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When is a Pyridine Not a Pyridine? Benzannulated *N*-Heterocyclic Ligands in Molecular Materials Chemistry

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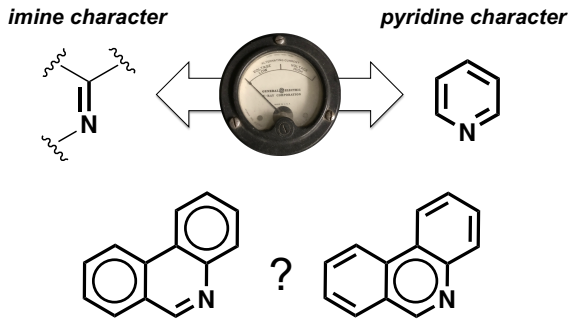
ABSTRACT

The C=N bond is a critical structural piece of many *N*-donor ligand scaffolds and is central to the properties and reactivity of important coordination complexes. For example, C=N units play a key role in the 'redox non-innocence' of α-diimine complexes and in making charge-transfer excited-state character available to complexes of *N*-heterocyclic ligands such as bipyridine. In *N*-heterocycles like pyridine, benzannulation can be used to extend the conjugated C=N containing π-system to quinoline (2,3-benzopyridine) to acridine (2,3-benzoquinoline). This stabilizes the lowest unoccupied molecular orbital (LUMO) of the molecule and boosts its electron-accepting properties, but the position of the benzannulation matters. For example, phenanthridine (3,4-benzoquinoline), an asymmetric isomer of acridine, bears a similarly electronically accessible extended π-system but with a more chemically isolated 'imine-like' C=N moiety. This Award Paper presents an overview of our work investigating the impact of such site-selective benzannulation on the chemistry and properties of phenanthridine as a molecule and ligand.

Keywords

ligand design, coordination chemistry, photophysics, molecular materials

Table of Contents Graphic



INTRODUCTION

Given the myriad applications of coordination complexes from homogenous catalysis to luminescent emitters, a detailed understanding of how molecular properties can be tuned through ligand design can be profitable in many ways.[1] Purposefully designed ligands have enabled, *inter alia*, the discovery of base metal hydrogenation catalysts,[2–4] sustainable-element emissive molecules,[5] and anolyte candidates for redox-flow batteries,[6] demonstrating the reach of ligand design to impact areas from synthesis to molecular materials chemistry to energy science. Ideally, a particular ligand framework would demonstrate wide versatility and be useful in imbuing reactivity and properties relevant to a variety of settings. Such an approach borrows from the concepts of 'privileged structures'[7] in medicinal chemistry – the discovery that particular biological ligands can bind a diverse library of receptors – and 'privileged catalysts'[8] in chiral catalysis – narrow classes of synthetic catalysts which can achieve enantioselective reactivity in a wide range of different reactions – and extend these ideas to electronic properties and the activation of small molecules. In thinking of a role for ligand design in these contexts, it might be noted that boundary-pushing ideas such as ligand 'redox non-innocence'[9] and 'metal-ligand cooperativity'[10] ('chemical non-innocence') both exploit ligand character in the frontier orbitals of a coordination complex. Similarly, the useful photoredox of prototypical sensitizers such as ruthenium(II) *tris*(2,2'-bipyridine) ($[Ru^{II}(bpy)_3]^{2+}$) is derived from ligand participation in forming long-lived metal-to-ligand charge-transfer (MLCT) excited states.[11] This raises a question: can common molecular features be identified that could in one context favour ligand-based equilibrium redox, while in another confer charge-transfer character to excited-states, and in yet another help stabilize reactive intermediates in catalysis (Figure 1)?

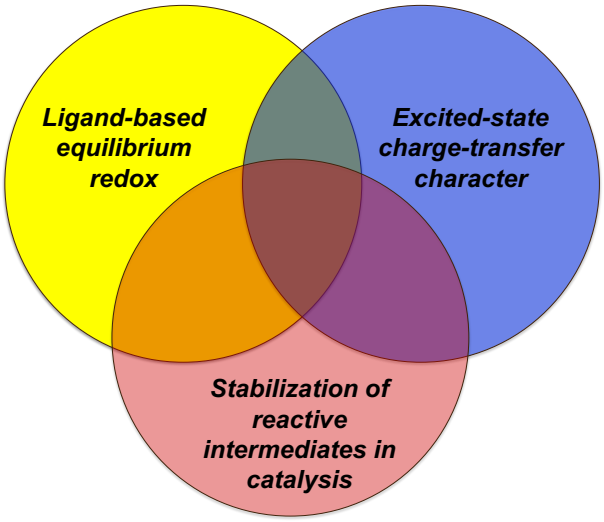


Figure 1. Seeking commonalities in ligand designs in pursuit of 'privileged ligand scaffolds' for applications of coordination complexes in organometallic chemistry.

C=N units appear ubiquitously in ligands whose complexes exhibit a wide range of exciting reactivity that makes use of both strong Lewis basic nitrogen coordination to metals and the presence of energetically accessible, vacant π* orbitals. Such ligands include C=N units as isolated imines, prominent examples of which include α-diimines[12] and pyridyldiimines[13] (PDIs), and as part of delocalized *N*-heterocycles such as 2,2'-bipyridine (bpy) and 2,2':6',2"-terpyridine (tpy; Figure 2).[14] The vacant, localized C=N π* orbitals of imine-based ligands like PDIs can be exploited to access ligand-centred redox in transition metal[15] and main-group complexes.[16] For example, (PDI)Fe(L) (L = N_2, NH_3) complexes contain ligand-centered triplet PDI diradical dianions antiferromagnetically coupled to ferrous iron centres, not neutral closed-shell singlet PDIs bound to Fe(0).[17] PDI ligands can thus serve as 'electron reservoirs', storing reducing equivalents which may then be used profitably in chemical reactions. For example, oxidative addition of halogens to U(IV) complexes bearing triply reduced $[PDI]^{3-}$ units has been shown to occur without a change to the metal oxidation state.[18] Similarly, pseudo-octahedral bis(PDI) complexes of Fe(II) present two PDI-based ligand reductions at accessible potentials.[19] A range of

$[(PDI)_2Fe]^{2+}$ complexes can be prepared with *N*-aryl rings containing both electron-releasing and electron-withdrawing substituents at the *para*-positions through direct condensation of substituted anilines with 2,6-diacetylpyridine (for electron-releasing substituents)[19,20] or via Zn-templated proligand synthesis for electron-withdrawing anilines.[21] Controlled potential electrolysis experiments show the reduced species are: (a) as soluble as the dications in organic solvents such as acetonitrile; (b) relatively stable over extended cycling with high Coulombic efficiencies;[20] and (c) able to mediate transfer of up to $2e^-$ per molecule,[21] which portends possible application of ligand-based redox activity in flow batteries for energy storage.[22]

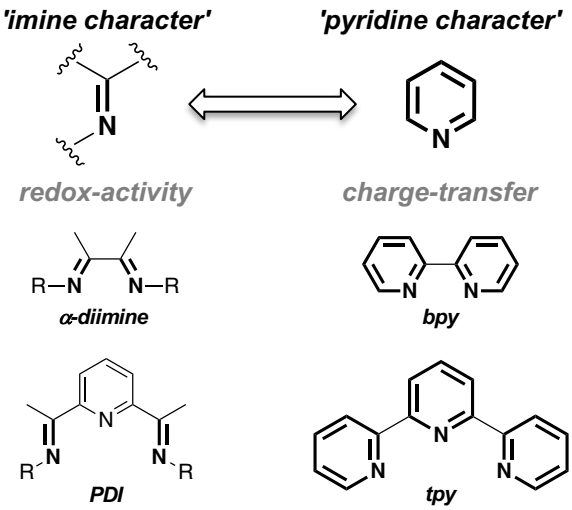


Figure 2. C=N containing ligand platforms.

At the other extreme, C=N units that comprise delocalized *N*-heterocyclic rings ('pyridine character') form excellent 'acceptors' for metal-to-ligand charge-transfer (MLCT) electronic excitations in transition metal coordination complexes. The best studied example[23] is likely the absorption of visible light by $[Ru^{II}(bpy)_3]^{2+}$ which leads to the formation of a long-lived triplet excited state through initial MLCT excitation that moves electron density from metal t_{2g}-type

orbitals into the delocalized π* manifold of a bpy ligand.[11] Given this conceptual continuum of localized to delocalized character, and the prevalence of these systems in exhibiting chemistry from ligand-localized redox to stabilized charge-transfer transitions, we were curious about molecular designs that might enable access to a C=N sub-unit with character intermediate between that of an isolated imine and a more delocalized pyridine.

