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Combined Nucleophilic and Electrophilic Functionalization to Optimize Blue Phosphorescence in Cyclometalated Platinum Complexes

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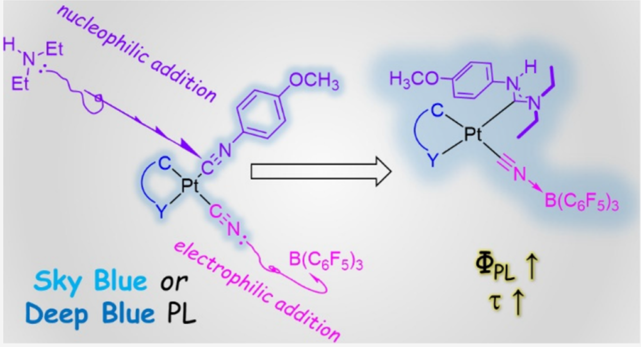
ABSTRACT: Ligand-based functionalization strategies have emerged as powerful approaches to tune and optimize blue phosphorescence, which can involve nucleophilic addition to coordinated ligands or electrophilic functionalization via the coordination of exogenous Lewis acids. Whereas both have been used separately to enhance the photophysical properties of organometallic compounds with high-energy triplet states, in this work, we show that these two strategies can be used together on the same platform. Isocyanide-supported cyclometalated platinum compounds undergo nucleophilic addition with diethylamine to form a strong σ-donor acyclic diaminocarbene-supporting ligand. In a subsequent step, a cyanide ancillary ligand is converted into a more strongly π-acidic isocyanoborate via the coordination of a borane Lewis acid. Importantly, both of these ligand-based functionalization steps improve the quantum yields and lifetimes of the blue-phosphorescent complexes. This synergy results in complexes with photoluminescence quantum yields up to 0.40 for deep blue and 0.75 for sky blue regions and PL lifetimes on the order of 10^{-5} s.



■ INTRODUCTION

Over the past few decades, phosphorescent metal complexes with emission colors spanning the entire visible range and beyond have been widely studied. Organic light-emitting diodes (OLEDs) are one of the most intensely investigated and technologically successful applications of molecular phosphorescence, and devices can approach 100% internal efficiency when phosphorescent dopants are used.[1−3] The dearth of effective blue-phosphorescent compounds stands as both a significant hindrance in the OLED sector as well as a fundamental challenge that has been pursued by several groups.[4−7] It is difficult to simultaneously optimize the color purity, quantum yield, and stability of a blue-phosphorescent compound, and success in this area requires innovative synthetic approaches and creative molecular designs.

Blue phosphorescence requires high triplet-state (T_1) energies, necessitating a careful choice of supporting ligands to engender large HOMO−LUMO gaps. A well-established concept in the design of organometallic blue phosphors is that the thermal population of higher-lying ligand-field states is deleterious to the efficiency and stability of blue phosphorescence. These states are also triplet in nature for Ir(III) and Pt(II) and are often termed as "metal-centered (^{3}MC) states." As such, successful designs of blue phosphors include supporting ligands that not only result in large HOMO−LUMO gaps to beget blue phosphorescence but also are strong σ-donors capable of destabilizing the ^{3}MC states. For these reasons, monodentate or polydentate ligands featuring *N*-heterocyclic carbenes (NHCs) have become popular and effective choices when designing blue-phosphorescent compounds.[4−12]

An emerging and complementary strategy, which has gained traction in recent years, is to use ligand-based functionalization strategies to install or modify supporting ligands to optimize blue phosphorescence. These approaches can give access to supporting ligands that are not readily installed by traditional synthetic methods and fall into two main categories: The first is nucleophilic addition to coordinated isocyanides, which generates acyclic diaminocarbenes (ADCs), even stronger σ-donors than NHCs and thus particularly well-suited for blue phosphorescence (Figure 1a). There are a few prior reports on ADC-supported complexes that luminesce outside of the blue region,[13−15] with our group spearheading the use of ADC ligands in compounds that phosphorescence in the higher-energy regions of the spectrum. We have installed ADCs onto

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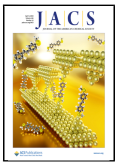

