ_{0-0} in the two cyanamido products, most pronounced in the bimetallic complex 5^{piq-OMe}. The azide-produced ancillary ligands also have pronounced impacts on the photoluminescence quantum yield (Φ_{PL}) and lifetime (τ). Table S5 in the Supporting Information gives a more

comprehensive summary of excited-state dynamics in solution, which includes k_r and k_{nr} values. The sky-blue emitting aryl cyanamido complex 2^{F₂ppy-CF₃} and chelate complex 4^{F₂ppy-OMe} have very weak luminescence in solution, which is turned on considerably in PMMA film ($\Phi_{PL} = 0.36$ and 0.39, respectively). However, exceptionally bright sky-blue luminescence occurs in solution for tetrazolato complex 3^{F₂ppy-xy1}, which has a photoluminescence quantum yield of 0.81 in CH₂Cl₂. The quantum yield in this complex is over twice as high as the bis-isocyanide precursor 1^{F₂ppy-xy1} ($\Phi_{PL} = 0.37$),⁴¹ and the much shorter lifetime in the tetrazolato complex (10 μ s vs 41 μ s) indicates that a nearly 10-fold increase in the radiative rate constant, k_r , is responsible. Interestingly, the 4-methoxyphenyl analogue 3^{F₂ppy-OMe} has a much lower Φ_{PL} of 0.23 in solution, suggesting that the rigidity afforded by the *ortho* methyl groups in the xylyl analogue may play an important role.

In the yellow-emitting C^N = bt series, photoluminescence quantum yields are consistently high, except for nitro-substituted aryl cyanamido complex 2^{bt-NO₂}. In both cases, for aryl cyanamido product 2^{bt-CF₃} and chelated *N*-tetrazolato-ADC complex 4^{bt-OMe}, the photoluminescence quantum yields are significantly higher than the respective bis-isocyanide precursor. Particularly outstanding outcomes were observed in 4^{bt-OMe}, which has a Φ_{PL} of 0.62 in solution and 0.87 in PMMA, with the short lifetime in solution ($\tau = 1.8$ μ s) and very fast radiative decay far exceeding isocyanide precursor 1^{bt-OMe} and comparable to other C^N = bt complexes used in optoelectronic applications.⁴⁸ Motivated by this outcome, we also prepared the C^N = piq analogue 4^{piq-OMe} with even lower-energy phosphorescence. The orange-red phosphorescence of this compound has Φ_{PL} values of 0.28 in solution and 0.65 in PMMA, slightly lower than the yellow-emitting analogues on account of the energy-gap law.⁴⁹ Still, these values are more than twice as high as the isocyanide precursor 1^{piq-OMe} with a much faster radiative rate constant, and comparable to other red-phosphorescent iridium complexes used in efficient OLED designs ($\Phi_{PL} \approx 0.5$).^{48,50–52} Even better outcomes are realized in the bimetallic cyanamido-bridged complex 5^{piq-OMe}, which has the fastest radiative rate and the highest quantum yield (0.54) in fluid solution of the three red-phosphorescent compounds studied.

To summarize the photophysical observations, the most consistent outcome, observed in all but two cases, is that azide addition results in higher radiative rates in solution than the bis-isocyanide precursors, which is desirable for certain optoelectronic applications.²⁰ Quantum yield values are variable in solution for the blue-emitting F₂ppy complexes although one compound, 3^{F₂ppy-xy1}, is very strongly luminescent in solution, and moderate Φ_{PL} values are observed in PMMA films across the series. More consistent outcomes were observed in the C^N = bt series, where the bis-isocyanide precursors and azide addition products all can have good quantum yields, albeit with much faster radiative rate constants and shorter lifetimes in the latter. In the orange-red C^N = piq set of complexes, azide addition to form 4^{piq-OMe} and 5^{piq-OMe} has the same effect of increasing k_r and decreasing τ , while also resulting in significant increases in Φ_{PL} . Importantly, these results show that azide addition to isocyanides can have pronounced and in some cases beneficial effects on the photoluminescence, motivating continued exploration of ligand-functionalization strategies to control and optimize excited-state dynamics.

CONCLUSIONS

Here we showed that azide addition to bis-cyclometalated iridium bis-isocyanide compounds gives access to a diverse set of new structures, with the fate of the reaction controlled primarily by the substituent pattern on the isocyanide with a secondary effect of the cyclometalating ligand. Previous work using isocyanide functionalization as a synthetic strategy for cyclometalated iridium complexes exclusively involved nucleophilic addition of nitrogen-based reagents, which gives access to acyclic diaminocarbenes.^{25,27,28} The reactions described here lead to more diverse outcomes, and presumably all initiate with a [3 + 2] azide-isocyanide cycloaddition. This cycloaddition can give a stable tetrazolato when the isocyanide is substituted with electron-donating groups, which is followed by N₂ extrusion to leave an aryl cyanamido with electron-withdrawing groups. Interestingly, isocyanides with electron-donating groups can give two other possible outcomes, one of which involves coupling and rearrangement of a tetrazolato and aryl cyanamido, the other the formation of a bridged bimetallic aryl cyanamido species. All observed structures would not be easily obtainable by traditional coordination-chemistry approaches, showing the value of ligand-based functionalization reactions in introducing new structure types. Importantly, azide addition has pronounced and, in some cases, positive impacts on the photoluminescence metrics. Mild spectral red shifts are observed as each isocyanide is functionalized, but more significantly, large increases in radiative rates occur in most cases. As a result, some of the azide-addition products have photoluminescence quantum yields in solution and/or polymer film that are not only higher than the respective bis-isocyanide precursor but also exceptional in an absolute sense. We will continue to use ligand-centered functionalization schemes to diversify the structure space of cyclometalated iridium and other phosphorescent organometallics and use these strategies to optimize photoluminescence attributes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.2c11062>.

Experimental details, X-ray crystallography summary tables, NMR spectra, IR spectra, crystal structures, cyclic voltammetry data, and additional photophysical data. (PDF)

Accession Codes

CCDC 2208150–2208155 and 2210106 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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Notes

The authors declare no competing financial interest.

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