To achieve this, we turned to site-selective benzannulation. Extending benzannulation in pyridine to formulate quinoline (benzo[*b*]pyridine), then the symmetric acridine (dibenzo[*b*,*e*]pyridine), lowers the energy of the unoccupied orbital manifold, resulting in what should ostensibly be a better acceptor.[24] However, if this second benzannulation occurs at the 3,4-position, the asymmetric, tricyclic molecule phenanthridine (benzo[*c*]quinoline) is formed. Compared with quinoline, acridine or the readily cyclometallated benzo[*h*]quinoline (7,8-benzoquinoline)[25], phenanthridine (3,4-benzoquinoline) has been much less explored as a ligand in transition metal chemistry. Phenanthridine is not without attractive features: it is respectably fluorescent, which has been exploited in dyes like ethidium bromide and related compounds;[26] its planarity has been leveraged in the construction of platinum anti-cancer compounds such as phenanthriplatin (*cis*-[$Pt^{II}(NH_3)_2$(phenanthridine)Cl]NO_3);[27] and it can be reversibly (de)hydrogenated, enabling application as a co-catalyst in hydrogenation reactions.[28,29] This latter reactivity can be realized electrochemically,[30] with implications for *N*-heterocycle-mediated electrochemical CO_2 reduction[31] and methodologies for electrochemical hydrogenation.[32] The ease with which phenanthridine's C=N bond can be selectively reduced can be understood by considering that phenanthridine has three (fused) six-membered rings but only 14π electrons. The 'imine-bridged biphenyl' resonance structure contributes most strongly to the ground state structure as it maximizes the number of aromatic sextets which can be drawn (Figure 3a).[33] This

manifests in a solid-state structure with a particularly short C=N bond (1.296(3) Å[34]) and an unusually downfield chemical shift for the hydrogen nucleus in the C_6 position (9.27 ppm) compared to the *ortho* CH signals in pyridine (8.6 ppm). Benzannulation in this case thus renders the central C_5N ring *less* aromatic (i.e., less 'pyridine-like'). The lowest unoccupied molecular orbital (LUMO) is accordingly localized at the C=N sub-unit (Figure 3b), lending phenanthridines conceptually similar electron-accepting character as the prototypical redox non-innocent PDI scaffolds discussed above.

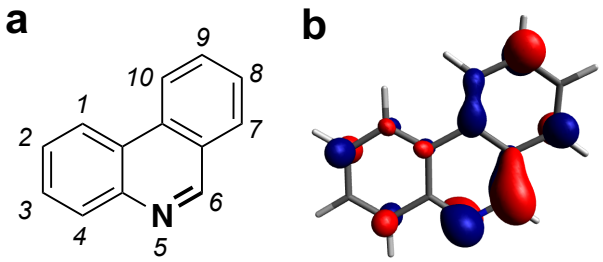


Figure 3. (a) Resonance structure of phenanthridine highlighting the 'imine-like' character of the C=N sub-unit with the IUPAC numbering scheme given in italics; (b) LUMO of phenanthridine (SMD-M06/Def2-TZVPD//SMD-M06L/Def2-TZVP).

These observations prompted our investigations into the photophysical properties of phenanthridine-containing coordination complexes. To introduce phenanthridine into the coordination sphere of metals, we targeted bromo- and amino-substituted analogs amenable for elaboration into multidentate scaffolds (Figure 4). We generally access these via a one-pot, tandem Pd-catalyzed cross-coupling/condensation protocol between appropriately substituted anilines and 2-formylphenyl boronic acid derivatives.[35] From 4-bromo/4-amino phenanthridines, we can then construct P^N[35], N^N[36,37], N^N^N[38,39], N^N^O[40–42], N^C^N[43] and N^N^P[44] proligands; C^N and

bpy-style (N^N)$_2$ biphenanthridine[45] proligands are available from (6-halo)phenanthridines.[46] Coordination complexes of these ligands can be used in the Ni-catalyzed direct alkylation of C-H bonds in azoles,[39] as well as to effect acceptorless dehydrogenative coupling reactions in which alcohols can be employed as electrophiles.[47] Ru complexes of phenanthridine-containing P^N ligands can be used in this way to prepare a host of *N*-heterocycles,[48] including luminescent[49] and donor-acceptor-donor/donor-acceptor-acceptor type pyrimidines.[50]

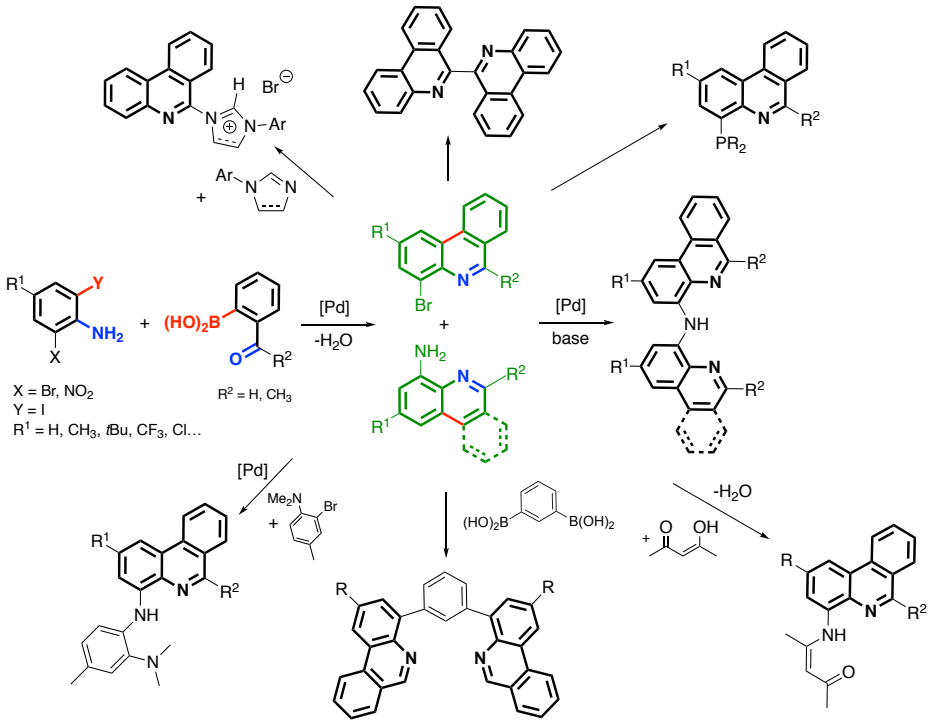


Figure 4. Examples of multidentate phenanthridine-containing proligands.

Our preparative route to phenanthridine-containing N^N^N ligands followed the methodology reported by Peters and co-workers for the preparation of *bis*(8-quinolinyl)amido 'pincer-type' ligands.[51] Using Pd-catalyzed coupling of bromo- and amino-substituted 8-quinolines and 4-phenanthridines, we prepared a series of ligands in which benzannulation is sequentially expanded from *bis*(8-quinolinyl)amido to (8-quinolinyl)(4-phenanthridinyl)amido to

bis(4-phenanthridinyl)amido frameworks. These ligands could then be installed on divalent Group 10 metal centres to yield a series of complexes that can be thought of as a platform for exploring the impact of systematic, site-selective ligand π-extension.[38] Expanding a molecule's π-system is usually associated with a bathochromic shift to its lowest energy absorption and emission processes. This holds true for main-group complexes[52] as well as transition metal chromophores[53] and is typically a result of the frontier orbitals growing closer in energy. However, there is a growing literature that describes 'counter-intuitive' hypsochromic blue shifts to both absorption and emission.[54,55] In one prominent example, Hanson *et al.* demonstrated that (N^N^N)Pt^{II}Cl complexes of benzannulated *bis*(pyridine)pyrrolate ligands can exhibit either red or blue shifts to absorption and emission maxima.[56] These observations were rationalized in terms of the site-selective influence of appending a butadiene fragment on the energy of the lowest-unoccupied molecular orbital (LUMO); the highest-occupied molecular orbital (HOMO) was found to be generally unperturbed by benzannulation. This orbital argument was extended to a broader paradigm for small molecules with the caveat that its validity relies on there being a single dominant character to the excitation (absorption) under examination (e.g., HOMO→LUMO). This enables application of the Tamm-Dancoff approximation to time-dependent density functional theory (TDDFT)[57,58] which can be used to validate the orbital analysis.

Curiously, our diarylamido-supported Ni(II), Pd(II) and Pt(II) complexes exhibited isoenergetic lowest energy absorption manifolds. For (N^N^N)Pt^{II}Cl complexes, the character of this excitation was dominantly HOMO→LUMO+1.[59] While the LUMO was found to stabilize with increasing benzannulation in keeping with conventional expectations, the HOMO and LUMO+1 were far less perturbed, leading our complexes to essentially absorb the same energy of visible light irrespective of the presence of quinolinyl or phenanthridinyl side-arms. Interestingly,

halide-bridged binuclear Cu(I) complexes of phenanthridinyl-containing P^N ligands did exhibit the 'expected' red-shift to the lowest energy absorption manifold compared to quinoline-containing congeners.[60] However, both Cu(I) and Pt(II) complexes supported by phenanthridinyl ligands phosphoresce at higher energy, with longer excited state lifetimes and higher quantum yields. Contrary to expectations, the quinoline-containing molecules emitted deeper to the red than those exclusively containing phenanthridine heterocycles.

In phosphorescent complexes, the (pseudo)Stokes shift is indicative of the degree of geometry reorganization upon excitation and subsequent relaxation to the emissive triplet state.[61] Comparing the DFT-optimized ground state (S_0) and lowest-lying triplet states (T_1) for our Pt(II) series, we note that the largest changes to bond lengths in the ligand are localized to the C=N sub-unit for the *bis*(phenanthridinyl)amido complex.[62] This is not the case in the quinoline-supported complexes, where the distortions in the excited state are more evenly spread about the heterocyclic ligand arms. The imine-localized structure to phenanthridine seems to buffer the rest of the rings from bigger changes upon photoexcitation. So while the formation of triplet states in arenes is generally accompanied by considerable distortion,[63,64] benzannulation of quinoline to phenanthridine may destabilize the emissive triplet state by inhibiting what would otherwise be an electronically desirable distortion. Overall, phenanthridine-supported Pt(II)[59,62] and Cu(I) species[60] are more rigid, with smaller differences in the torsion angles estimated for the T_1/S_0 states of the phenanthridine-based systems compared to quinoline-supported analogs - something that can be further exploited through counterion interactions to access even brighter, higher-energy solid-state emitters.[65] The unexpected blue-shifted emission from phenanthridine-supported Cu(I) and Pt(II) complexes can therefore be ascribed to both a destabilized triplet excited state ($E(T_1)$) and a smaller reorganization energy (λ_T)[66] upon relaxation back to the ground state (Figure 5).