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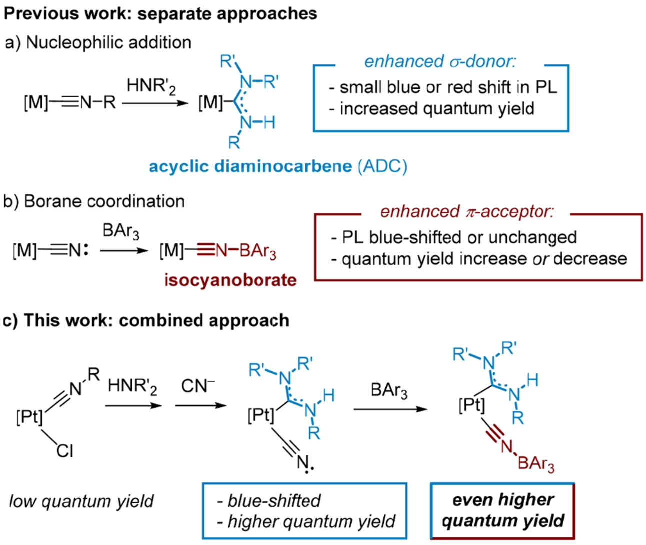


Figure 1. Previous ligand-based strategies to modify and optimize blue-phosphorescent organometallics and the combined approach used in this work.

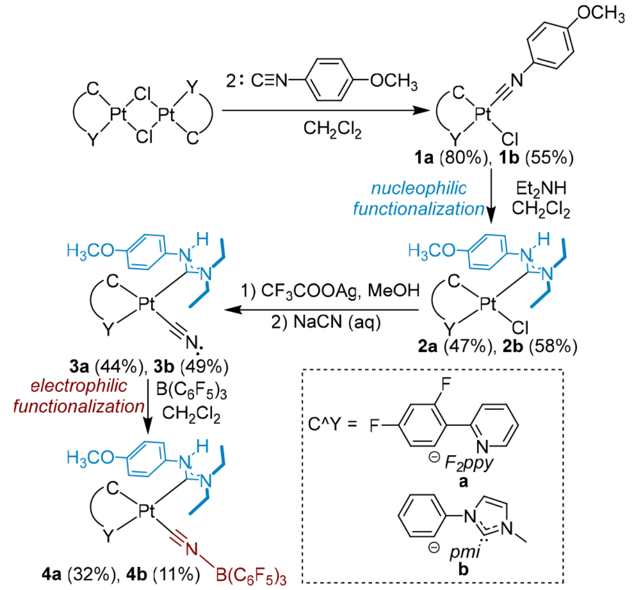
both cyclometalated iridium[16,17] and platinum acetylide complexes,[18−21] via nucleophilic addition to isocyanide precursors, generating compounds that luminesce in the sky blue[16,19,21] or deep blue[17,18,20] regions. In the vast majority of cases, installation of the ADC results in higher photoluminescence (PL) quantum yields and smaller nonradiative rate constants (k_{nr}) than the isocyanide precursor, which computational analysis concluded is a result of the destabilization of the ^{3}MC states by the strong σ-donor ADCs.[20] The second major approach to ligand-based functionalization, which has been less explored in the context of blue phosphorescence, is electrophilic functionalization, i.e., Lewis acid coordination; Figure 1b. Most commonly, a cyanide-supporting ligand coordinates to a triarylborane via its nitrogen lone pair, forming an isocyanoborate $[\text{CNBAr}_3]^-$, a better π-acceptor and thus a stronger-field ligand than CN^-. The photophysical consequences of this synthetic modification are less consistent; in cyclometalated iridium complexes, cyanide−borane coordination blue-shifts the phosphorescence and, in most cases, increases the PL quantum yield,[22,23] which in one recent example was ascribed to a steep reduction in k_{nr}.[23] In a report on terdentate cyclometalated platinum complexes with isocyanoborate ancillary ligands, it was shown that the borane coordination had minimal effect on the PL wavelength, but it led to significant increases in PL quantum yield.[24]