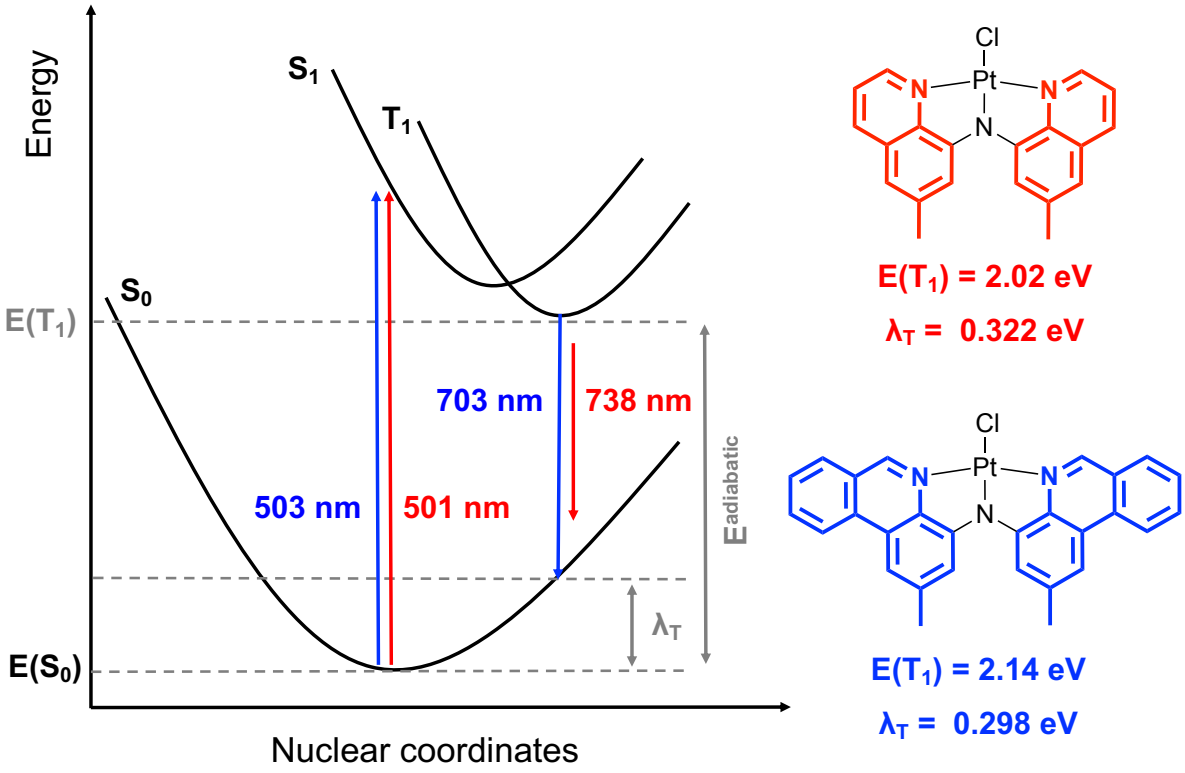


Figure 5. Deep-red phosphorescent Pt(II) complexes supported by phenanthridine-containing ligands. Experimental absorption and emission maxima are reported in nm; DFT-calculated triplet excited state energies ($E(T_1)$) and reorganization energies (λ_T) are given in eV.

Site-selective benzannulation can also help address a curious discrepancy in the literature noted for emissive Pt(II) complexes of N^N^N and N^C^N polypyridyl-type ligands. Namely, *bis*(quinolinyl)pyridine-supported Pt(II) complexes that form six-membered rings display much more intense emission than tpy analogs with five-membered rings, an observation attributed to improved orbital overlap on changing the ligand's bite angle.[67] However, for cyclometallated N^C$^-$^N-coordinated Pt(II) emitters, increasing chelate ring size has the opposite effect: complexes of 6-membered ring forming ligands exhibit much smaller quantum yields (Φ_{lum} = 1.6% for *bis*(8-quinolinyl)benzene platinum(II) chloride[67] compared to 60% for *bis*(2-pyridinyl)benzene

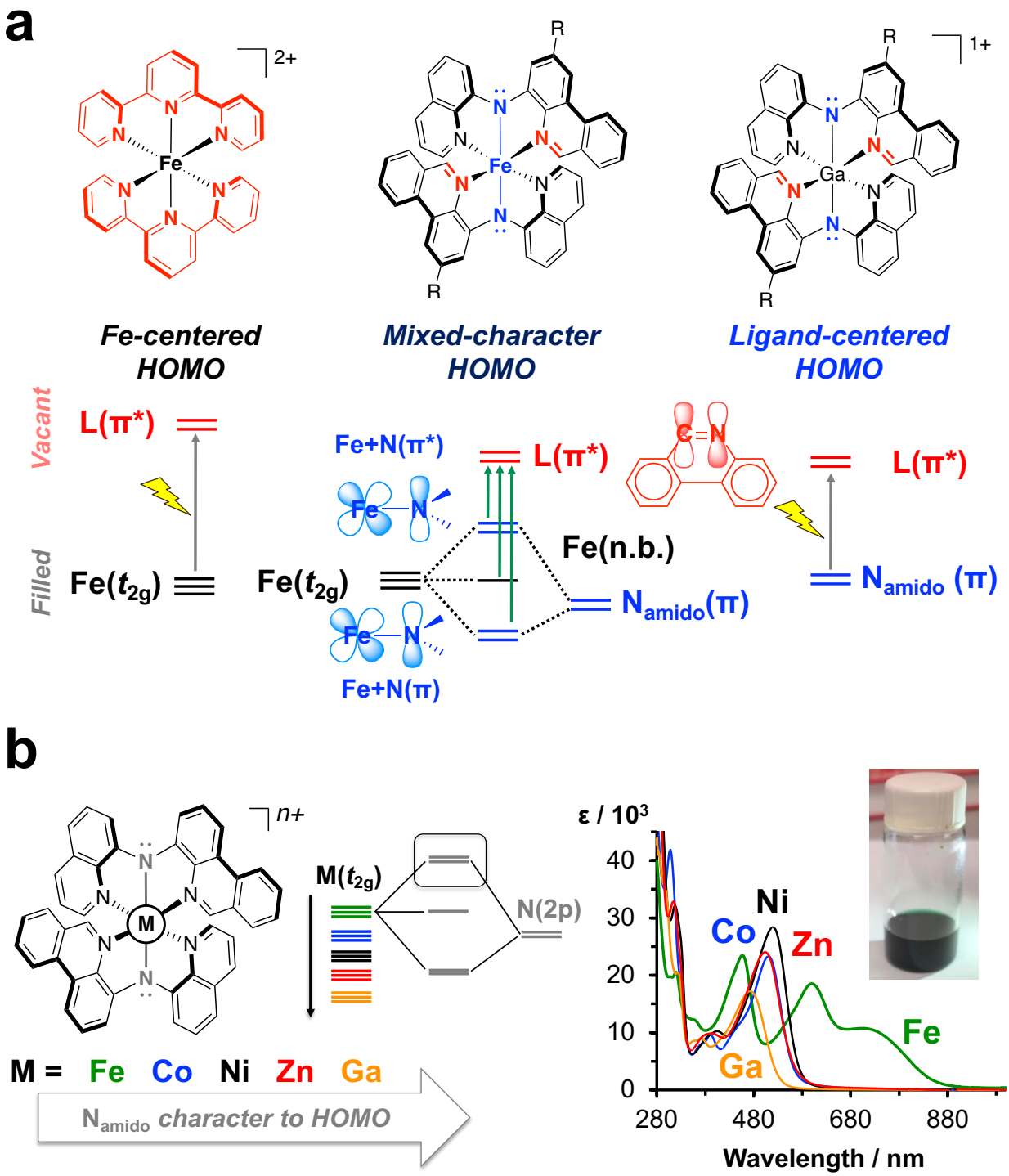
platinum(II) chloride[68]). This was traced to significantly lower radiative rate constants attributed to diminished metal participation in the excited state. Site-selective benzannulation of the quinolinyl side-arms to phenanthridine can offset this deleterious effect of changing the chelate ring-size, returning some of the lost emission intensity (Φ_{lum} = 9%). Computational analysis suggests benzannulation again destabilizes the emissive triplet state compared to the smaller π-system leading to a smaller (pseudo)Stokes shift, with the localized 'imine-bridged biphenyl' form of the phenanthridinyl arms cushioning against larger molecular distortions, improving the quantum yields.[43]

Having established that phenanthridine-containing ligands can present improved 'acceptor' properties, enhancing molecular rigidity and boosting photophysical properties such as quantum yields and triplet excited state lifetimes, we turned to investigating the impact of these ligand designs on the photoactivity of iron(II) coordination complexes. The question of how to replicate the favourable photophysical properties of precious-metal sensitizers such as $[Ru^{II}(bpy)_3]^{2+}$ in complexes of more sustainable elements like iron has received renewed attention of late,[69] with some of the momentum in this area attributable to seminal experiments on charge-injection from photoexcited Fe(II) complexes into surfaces by Ferrere and Gregg.[70] The complicating challenge is that in direct analogs of $[Ru^{II}(bpy)_3]^{2+}$ such as $[Fe^{II}(bpy)_3]^{2+}$, photogenerated ^{1}MLCT states deactivate on an ultrafast (< 100 fs) timescale down to the ligand field manifold.[71] In most cases, this precludes the possibility for photoinduced electron transfer which typically happens through long-lived charge-transfer states,[72] although exciting work is emerging that hints at the utility of other mechanisms for excited-state electron transfer.[73] A clue as to why can be gleaned from comparing the potential energy curves representing the excited states typical of Ru(II)- and Fe(II)-polypyridyl complexes. Once formed, electron transfer in $[Ru^{II}(bpy)_3]^{2+}$ from $^{1/3}$MLCT states to

metal-centered (MC) states is an activated process, implying that it is slow on the nanosecond or longer time scale. In contrast, for Fe analogs, the crossing between the $^{1/3}$MLCT and MC states occurs close to the minimum of the MLCT potential energy curve, which leads to ultrafast decay.[74] This arises from the so-called 'primogenic effect'[75] that results in lower overlap and weaker metal-ligand bonds, in turn leading to inversion of excited state character for coordination complexes of the lighter (3d) transition metals compared to their heavier element (4d, 5d) analogs.[76]