Given the successes of these two approaches, we describe here platforms that are amenable to both nucleophilic *and* electrophilic functionalization, a synergy that we postulated would lead to sequential beneficial effects on blue-phosphorescence metrics (Figure 1c). To probe this hypothesis, we prepared two sets of blue-phosphorescent platinum complexes using 2-(2,4-difluorophenyl)pyridine (F$_2$ppy) and 1-methyl-3-phenylimidazol-2-ylidene (pmi) as the cyclometalating ligands. The compounds allow sequential installation of an ADC via nucleophilic addition and an isocyanoborate via borane coordination. Photophysical studies show that the ADC results in a blue shift of the PL while increasing the quantum yield by 3.3× or 12.3× relative to the isocyanide precursor. The addition of borane further boosts the PL quantum yield while retaining the blue emission profile. These increases in quantum yield are largely driven by decreases in k_{nr}, consistent with the strongly σ-donating ADC and strongly π-accepting isocyanoborate progressively destabilizing the nonradiative ^{3}MC states.

■ RESULTS AND DISCUSSION

Synthesis and Structural Characterization. Scheme 1 shows the approach used to sequentially functionalize cyclometalated platinum complexes via nucleophilic and electrophilic addition. Isocyanide-terminated platinum complexes **1a−b**, chelated respectively by the cyclometalating (C^Y) ligands F$_2$ppy and pmi, are synthesized by treating their chloro-bridged dimer precursors with 2 equiv of 4-methoxyphenyl isocyanide under reflux and isolated in good yields. The nucleophilic addition step was carried out next, with ADC complexes **2a−b** obtained by adding excess diethylamine to the isocyanide precursor in dichloromethane at room temperature, giving the desired products in a moderate isolated yield. From there, the platform was further derivatized to allow electrophilic functionalization. The ADC−chloride complexes **2a−b** were treated with silver trifluoroacetate in methanol to abstract the chloride, followed by the addition of an aqueous solution of sodium cyanide to install the cyanide ancillary ligand, producing complexes **3a−b**. The final electrophilic functionalization step, to produce borane adducts **4a−b**, was executed by combining **3a−b** with tris(pentafluorophenyl)borane in dichloromethane under an inert atmosphere, affording the products as colorless powders in modest yields following recrystallization. The moderate isolated yields we report are primarily due to product loss during recrystallization, necessary to ensure the products are free of any luminescent impurities.

Scheme 1. Synthesis of New Platinum Complexes[a]



[a]Isolated yields for each compound are shown in parentheses.

The new platinum compounds **1−4** were structurally validated by NMR spectroscopy (Figures S1−S17). Complexes **1a−4a** exhibit two well-defined ^{19}F signals within the range of −105 to −115 ppm. The conversion of the isocyanides into ADCs (**1** → **2**) led to the disappearance of the strong $\tilde{\nu}_{\text{C}\equiv\text{N}}$ peaks in the FT-IR spectra (Figures S18, S19, S22 and S23),

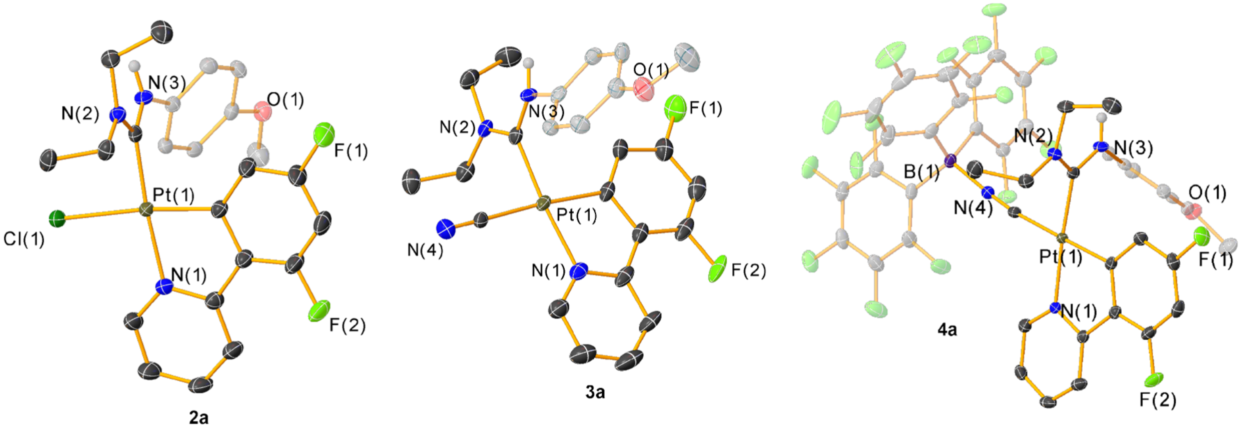


Figure 2. Molecular structures of new platinum complexes determined by single-crystal X-ray diffraction. Ellipsoids are shown at a 50% probability level with carbon-bound hydrogen atoms and solvent molecules omitted. Aryl substituents associated with the ADC and/or isocyanoborate ligand are shown in a lighter color for better contrast and perspective.

accompanied by the emergence of signals for the N-*H* protons in the ^{1}H NMR spectra, characterized by pronounced satellites arising from coupling interactions with the ^{195}Pt centers ($^3J_{\text{Pt-H}}$ = 88 Hz for **2a** and 68 Hz for **2b**).[18−21] Substituting the chloride ligand in **2a**−**b** with the cyanide ligand in **3a**−**b** led to the emergence of a $\tilde{\nu}_{\text{C≡N}}$ stretch near 2100 cm^{-1} (Figures S20 and S24), while coordination of the borane in **4a**−**b** increases the C≡N stretching frequency (Figures S21 and S25) and shifts the N-*H* protons downfield, both in alignment with the electron-withdrawing influence of the borane moiety.[25,26] For complexes **1a**, **3a**, and **4a**, the C≡N stretches are observed at higher frequency when compared to their counterparts **1b**, **3b**, and **4b**, indicating that the F$_2$ppy cyclometalating ligand is less electron-donating than pmi.

The structures of compounds **2a**−**4a**, **1b**, and **4b** were further characterized by single-crystal X-ray diffraction. Molecular structures for **2a**−**4a** are presented in Figure 2, while those for **1b** and **4b** are available in Figures S26 and S27, respectively. Detailed structural data for all five compounds are summarized in Tables S1 and S2 of the Supporting Information. The Pt centers in all of the complexes exhibit an almost perfectly planar geometry, with the neutral ancillary ligand (isocyanide in **1b**, ADC in the rest) arranged *trans* to the neutral heterocycle (pyridine or NHC) of the cyclometalated ligands. In all cases, the ADC ligand is nearly perpendicular to the Pt coordination plane, most likely to avoid a steric clash with the cyclometalated ligand. In the solid state, this arrangement effectively inhibits significant π-stacking interactions among the complexes. Selected bond lengths are summarized in Table 1, along with C≡N stretching frequencies determined by IR. One key takeaway is that the Pt−C$_{\text{ADC}}$ distance in pmi complex **4b** is substantially longer than the same distance in the F$_2$ppy complexes, again reflecting the difference in the trans influence between these two cyclometalating ligands. Another notable outcome is that the Pt−C$_{\text{aryl}}$ bond distance in chloride-terminated **2a** measures 1.976(3) Å, significantly shorter than those of **3a** and **4a**, originating from the weaker trans influence of chloride compared to that of cyanide or isocyanoborate. Interestingly, the C≡N bond distance in isocyanoborate complex **4a** is identical to the average of the two crystallographically independent C≡N distances in its cyano precursor **3a**, despite the large change in $\tilde{\nu}_{\text{C≡N}}$ that accompanies borane coordination.

Table 1. Selected Bond Lengths and $\tilde{\nu}_{\text{C≡N}}$ Values of the Crystallographically Characterized Platinum Complexes

complex	bond lengths/Å			$\tilde{\nu}_{\text{C≡N}}$/cm^{-1}
	Pt−C$_{\text{ADC}}$	Pt−C$_{\text{phenyl}}$	C≡N	
2a	1.982(3)	1.976(3)	N/A	N/A
3a	2.002(5), 1.984(5)[a]	2.026(5), 2.024(5)[a]	1.140(6), 1.151(6)[a]	2125
4a	1.990(2)	2.023(2)	1.146(3)	2187
1b	N/A	2.015(2)	1.152(3)	2175
4b	2.041(6), 2.048(6)[a]	2.053(6), 2.070(6)[a]	1.152(7), 1.152(7)[a]	2125

[a] Distances are listed for each of the crystallographically independent molecules.