Efforts to redress this in (pseudo)octahedral Fe(II) complexes have consequently focused on increasing ligand σ-donor strength in an effort to re-order MC/MLCT states by destabilizing metal-centered e_g*-type orbitals. Pioneering work incorporating increasingly strong σ-donating carbene ligands by the Gros[77] and Wärnmark[78,79] groups or cyclometallating C-donor ligands by Dixon,[80,81] Bauer[82] and Berkfeld[83] have demonstrated the effectiveness of this strategy, enabling high yields of photo-induced charge-injection[84,85] and the first example of observable room-temperature luminescence from an Fe(II) complex,[83] complementing the remarkable discovery of ^{2}LMCT spin-conserved emission from ferric congeners.[86,87] We were curious about a slightly different approach: what would be the impact of combining strong acceptors like phenanthridine with π-donor amido ligands? Prior to our work, Betley and Peters nicely demonstrated using a simple molecular orbital interaction diagram how orthogonal amido donors might impact the nature of the highest energy manifold in pseudo-octahedral Group VIII complexes,[88] consistent with the textbook MO treatment of weak-field π-donors.[89] Indeed, we found installing two equivalents of our phenanthridine-containing diarylamido N^N$^-$^N ligands on Fe(II) leads to mixed metal-ligand character of the HOMO through to HOMO-4 thanks to strong mixing between the fully filled, triply degenerate formally t_{2g} orbital set on Fe(II) and the two orthogonal filled N(2p) orbitals (Figure 6a).[90] This highly covalent character contrasts the situation in $[Fe^{II}(tpy)_2]^{2+}$

and Ga(III) complexes of our N^N$^-$^N ligands, and manifests in the Fe-N(amido) distances evident from the solid-state structures of the (N^N^N)$_2$Fe(II) and one-electron oxidized [(N^N^N)$_2$Fe]$^+$. Specifically, removal of an electron from the HOMO depopulates an orbital with Fe-N(amido) π-anti-bonding character and is accompanied by a contraction of the Fe-N(amido) distance from 1.932(3)/1.938(3) Å to 1.882(2)/1.901(2) Å for the two crystallographically distinct Fe-N(amido) bonds. The mixed character to the HOMOs also affects the non-zero electric field gradients that can be quantified using zero-field ^{57}Fe Mössbauer spectroscopy. Compared with other polypyridyl Fe complexes such as [Fe$^{II/III}$(tpy)$_2$]$^{2+/3+}$, the isomer shifts and quadrupole splitting are not nearly as affected by oxidation for [(N^N^N)$_2$Fe]$^{0/+}$.[90]



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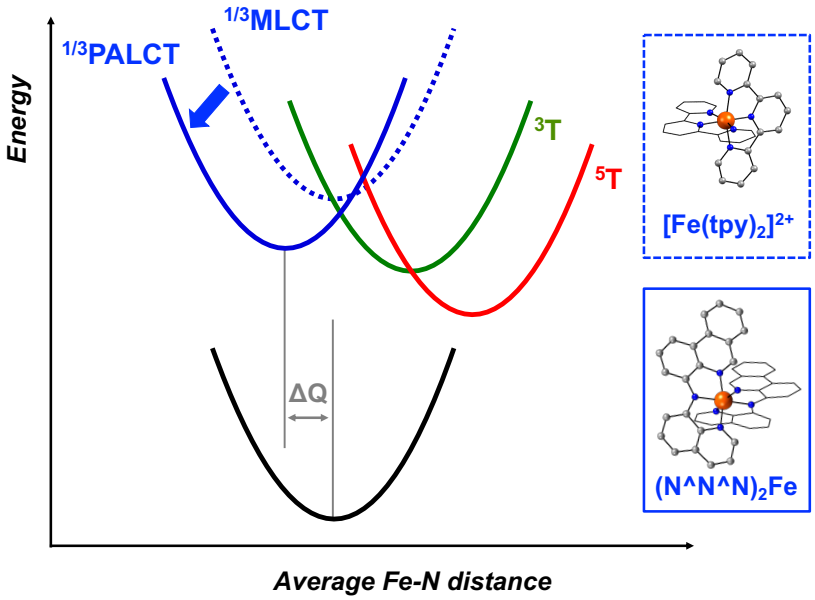
272 **Figure 6.** (a) MO description of strong mixing in iron complexes of weak-field π-donors. (b)

273 Comparing the panchromatic absorption of Fe(II)-amido complexes with increasingly ligand-

localized transitions in Co, Ni, Zn and Ga analogs (inset: photograph of a solution of the Fe(II) species).

These highly covalent Fe-N(amido) interactions lead to strong, panchromatic absorption across the visible range of the electromagnetic spectrum (Figure 6b), in keeping with the predictions of Jakubikova and coworkers about the impact of 'HOMO inversion' on the absorption properties of Fe(II) coordination complexes.[91] Altering the energy of the metal orbitals by changing the metal reduces the mixing and yields either metal- (e.g., Ni(II)) or ligand-centered (e.g., for Ga(III)) HOMOs.[92] Resonant inelastic X-ray scattering experiments confirm this strong covalency and reveal that compared to $[Fe^{II}(tpy)_2]^{2+}$, the nephelauxetic reduction in d-electron repulsion thanks to strong Fe-amido mixing counteracts the impact of using weak field π-donor amido ligands on the excited-state ordering at the ground-state geometry.[93] Electronic excitation, rather than producing a formally MLCT excited state as for $[Fe^{II}(tpy)_2]^{2+}$, forms a "π-anti-bonding-to-ligand" charge-transfer (PALCT) type excited state (Figure 7).[94] Transient absorption experiments reveal strong excited-state absorption features that persist for nanoseconds. Assignment of these transiently generated difference spectra using spectroelectrochemistry[95] is consistent with charge-transfer type character, however without corroborating evidence from the perspective of the metal[96] this assignment remains incomplete and is the subject of on-going investigations.



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294 **Figure 7.** Schematic potential energy diagram illustrating how increased covalency influences the
295 nature of the electronic excitation at the ground state geometry ($^{1/3}$MLCT for $[Fe^{II}(tpy)_2]^{2+}$ vs.
296 $^{1/3}$PALCT excitation in $(N^N^N)_2Fe^{II}$). The Fe-N bond contraction relative to the ground state
297 (ΔQ) expected on forming a $^{1/3}$PALCT is noted. Also shown are metal-centered triplet (^{3}T; green
298 curve) and quintet (^{5}T; red curve) excited states. These high-spin excited states represent the lowest
299 energy excited states for most pseudo-octahedral polypyridyl Fe(II) coordination complexes,
300 including $[Fe^{II}(tpy)_2]^{2+}$.

301

302 Consistent with the solid-state structures of the redox-related pair $[(N^N^N)_2Fe]^{0/+}$ noted
303 above, PALCT should similarly be accompanied by a contraction of the Fe-N(amido) bond
304 distance (ΔQ), as an anti-bonding orbital is depopulated upon charge-transfer type photoexcitation.
305 This would contrast the situation on formation of a metal-centered triplet (^{3}T) or quintet (^{5}T)
306 excited state in which metal-ligand σ* anti-bonding orbitals (i.e., the e_g sub-set) are populated,
307 causing an elongation of metal-ligand distances.[97] In principle, stabilizing the CT potential energy

surface (PES) and shifting it away from near-lying MC states along the metal-ligand bond coordinate could move the crossing point of the PESs away from the minimum of the PALCT surface. This could suggest a mechanism for introducing an activation barrier that might be used to retard electron transfer from a $^{1/3}$PALCT excited state to the MC manifold. Indeed, the enhanced covalency of π-donor amido ligands has been used to achieve near-IR-II emission in chromium(III) complexes[98] and stabilize MLCT excited states with cobalt(III).[99]

The amido character of monoanionic pincer-type ligands thus has a significant impact on the photophysical properties of phenanthridine-supported coordination complexes. When tempered by strong mixing with metal-based orbitals as in the Fe(II) example discussed above, or in divalent Group 10 compounds,[38,39] the presence of the formal nitrogen lone pair does not dominate the chemical reactivity of the complexes and these species are for the most part stable to air and ambient moisture. However, when ligated, for example, to Zn(II), this mixing is limited and Zn(II) complexes of bidentate *N*-aryl phenanthridinyl amides[36] or tridentate diarylamido ligands[92] are quite reactive towards protonolysis by even trace moisture. In contrast, N^N^O proligands comprised of 'nac-ac' style scaffolds can similarly be used to tone down the lone-pair character of amido ligands, but through contribution of an enolato-imine resonance structure (Figure 8a). Pt(II) complexes of such ligands are much more brightly emissive than phenanthridine-supported (N^N^N)Pt(II) chlorides, with phosphorescence quantum yields reaching 16% and 24 microsecond lifetimes.[41] These complexes are also substantially solvatochromic, with a strong influence of the solvent dielectric on the energy of the lowest energy absorption consistent with charge-transfer character.

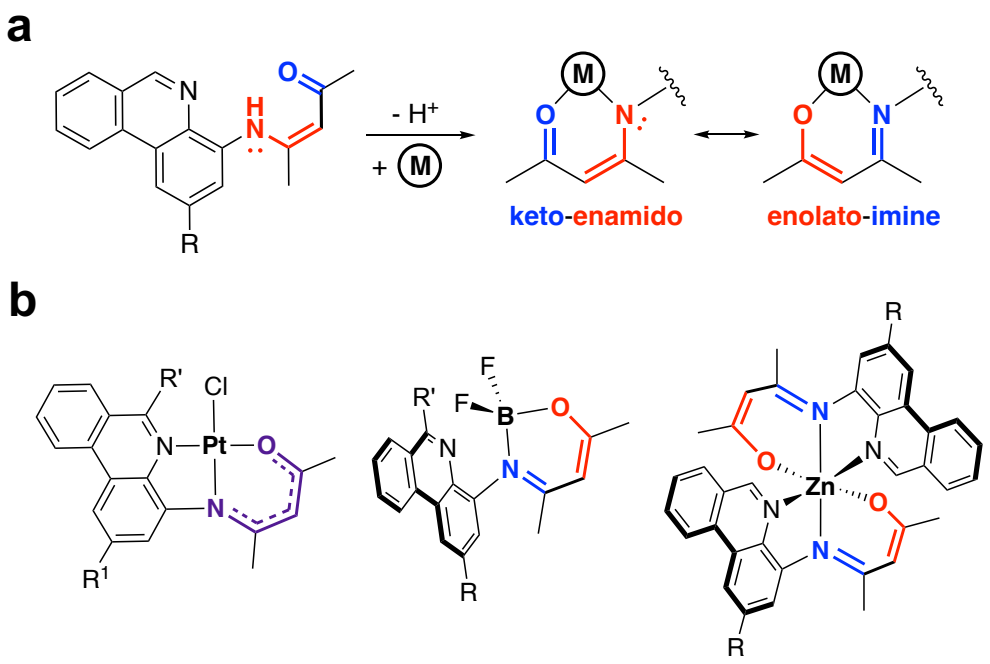

Figure 8. (a) 'Nac-ac' style N^N^O proligands and their resonance structures upon metalation; (b) Platinum(II), zinc(II) and boron complexes of N^N^O ligands.

Phenanthridinyl-decorated, β-ketoiminate chelating ligand scaffolds can also be used to construct boron difluoride complexes (Figure 8b).[42] Here, the BF_2 fragment is four-coordinate, ligated within the ketoiminate N^O pocket. $^{19}F–^{1}H$ NOE NMR spectroscopy measurements show well-resolved through-space interactions between a phenanthridinyl C–H and one fluorine indicating that in fluid solution the relative orientation of the pendent phenanthridinyl arm is still fixed despite not coordinating to boron. Nevertheless, with nonradiative decay pathways available thanks to rotation of the *N*-heterocycle, these compounds are only weakly luminescent; however, methylation of the phenanthridinyl nitrogen can be used to 'switch on' relatively strong emission by limiting this rotation and altering the character of the lowest energy excitation. Pseudo-octahedral Zn(II) complexes supported by such monoanionic, tridentate acetylacetone-derived N^N-^O ligands also emit weakly in solution but exhibit very long (millisecond) luminescence

lifetimes when rigidified in the solid state at room temperature or in a frozen glass at 77 K, consistent with phosphorescence from low-lying triplet excited states which is rare for Zn.[100] This is in sharp contrast to non-emissive, four-coordinate, amide-supported tetradentate Zn(II) complexes.[36] In addition, the six-coordinate Zn complexes are air- and moisture-stable, as well as unreactive towards mildly acidic solvents. The delocalized character of the central deprotonated NH upon coordination mitigates the amido character of the ligand, increasing chemical stability and provides a mechanism for switching on remarkably long-lived luminescence from *N*-heterocycle/amido-supported Zn(II) coordination complexes.

Finally, phenanthridines can be used to prepare doubly π-extended analogs of the canonical ligand 2,2-bipyridyl (bpy) we termed "biphe" (6,6'-biphenanthridine; Figure 9a).[45] The organic proligand itself displays blue fluorescence in solution, which shifts to even stronger yellow emission upon monoprotonation. *Tris*(6,6'-biphenanthridine)ruthenium(II) and *bis*(2,2'-bipyridine)(6,6'-biphenanthridine)ruthenium(II) dications can also be made and these display strongly bathochromically shifted emission at 77 K that is nearly 200 nm red-shifted compared to $[Ru^{II}(bpy)_3]^{2+}$. This phosphorescence is very weak and short-lived at ambient temperature, however, and rapid ligand photodissociation competes with radiative decay, especially in the heteroleptic complex. Nevertheless, this substantial low energy shift is consistent with the lower energy π* orbitals that accompany extended conjugation, which lowers the energy of the emissive ^{3}MLCT excited state. Indeed, biphe's stabilized vacant π* manifold can be addressed electrochemically, and multiple reversible reductions are observed by cyclic voltammetry at much less negative potentials compared with $[Ru^{II}(bpy)_3]^{2+}$. As can be seen from the solid-state structures in Figure 9b, the biphe ligand is significantly twisted despite chelating to the metal and

our current efforts are addressing this lack of planarity in order to boost the efficiency of any low-energy emission.

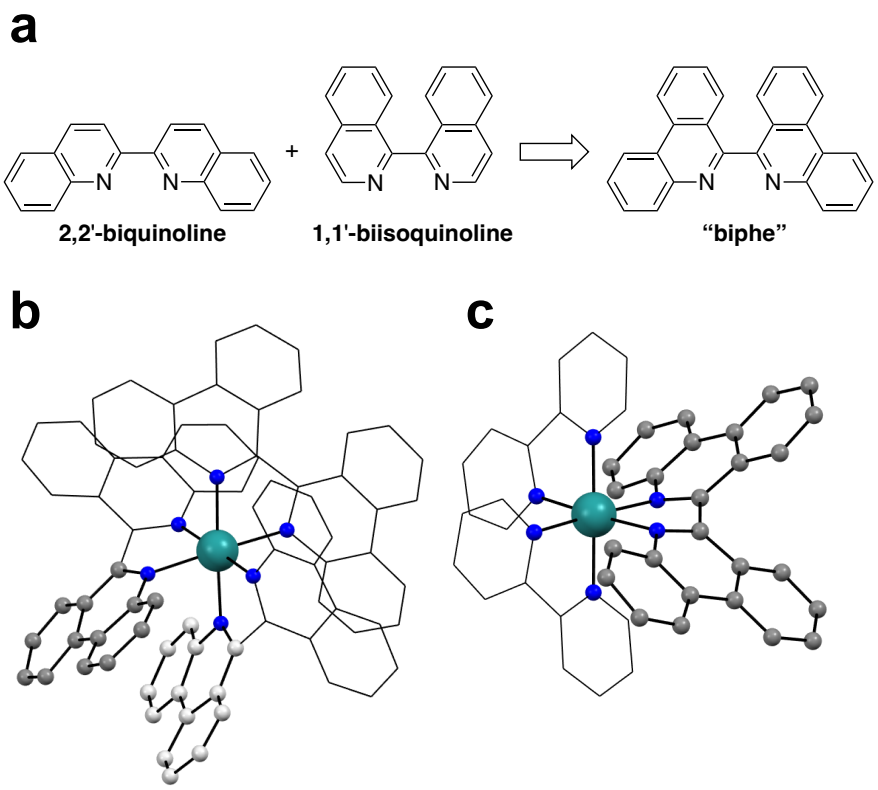

Figure 9. (a) π-extended bpy analogs and solid-state structures of (b) *tris*(6,6'-biphenanthridine)ruthenium(II) dication showing intramolecular π-stacking between biphe ligands and (c) *bis*(2,2'-bipyridine)(6,6'-biphenanthridine)ruthenium(II) dication illustrating the twist between phenanthridine units in coordinated biphe.

Conclusion and Outlook

Large, planar *N*-heterocyclic frameworks provide a rich playground for coordination chemistry,[101] one that is continually revealing interesting nuances with respect to the impact of site-selective benzannulation on commonly held conceptions regarding ligand π-extension. In particular, *N*-heterocycles, that through the quirks of their structures present 'imine-like' C=N units, can help rigidify molecular scaffolds, attenuating non-radiative decay and increasing both excited state lifetimes and quantum yields. When paired with weak-field amido donors, highly covalent molecules can be designed and constructed that strongly absorb wide swathes of visible light with unexpected excited-state properties. The findings surveyed in this article suggest that simple structural changes may continue to lead to the discovery of novel ligand and molecular designs with yet unanticipated fascinating fundamental properties and the possibility of useful applications.

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Competing Interests Statement

The author declares no competing interests.

Data Availability Statement

This manuscript is a review article and does not report new data.

REFERENCES

(1) Fryzuk, M. D. The 1992 Alcan Award Lecture Excursions around the Periodic Table: Ligand Design in Inorganic Chemistry. *Can. J. Chem.* **1992**, *70*, 2839–2845.

(2) Chirik, P. J.; Wieghardt, K. Radical Ligands Confer Nobility on Base-Metal Catalysts. *Science* **2010**, *327*, 794–795.

(3) Bullock, R. M. Abundant Metals Give Precious Hydrogenation Performance. *Science* **2013**, *342*, 1054–1055.

(4) Chirik, P. J. Iron- and Cobalt-Catalyzed Alkene Hydrogenation: Catalysis with Both Redox-Active and Strong Field Ligands. *Acc. Chem. Res.* **2015**, *48*, 1687–1695.