Photophysical Properties. UV−vis absorption spectra in CH$_2$Cl$_2$ solution and PL spectra in 2 wt% poly(methyl methacrylate) (PMMA) films are shown in Figure 3 (absorption spectra are shown as black lines, and PL spectra as blue lines). The data are summarized in Table 2, and for better comparison, UV−vis spectra are overlaid in Figures S28 and S29, and PL spectra in Figures S30 and S31. All compounds display strong absorption in the λ < 300 nm region, with weaker, overlapping bands tailing off before 400 nm. The high-energy absorption bands in complexes **1**−**4** likely arise from $\pi \to \pi^*$ transitions centered on the conjugated ligands. The low-energy bands are assigned as MLCT bands involving the highest-occupied 5*d* orbital and C^Y-centered LUMO.

In PMMA films at room temperature, all platinum complexes luminesce in the blue region with λ_{0-0} between 415−433 nm (deep blue) when C^Y = pmi and 453−462 nm (sky blue) when C^Y = F$_2$ppy. A more detailed description of the color profiles is given below. At room temperature in CH$_2$Cl$_2$ solvent, only C^Y = F$_2$ppy complexes **2a**−**4a** exhibit luminescence, as shown in Figures S32 and S34 and summarized in Table S3, whereas none of the C^Y = pmi complexes luminesce in solution.

The most significant photophysical outcome is that both the nucleophilic and electrophilic ligand-based functionalization strategies improve the PL quantum yield (Φ_{PL}). First, conversion of the isocyanide into an ADC leads to a 12.3-fold increase in the quantum yield of the F$_2$ppy complexes (**1a** → **2a**) and 3.3-fold increase in the quantum yield of the pmi

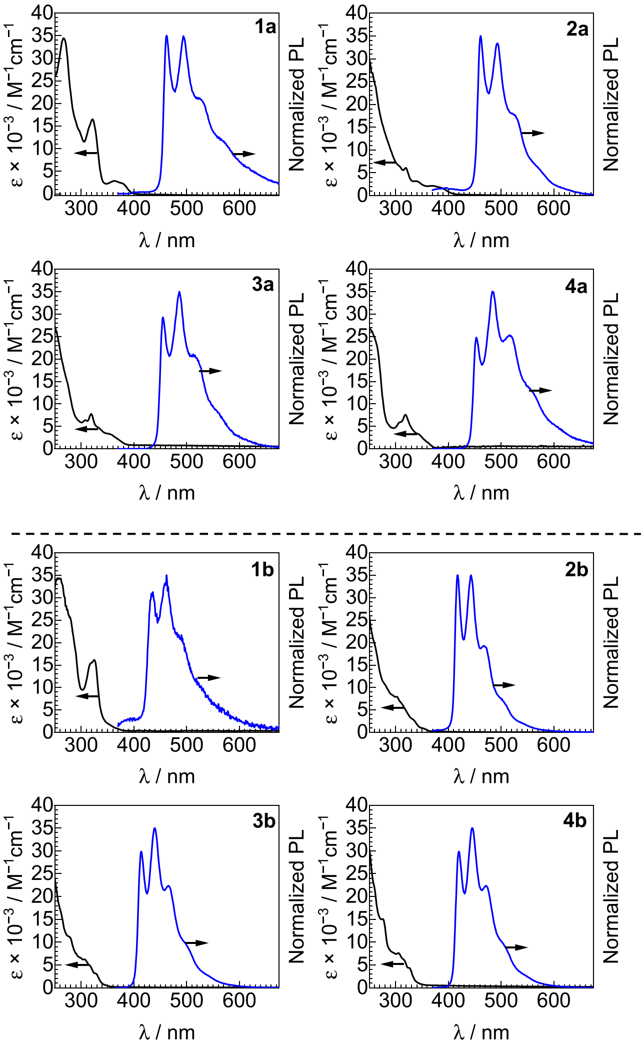


Figure 3. Overlaid UV−vis absorption (black lines) and normalized PL spectra (blue lines) of all cyclometalated platinum complexes. Absorption spectra were recorded in CH_2Cl_2 at room temperature, and PL spectra were recorded in 2 wt% PMMA films at room-temperature.