(5) Dierks, P.; Vukadinovic, Y.; Bauer, M. Photoactive Iron Complexes: More Sustainable, but Still a Challenge. *Inorg. Chem. Front.* **2022**, *9*, 206–220.

(6) Zhang, C.; Zhang, L.; Ding, Y.; Peng, S.; Guo, X.; Zhao, Y.; He, G.; Yu, G. Progress and Prospects of Next-Generation Redox Flow Batteries. *Energ. Stor. Mater.* **2018**, *15*, 324–350.

(7) Evans, B. E.; Rittle, K. E.; Bock, M. G.; DiPardo, R. M.; Freidinger, R. M.; Whitter, W. L.; Lundell, G. F.; Veber, D. F.; Anderson, P. S.; Chang, R. S. L.; Lotti, V. J.; Cerino, D. J.; Chen, T. B.; Kling, P. J.; Kunkel, K. A.; Springer, J. P.; Hirshfield, J. Methods for Drug Discovery: Development of Potent, Selective, Orally Effective Cholecystokinin Antagonists. *J. Med. Chem.* **1988**, *31*, 2235–2246.

(8) Yoon, T. P.; Jacobsen, E. N. Privileged Chiral Catalysts. *Science* **2003**, *299*, 1691–1693.

(9) Lyaskovskyy, V.; de Bruin, B. Redox Non-Innocent Ligands: Versatile New Tools to Control Catalytic Reactions. *ACS Catal.* **2012**, *2*, 270–279.

(10) Gunanathan, C.; Milstein, D. Metal-Ligand Cooperation by Aromatization-Dearomatization: A New Paradigm in Bond Activation and "Green" Catalysis. *Acc. Chem. Res.* **2011**, *44*, 588–602.

(11) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. Ruthenium(II) Polypyridine Complexes: Photophysics, Photochemistry, Electrochemistry, and Chemiluminescence. *Coord. Chem. Rev.* **1988**, *84*, 85–277.

(12) Koten, G. V.; Vrieze, K. 1,4-Diaza-1,3-Butadiene (α-Diimine) Ligands: Their Coordination Modes and the Reactivity of Their Metal Complexes. *Adv. Organomet. Chem.* **1982**, *21*, 151–239.

(13) Flisak, Z.; Sun, W.-H. Progression of Diiminopyridines: From Single Application to Catalytic Versatility. *ACS Catal.* **2015**, *5*, 4713–4724.

(14) Thummel, R. P. Terpyridine, Oligopyridine, and Polypyridine Ligands. In *Compr. Coord. Chem. II*; Elsevier Ltd., 2004; Vol. 1, pp 41–53.

(15) Singh, K.; Kundu, A.; Adhikari, D. Ligand-Based Redox: Catalytic Applications and Mechanistic Aspects. *ACS Catal.* **2022**, *12*, 13075–13107.

(16) Gray, P. A.; Braun, J. D.; Rahimi, N.; Herbert, D. E. Diiminepyridine-Supported Phosphorus(I) and Phosphorus(III) Complexes: Synthesis, Characterization, and Electrochemistry. *Eur. J. Inorg. Chem.* **2020**, *2020*, 2105–2111.

(17) Tondreau, A. M.; Stieber, S. C. E.; Milsmann, C.; Lobkovsky, E.; Weyhermuller, T.; Semproni, S. P.; Chirik, P. J. Oxidation and Reduction of Bis(Imino)Pyridine Iron Dinitrogen Complexes: Evidence for Formation of a Chelate Trianion. *Inorg. Chem.* **2013**, *52*, 635–646.

(18) Kiernicki, J. J.; Fanwick, P. E.; Bart, S. C. Utility of a Redox-Active Pyridine(Diimine) Chelate in Facilitating Two Electron Oxidative Addition Chemistry at Uranium. *Chem. Commun.* **2014**, *50*, 8189–8192.
(19) de Bruin, B.; Bill, E.; Bothe, E.; Weyhermueller, T.; Wieghardt, K. Molecular and Electronic Structures of Bis(Pyridine-2,6-Diimine)Metal Complexes $[ML_2](PF_6)_n$ (n = 0, 1, 2, 3; M = Mn, Fe, Co, Ni, Cu, Zn). *Inorg. Chem.* **2000**, *39*, 2936–2947.
(20) Duarte, G. M.; Braun, J. D.; Giesbrecht, P. K.; Herbert, D. E. Redox Non-Innocent Bis(2,6-Diimine-Pyridine) Ligand-Iron Complexes as Anolytes for Flow Battery Applications. *Dalton Trans.* **2017**, *46*, 16439–16445.
(21) Braun, J. D.; Gray, P. A.; Sidhu, B. K.; Nemez, D. B.; Herbert, D. E. Zn-Templated Synthesis of Substituted (2,6-Diimine)Pyridine Proligands and Evaluation of Their Iron Complexes as Anolytes for Flow Battery Applications. *Dalton Trans.* **2020**, *49*, 16175–16183.
(22) Soloveichik, G. L. Flow Batteries: Current Status and Trends. *Chem. Rev.* **2015**, *115*, 11533–11558.
(23) Arias-Rotondo, D. M. The Fruit Fly of Photophysics. *Nat. Chem.* **2022**, *14*, 716–716.
(24) Katritzky, A. R. *Handbook of Heterocyclic Chemistry*, 3rd ed.; Oxford : Elsevier: Oxford, 2010.
(25) Neufeldt, S. R.; Sanford, M. S. Controlling Site Selectivity in Palladium-Catalyzed C–H Bond Functionalization. *Acc. Chem. Res.* **2012**, *45*, 936–946.
(26) Tumir, L.-M.; Stojkovic, M. R.; Piantanida, I. Come-Back of Phenanthridine and Phenanthridinium Derivatives in the 21st Century. *Beilstein J. Org. Chem.* **2014**, *10*, 2930–2954.
(27) Johnstone, T. C.; Park, G. Y.; Lippard, S. J. Understanding and Improving Platinum Anticancer Drugs - Phenanthriplatin. *Anticancer Res.* **2014**, *34*, 471–476.
(28) Chen, Q.-A.; Gao, K.; Duan, Y.; Ye, Z.-S.; Shi, L.; Yang, Y.; Zhou, Y.-G. Dihydrophenanthridine: A New and Easily Regenerable NAD(P)H Model for Biomimetic Asymmetric Hydrogenation. *J. Am. Chem. Soc.* **2012**, *134*, 2442–2448.
(29) Lu, L.-Q.; Li, Y.; Junge, K.; Beller, M. Iron-Catalyzed Hydrogenation for the In Situ Regeneration of an NAD(P)H Model: Biomimetic Reduction of α-Keto-/α-Iminoesters. *Angew. Chem., Int. Ed.* **2013**, *52*, 8382–8386.
(30) Giesbrecht, P. K.; Nemez, D. B.; Herbert, D. E. Electrochemical Hydrogenation of a Benzannulated Pyridine to a Dihydropyridine in Acidic Solution. *Chem. Commun.* **2018**, *54*, 338–341.
(31) Giesbrecht, P. K.; Herbert, D. E. Electrochemical Reduction of Carbon Dioxide to Methanol in the Presence of Benzannulated Dihydropyridine Additives. *ACS Energy Lett.* **2017**, *2*, 549–555.
(32) Nemez, D. B.; Sidhu, B. K.; Giesbrecht, P. K.; Braun, J. D.; Herbert, D. E. Electrochemical Hydrogenation of α-Ketoesters and Benzoxazinones Using Carbon Electrodes and a Sustainable Brønsted Acid. *Org. Chem. Front.* **2021**, *8*, 549–554.
(33) Maksic, Z. B.; Baric, D.; Mueller, T. Clar's Sextet Rule Is a Consequence of the σ-Electron Framework. *J. Phys. Chem. A* **2006**, *110*, 10135–10147.
(34) Brett, W. A.; Rademacher, P.; Boese, R. Redetermination of the Structure of Phenanthridine. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1993**, *C49*, 1564–1566.

(35) Mondal, R.; Giesbrecht, P. K.; Herbert, D. E. Nickel(II), Copper(I) and Zinc(II) Complexes Supported by a (4-Diphenylphosphino)Phenanthridine Ligand. *Polyhedron* **2016**, *108*, 156–162.
(36) Lozada, I. B.; Murray, T.; Herbert, D. E. Monomeric Zinc(II) Amide Complexes Supported by Bidentate, Benzannulated Phenanthridine Amido Ligands. *Polyhedron* **2019**, *161*, 261–267.
(37) Gaire, S.; Ortiz, R. J.; Schrage, B. R.; Lozada, I. B.; Mandapati, P.; Osinski, A. J.; Herbert, D. E.; Ziegler, C. J. (8-Amino)Quinoline and (4-Amino)Phenanthridine Complexes of $Re(CO)_3$ Halides. *J. Organomet. Chem.* **2020**, *921*, 121338.
(38) Mandapati, P.; Giesbrecht, P. K.; Davis, R. L.; Herbert, D. E. Phenanthridine-Containing Pincer-like Amido Complexes of Nickel, Palladium, and Platinum. *Inorg. Chem.* **2017**, *56*, 3674–3685.
(39) Mandapati, P.; Braun, J. D.; Sidhu, B. K.; Wilson, G.; Herbert, D. E. Catalytic C–H Bond Alkylation of Azoles with Alkyl Halides Mediated by Nickel(II) Complexes of Phenanthridine-Based N^N$^-$^N Pincer Ligands. *Organometallics* **2020**, *39*, 1989–1997.
(40) Lozada, I. B.; Huang, B.; Stilgenbauer, M.; Beach, T.; Qiu, Z.; Zheng, Y.; Herbert, D. E. Monofunctional Platinum(II) Anticancer Complexes Based on Multidentate Phenanthridine-Containing Ligand Frameworks. *Dalton Trans.* **2020**, *49*, 6557–6560.
(41) Lozada, I. B.; Williams, J. A. G.; Herbert, D. E. Platinum(II) Complexes of Benzannulated N^N$^-$^O-Amido Ligands: Bright Orange Phosphors with Long-Lived Excited States. *Inorg. Chem. Front.* **2022**, *9*, 10–22.
(42) Lozada, I. B.; Ortiz, R. J.; Braun, J. D.; Williams, J. A. G.; Herbert, D. E. Donor–Acceptor Boron-Ketoiminate Complexes with Pendent *N*-Heterocyclic Arms: Switched-on Luminescence through *N*-Heterocycle Methylation. *J. Org. Chem.* **2022**, *87*, 184–196.
(43) Ortiz, R. J.; Braun, J. D.; Williams, J. A. G.; Herbert, D. E. Brightly Luminescent Platinum Complexes of N^C$^-$^N Ligands Forming Six-Membered Chelate Rings: Offsetting Deleterious Ring Size Effects Using Site-Selective Benzannulation. *Inorg. Chem.* **2021**, *60*, 16881–16894.
(44) Sidhu, B. K.; Braun, J. D.; Herbert, D. E. P–C Bond Activation and Transfer of a Diphenylphosphino Unit from 1,1′-Bis(Diphenylphosphino)Ferrocene: Unexpected Templated Synthesis of an N^N$^-$^P Pincer Ligand Palladium Complex. *Organometallics* **2021**, *40*, 2538–2545.
(45) Nemez, D. B.; Lozada, I. B.; Braun, J. D.; Williams, J. A. G.; Herbert, D. E. Synthesis and Coordination Chemistry of a Benzannulated Bipyridine: 6,6′-Biphenanthridine. *Inorg. Chem.* **2022**, *61*, 13386–13398.
(46) Mondal, R.; Ortiz, R. J.; Braun, J. D.; Herbert, D. E. Synthesis, Characterization, and Coordination Chemistry of a Phenanthridine-Containing N-Heterocyclic Carbene Ligand. *Can. J. Chem.* **2021**, *99*, 245–252.
(47) Gunanathan, C.; Milstein, D. Applications of Acceptorless Dehydrogenation and Related Transformations in Chemical Synthesis. *Science* **2013**, *341*, 249.
(48) Mondal, R.; Herbert, D. E. Synthesis of Pyridines, Quinolines, and Pyrimidines via Acceptorless Dehydrogenative Coupling Catalyzed by a Simple Bidentate P^N Ligand Supported Ru Complex. *Organometallics* **2020**, *39*, 1310–1317.
(49) Mondal, R.; Lozada, I. B.; Stotska, O.; Herbert, D. E. Catalytic Synthesis of Luminescent Pyrimidines via Acceptor-Less Dehydrogenative Coupling. *J. Org. Chem.* **2020**, *85*, 13747–13756.

(50) Mondal, R.; Braun, J. D.; Sidhu, B. K.; Nevonen, D. E.; Nemykin, V. N.; Herbert, D. E. Catalytic Synthesis of Donor-Acceptor-Donor (D-A-D) and Donor-Acceptor-Acceptor (D-A-A) Pyrimidine-Ferrocenes via Acceptorless Dehydrogenative Coupling: Synthesis, Structures, and Electronic Communication. *Organometallics* **2021**, *40*, 1765–1775.
(51) Peters, J. C.; Harkins, S. B.; Brown, S. D.; Day, M. W. Pincer-like Amido Complexes of Platinum, Palladium, and Nickel. *Inorg. Chem.* **2001**, *40*, 5083–5091.
(52) Barbon, S. M.; Staroverov, V. N.; Gilroy, J. B. Effect of Extended π Conjugation on the Spectroscopic and Electrochemical Properties of Boron Difluoride Formazanate Complexes. *J. Org. Chem.* **2015**, *80*, 5226–5235.
(53) Li, Z.; Cui, P.; Wang, C.; Kilina, S.; Sun, W. Nonlinear Absorbing Cationic Bipyridyl Iridium(III) Complexes Bearing Cyclometalating Ligands with Different Degrees of π-Conjugation: Synthesis, Photophysics, and Reverse Saturable Absorption. *J. Phys. Chem. C* **2014**, *118*, 28764–28775.
(54) Bossi, A.; Rausch, A. F.; Leitl, M. J.; Czerwieniec, R.; Whited, M. T.; Djurovich, P. I.; Yersin, H.; Thompson, M. E. Photophysical Properties of Cyclometalated Pt(II) Complexes: Counterintuitive Blue Shift in Emission with an Expanded Ligand π System. *Inorg. Chem.* **2013**, *52*, 12403–12415.
(55) Liu, B.; Lystrom, L.; Brown, S. L.; Hobbie, E. K.; Kilina, S.; Sun, W. Impact of Benzannulation Site at the Diimine (N^N) Ligand on the Excited-State Properties and Reverse Saturable Absorption of Biscyclometalated Iridium(III) Complexes. *Inorg. Chem.* **2019**, *58*, 5483–5493.
(56) Hanson, K.; Roskop, L.; Djurovich, P. I.; Zahariev, F.; Gordon, M. S.; Thompson, M. E. A Paradigm for Blue- or Red-Shifted Absorption of Small Molecules Depending on the Site of π-Extension. *J. Am. Chem. Soc.* **2010**, *132*, 16247–16255.
(57) Hirata, S.; Head-Gordon, M. Time-Dependent Density Functional Theory within the Tamm–Dancoff Approximation. *Chem. Phys. Lett.* **1999**, *314*, 291–299.
(58) Dreuw, A.; Head-Gordon, M. Single-Reference Ab Initio Methods for the Calculation of Excited States of Large Molecules. *Chem. Rev.* **2005**, *105*, 4009–4037.
(59) Mandapati, P.; Braun, J. D.; Killeen, C.; Davis, R. L.; Williams, J. A. G.; Herbert, D. E. Luminescent Platinum(II) Complexes of N^N$^-$^N Amido Ligands with Benzannulated *N*-Heterocyclic Donor Arms: Quinolines Offer Unexpectedly Deeper Red Phosphorescence than Phenanthridines. *Inorg. Chem.* **2019**, *58*, 14808–14817.
(60) Mondal, R.; Lozada, I. B.; Davis, R. L.; Williams, J. A. G.; Herbert, D. E. Site-Selective Benzannulation of *N*-Heterocycles in Bidentate Ligands Leads to Blue-Shifted Emission from $[(P\text{^}N)Cu]_2(\mu\text{-}X)_2$ Dimers. *Inorg. Chem.* **2018**, *57*, 4966–4978.
(61) Shon, J.-H.; Teets, T. S. Molecular Photosensitizers in Energy Research and Catalysis: Design Principles and Recent Developments. *ACS Energy Lett.* **2019**, *4*, 558–566.
(62) Mandapati, P.; Braun, J. D.; Lozada, I. B.; Williams, J. A. G.; Herbert, D. E. Deep-Red Luminescence from Platinum(II) Complexes of N^N$^-$^N-Amido Ligands with Benzannulated N-Heterocyclic Donor Arms. *Inorg. Chem.* **2020**, *59*, 12504–12517.
(63) de Groot, M. S.; van der Waals, J. H. Paramagnetic Resonance in Phosphorescent Aromatic Hydrocarbons. III. Conformational Isomerism in Benzene and Triptycene. *Mol. Phys.* **1963**, *6*, 545.
(64) Papadakis, R.; Ottosson, H. The Excited State Antiaromatic Benzene Ring: A Molecular Mr Hyde? *Chem. Soc. Rev.* **2015**, *44*, 6472–6493.