complexes (**1b** → **2b**). These increases in quantum yield are accompanied by noticeable increases in PL lifetime and in each case involve both a sharp increase in the radiative rate constant (k_r) and a pronounced reduction in the nonradiative rate constant (k_{nr}), the latter attributed to destabilization of ^{3}MC states by the strong σ-donor ADC. Notably, the relative decreases in k_{nr} are similar in **2a** and **2b**, but the larger quantum yield enhancement in the former arises from a larger increase in k_r. The decreases in k_{nr} we observe upon installation of an ADC align well with our previous reports on ADC-supported platinum acetylide complexes.[18−21] However, the significant enhancement in k_r is unique to the cyclometalated complexes described here, which we believe arises from these compounds having greater ^{3}MLCT character in their emissive T_1 state, and thus having radiative decay dynamics that are more strongly affected by the ancillary ligands, in contrast to the platinum acetylide complexes where the excited state is almost exclusively acetylide-localized $^3(\pi \rightarrow \pi^*)$ in nature. In both **2a** and **2b**, the installment of the ADC leads to a subtle blue shift of the phosphorescence, as judged by the λ_{0-0} value (Table 2) and the CIE coordinates (Figure 4).

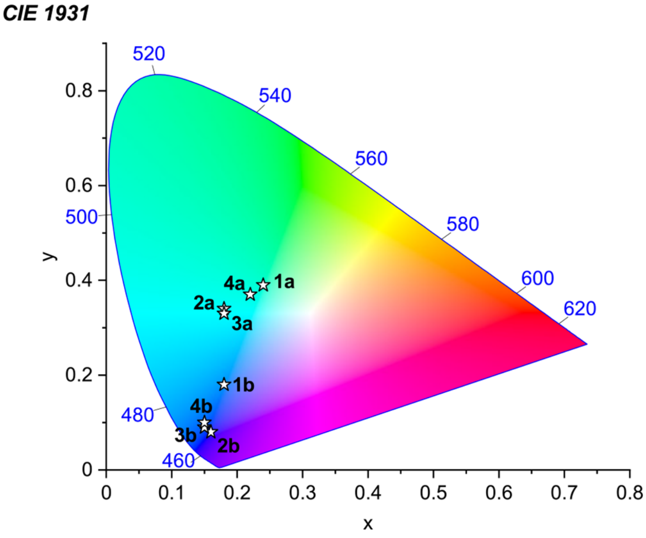


Figure 4. Chromaticity diagram showing the (CIEx, CIEy) coordinates of **1**−**4**.

Further derivatization of the compounds leads to additional increases in the blue-phosphorescence metrics. Substitution of the chloride ligand with the cyanide ligand (**2** → **3**) nearly doubles Φ_{PL} in both cases, with the lifetimes increasing ca. 1.5-fold. The phosphorescence λ_{0-0} values in complexes **3a**−**b** are blue-shifted relative to their respective chloride precursors **2a**−**b**, with minimal changes in the CIE coordinates (see Figure 4). The increases in quantum yield and lifetime originate from the strong-field nature of the cyanide ligand relative to chloride, which increases the energy of the ^{3}MC states and slows

Table 2. Summary of UV−Vis Absorption and PL Data

	UV−vis absorption[a]	PL[b]					
complex	λ_{max}/nm ($\varepsilon \times 10^{-3}$/$M^{-1}cm^{-1}$)	λ_{0-0}/nm	Φ_{PL}	τ/μs	k_r/s^{-1}	k_{nr}/s^{-1}	(CIEx, CIEy)
1a	267 (35), 322 (16), 363 (3)	462	0.03	5.4	6×10^3	2×10^5	(0.24, 0.39)
2a	316 (6)	461	0.37	9.4	3.9×10^4	6.7×10^4	(0.18, 0.34)
3a	319(8)	455	0.67	14	4.8×10^4	2.4×10^4	(0.18, 0.33)
4a	319 (8)	453	0.75	30	2.5×10^4	8.3×10^3	(0.22, 0.37)
1b	258 (34), 279 (26) (sh)[c], 325(16)	433	0.03	1.3	2×10^4	7×10^5	(0.18, 0.18)
2b	304 (8) (sh)	418	0.10	3.9	2.6×10^4	2.3×10^5	(0.16, 0.08)
3b	280 (11), 307 (6) (sh), 328 (3) (sh)	415	0.23	4.6	5.0×10^4	1.7×10^5	(0.15, 0.09)
4b	276 (15), 305 (8), 325 (4)	419	0.40	11	3.6×10^4	5.5×10^4	(0.15, 0.10)