(65) Mondal, R.; Lozada, I. B.; Davis, R. L.; Williams, J. A. G.; Herbert, D. E. Exploiting Synergy between Ligand Design and Counterion Interactions to Boost Room Temperature Phosphorescence from Cu(I) Compounds. *J. Mater. Chem. C* **2019**, *7*, 3772–3778.
(66) Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. Highly Efficient Organic Light-Emitting Diodes From Delayed Fluorescence. *Nature* **2012**, *492*, 234–238.
(67) Garner, K. L.; Parkes, L. F.; Piper, J. D.; Williams, J. A. G. Luminescent Platinum Complexes with Terdentate Ligands Forming 6-Membered Chelate Rings: Advantageous and Deleterious Effects in N^N^N and N^C^N-Coordinated Complexes. *Inorg. Chem.* **2010**, *49*, 476–487.
(68) Williams, J. A. G. The Coordination Chemistry of Dipyridylbenzene: N-Deficient Terpyridine or Panacea for Brightly Luminescent Metal Complexes? *Chem. Soc. Rev.* **2009**, *38*, 1783–1801.
(69) Wenger, O. S. Is Iron the New Ruthenium? *Chem. - Eur. J.* **2019**, *25*, 6043–6052.
(70) Ferrere, S.; Gregg, B. A. Photosensitization of TiO_2 by $[Fe^{II}(2,2'$-Bipyridine-4,4'-Dicarboxylic Acid$)_2(CN)_2]$: Band Selective Electron Injection from Ultra-Short-Lived Excited States. *J. Am. Chem. Soc.* **1998**, *120*, 843–844.
(71) Juban, E. A.; Smeigh, A. L.; Monat, J. E.; McCusker, J. K. Ultrafast Dynamics of Ligand-Field Excited States. *Coord. Chem. Rev.* **2006**, *250*, 1783–1791.
(72) Arias-Rotondo, D. M.; McCusker, J. K. The Photophysics of Photoredox Catalysis: A Roadmap for Catalyst Design. *Chem. Soc. Rev.* **2016**, *45*, 5803–5820.
(73) Woodhouse, M. D.; McCusker, J. K. Mechanistic Origin of Photoredox Catalysis Involving Iron(II) Polypyridyl Chromophores. *J. Am. Chem. Soc.* **2020**, *142* (38), 16229–16233.
(74) Ponseca, C. S.; Chabera, P.; Uhlig, J.; Persson, P.; Sundstroem, Villy. Ultrafast Electron Dynamics in Solar Energy Conversion. *Chem. Rev.* **2017**, *117*, 10940–11024.
(75) Kaupp, M. The Role of Radial Nodes of Atomic Orbitals for Chemical Bonding and the Periodic Table. *J. Comput. Chem.* **2007**, *28*, 320–325.
(76) McCusker, J. K. Electronic Structure in the Transition Metal Block and Its Implications for Light Harvesting. *Science* **2019**, *363*, 484.
(77) Duchanois, T.; Liu, L.; Pastore, M.; Monari, A.; Cebrián, C.; Trolez, Y.; Darari, M.; Magra, K.; Francés-Monerris, A.; Domenichini, E.; Beley, M.; Assfeld, X.; Haacke, S.; Gros, P. C. NHC-Based Iron Sensitizers for DSSCs. *Inorganics* **2018**, *6*, 63.
(78) Liu, Y.; Warnmark, K.; Liu, Y.; Sundstrom, V.; Persson, P. Fe N-Heterocyclic Carbene Complexes as Promising Photosensitizers. *Acc. Chem. Res.* **2016**, *49*, 1477–1485.
(79) Chábera, P.; Kjaer, K. S.; Prakash, O.; Honarfar, A.; Liu, Y.; Fredin, L. A.; Harlang, T. C. B.; Lidin, S.; Uhlig, J.; Sundström, V.; Lomoth, R.; Persson, P.; Wärnmark, K. FeII Hexa N-Heterocyclic Carbene Complex with a 528 Ps Metal-to-Ligand Charge-Transfer Excited-State Lifetime. *J. Phys. Chem. Lett.* **2018**, *9*, 459–463.
(80) Dixon, I. M.; Alary, F.; Boggio-Pasqua, M.; Heully, J.-L. The (N4C2)2- Donor Set as Promising Motif for Bis(Tridentate) Iron(II) Photoactive Compounds. *Inorg. Chem.* **2013**, *52*, 13369–13374.
(81) Dixon, I. M.; Alary, F.; Boggio-Pasqua, M.; Heully, J.-L. Reversing the Relative ^{3}MLCT-^{3}MC Order in Fe(II) Complexes Using Cyclometallating Ligands: A Computational Study Aiming at Luminescent Fe(II) Complexes. *Dalton Trans.* **2015**, *44*, 13498–13503.
(82) Dierks, P.; Kruse, A.; Bokareva, O. S.; Al-Marri, M. J.; Kalmbach, J.; Baltrun, M.; Neuba, A.; Schoch, R.; Hohloch, S.; Heinze, K.; Seitz, M.; Kühn, O.; Lochbrunner, S.; Bauer, M.

Distinct Photodynamics of κ-N and κ-C Pseudoisomeric Iron(II) Complexes. *Chem. Commun.* **2021**, *57*, 6640–6643.
(83) Leis, W.; Argüello Cordero, M. A.; Lochbrunner, S.; Schubert, H.; Berkefeld, A. A Photoreactive Iron(II) Complex Luminophore. *J. Am. Chem. Soc.* **2022**, *144*, 1169–1173.
(84) Epstein, L. M. Moessbauer Isomer Shifts of Ferrous Phenanthroline and Related Complexes. *J. Chem. Phys.* **1964**, *40*, 435–439.
(85) Reiff, W. M.; Baker, W. A., Jr.; Erickson, N. E. Binuclear, Oxygen-Bridged Complexes of Iron(III). New Iron(III)-2,2',2"-Terpyridine Complexes. *J. Amer. Chem. Soc.* **1968**, *90*, 4794–4800.
(86) Chábera, P.; Liu, Y.; Prakash, O.; Thyrhaug, E.; Nahhas, A. E.; Honarfar, A.; Essén, S.; Fredin, L. A.; Harlang, T. C. B.; Kjær, K. S.; Handrup, K.; Ericson, F.; Tatsuno, H.; Morgan, K.; Schnadt, J.; Häggström, L.; Ericsson, T.; Sobkowiak, A.; Lidin, S.; Huang, P.; Styring, S.; Uhlig, J.; Bendix, J.; Lomoth, R.; Sundström, V.; Persson, P.; Wärnmark, K. A Low-Spin Fe(III) Complex With 100-Ps Ligand-to-Metal Charge Transfer Photoluminescence. *Nature* **2017**, *543*, 695.
(87) Kjær, K. S.; Kaul, N.; Prakash, O.; Chábera, P.; Rosemann, N. W.; Honarfar, A.; Gordivska, O.; Fredin, L. A.; Bergquist, K.-E.; Häggström, L.; Ericsson, T.; Lindh, L.; Yartsev, A.; Styring, S.; Huang, P.; Uhlig, J.; Bendix, J.; Strand, D.; Sundström, V.; Persson, P.; Lomoth, R.; Wärnmark, K. Luminescence and Reactivity of a Charge-Transfer Excited Iron Complex with Nanosecond Lifetime. *Science* **2019**, *363*, 249.
(88) Betley, T. A.; Qian, B. A.; Peters, J. C. Group VIII Coordination Chemistry of a Pincer-Type Bis(8-Quinolinyl)Amido Ligand. *Inorg. Chem.* **2008**, *47*, 11570–11582.
(89) Basch, H.; Viste, A.; Gray, H. B. Molecular Orbital Theory for Octahedral and Tetrahedral Metal Complexes. *J. Chem. Phys.* **1966**, *44*, 10–19.
(90) Braun, J. D.; Lozada, I. B.; Kolodziej, C.; Burda, C.; Newman, K. M. E.; van Lierop, J.; Davis, R. L.; Herbert, D. E. Iron(II) Coordination Complexes with Panchromatic Absorption and Nanosecond Charge-Transfer Excited State Lifetimes. *Nat. Chem.* **2019**, *11*, 1144–1150.
(91) Mukherjee, S.; Torres, D. E.; Jakubikova, E. HOMO Inversion as a Strategy for Improving the Light-Absorption Properties of Fe(II) Chromophores. *Chem. Sci.* **2017**, *8*, 8115–8126.
(92) Braun, J. D.; Lozada, I. B.; Herbert, D. E. In Pursuit of Panchromatic Absorption in Metal Coordination Complexes: Experimental Delineation of the HOMO Inversion Model Using Pseudo-Octahedral Complexes of Diarylamido Ligands. *Inorg. Chem.* **2020**, *59*, 17746–17757.
(93) Larsen, C. B.; Braun, J. D.; Lozada, I. B.; Kunnus, K.; Biasin, E.; Kolodziej, C.; Burda, C.; Cordones, A. A.; Gaffney, K. J.; Herbert, D. E. Reduction of Electron Repulsion in Highly Covalent Fe-Amido Complexes Counteracts the Impact of a Weak Ligand Field on Excited-State Ordering. *J. Am. Chem. Soc.* **2021**, *143*, 20645–20656.
(94) Dixon, I. M.; Khan, S.; Alary, F.; Boggio-Pasqua, M.; Heully, J.-L. Probing the Photophysical Capability of Mono and Bis(Cyclometallated) Fe(II) Polypyridine Complexes Using Inexpensive Ground State DFT. *Dalton Trans.* **2014**, *43*, 15898–15905.
(95) Brown, A. M.; McCusker, C. E.; McCusker, J. K. Spectroelectrochemical Identification of Charge-Transfer Excited States in Transition Metal-Based Polypyridyl Complexes. *Dalton Trans.* **2014**, *43*, 17635–17646.

(96) Gaffney, K. J. Capturing Photochemical and Photophysical Transformations in Iron Complexes with Ultrafast X-Ray Spectroscopy and Scattering. *Chem. Sci.* **2021**, *12*, 8010–8025.
(97) Smeigh, A. L.; Creelman, M.; Mathies, R. A.; McCusker, J. K. Femtosecond Time-Resolved Optical and Raman Spectroscopy of Photoinduced Spin Crossover: Temporal Resolution of Low-to-High Spin Optical Switching. *J. Am. Chem. Soc.* **2008**, *130*, 14105–14107.
(98) Sinha, N.; Jiménez, J.-R.; Pfund, B.; Prescimone, A.; Piguet, C.; Wenger, O. S. A Near-Infrared-II Emissive Chromium(III) Complex. *Angew. Chem., Int. Ed.* **2021**, *60*, 23722–23728.
(99) Sinha, N.; Pfund, B.; Wegeberg, C.; Prescimone, A.; Wenger, O. S. Cobalt(III) Carbene Complex with an Electronic Excited-State Structure Similar to Cyclometalated Iridium(III) Compounds. *J. Am. Chem. Soc.* **2022**, *144*, 9859–9873.
(100) Lozada, I. B.; Braun, J. D.; Williams, J. A. G.; Herbert, D. E. Yellow-Emitting, Pseudo-Octahedral Zinc Complexes of Benzannulated N^N^O Pincer-Type Ligands. *Inorg. Chem.* **2022**, *61*, 17568–17578.
(101) Constable, E. C.; Hartshorn, R. M.; Housecroft, C. E. 1,1'-Biisoquinolines-Neglected Ligands in the Heterocyclic Diimine Family That Provoke Stereochemical Reflections. *Molecules* **2021**, *26*, 1584.