[a]Recorded in CH_2Cl_2 at room temperature. [b]Recorded in 2 wt% PMMA films at room temperature. [c]sh = shoulder.

nonradiative decay. The blue shifts can be ascribed to the π-accepting nature of cyanide versus the π-donating nature of chloride, which stabilizes $5d\pi$ orbitals, consequently leading to higher-energy ^{3}MLCT states. These photophysical consequences of replacing chloride with cyanide are in line with well-characterized effects observed in cyclometalated iridium complexes,[27,28] with recent computational analyses explicitly showing that substituting chloride for cyanide stabilizes the $5d\pi$ orbitals and substantially raises the energy of the higher-lying ^{3}MC states.[28]

Finally, coordination of the borane $B(C_6F_5)_3$ (**3** → **4**) gives an additional layer of control over the excited-state dynamics and, yet again, enhances both the PL quantum yields and lifetimes. The addition of borane causes a slight decrease in k_r but an even larger suppression of k_{nr}, leading to a 1.2× increase in Φ_{PL} for the F_2ppy complex **4a**, and a larger 1.7× increase for the deeper blue pmi complex **4b**. Compared to cyanide, isocyanoborates are stronger π-acids and weaker σ-donors.[29] Despite these competing effects, previous spectroscopic[30] and computational[29,31] studies on metal isocyanoborate complexes consistently show that borane addition increases the ligand-field strength and d−d splitting, which in turn leads to higher-energy ^{3}MC states. Thus, we propose that the decreases in k_{nr} we observe in **4a** and **4b** relative to their cyanide precursors occur because of the increased ligand-field strength upon borane addition, which destabilizes the deleterious ^{3}MC states. The effects of the isocyanoborate ligand on the color profile are subtle and inconsistent among the two members of the series. The λ_{0-0} value of F_2ppy complex **4a** is slightly blue-shifted relative to **3a**, but the more pronounced λ_{0-2} peak in **4a** furnishes CIE coordinates that suggest less blue coloration. In **4b** λ_{0-0} is slightly longer than that in **3b**, but the overall spectral profile, as judged by CIE coordinates, is minimally different.

To summarize the photophysical consequences of combined nucleophilic/electrophilic functionalization, we have observed a consistent pattern whereby the lifetimes and quantum yields all progressively increase in the sequence **1** < **2** < **3** < **4**. These results underscore the effectiveness of our combined functionalization strategy, which allows us to fine-tune and optimize the energy and dynamics of the triplet state. The luminescence colors can be evaluated via the CIE 1931 coordinates determined from PMMA film PL data, as depicted in Figure 4. Compounds with C^Y = F_2ppy luminesce in the sky blue region, as typically observed for platinum complexes with this cyclometalating ligand.[32] Conversely, compounds with the NHC-based C^Y ligand pmi exhibit a much deeper blue hue, with compounds **2b** and **3b** classified as deep blue emitters and **4b** as a pure-blue emitter, with spectral profiles similar to other platinum complexes with pmi as the chromophoric ligand.[6,33]

CONCLUSIONS

In this study, we introduced an innovative strategy to optimize both the color profiles and PL quantum yields of blue-phosphorescent cyclometalated platinum complexes, which combines nucleophilic and electrophilic ligand-based functionalization strategies. ADCs, strong σ-donating ancillary ligands, are installed by nucleophilic addition to an isocyanide precursor. Borane coordination by a cyanide ancillary ligand produces a strong π-accepting isocyanoborate. Both of these modifications result in significant increases in Φ_{PL}, driven by significant decreases in nonradiative decay rates (k_{nr}), true for both sky blue and deep blue emitters. Nucleophilic and electrophilic functionalization strategies have been separately used to optimize PL or other excited-state properties, and in this work, we report platforms where both can be executed sequentially. This effort shows that the two types of synthetic modification synergistically combine to give progressive increases in blue-phosphorescence performance metrics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c00203.

Experimental details, X-ray crystallography data, NMR spectra, additional crystal structures, IR spectra, and additional PL data (PDF)

Accession Codes

CCDC 2303687−2303691 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, U.K.; fax: +44 1223 336033.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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