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Beyond BODIPY: Dipyrrin Complexes of P-Block Elements

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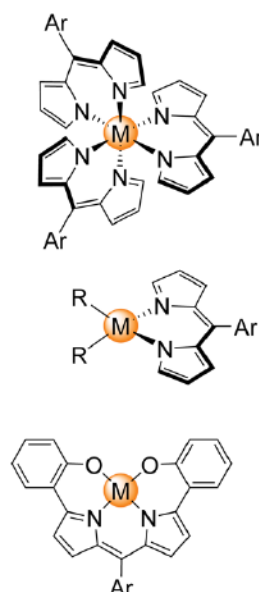
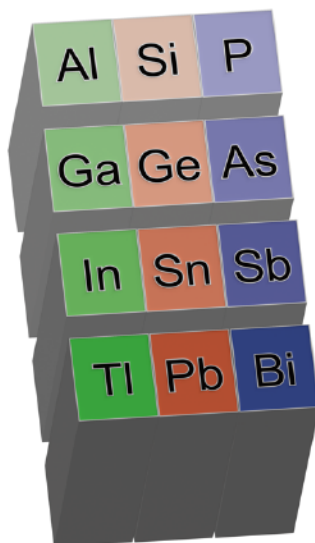
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Abstract

Dipyrin has proven to be a versatile ligand platform for metals across the periodic table. Since much of the coordination chemistry has focused on transition metals, main-group dipyrin chemistry has been underexplored, particularly in the case of heavy p-block elements. Boron dipyrin complexes (also known as BODIPY) were initially reported in 1968, yet the first well-characterized example of a heavy p-block dipyrin complex was in 2006. This nascent area of research has undergone a significant surge, where nearly half of the reports in this field have been published since 2019. Given this renewed interest and rapid development, we provide a focused review on heavy p-block dipyrin complexes, describing the synthesis, structure, and spectroscopy of these molecules. One significant aspect of these complexes is their optical properties, which access red and near-infrared wavelengths with high quantum yields. While these main-group dipyrins have been used as catalysts, they have also been leveraged for a variety of biological applications including photodynamic therapy, tumor imaging, and cytotoxic drugs. With the advent of synthetic methods for these novel p-block complexes, dipyrins can begin to interface with recent advances and applications of main-group chemistry, potentially offering advantages over other ligand platforms.



Keywords:

dipyrin, main-group, p-block, X-ray structure, emission, photodynamic therapy (PDT), bioimaging, catalysis

1. Introduction

Dipyrrens, or half-porphyrins, are versatile bidentate ligands that can bind main-group elements, d-block metals, and f-block metals [1]. The dipyrryn ligand originates from the early pyrrole chemistry of Hans Fisher [2] and later Alfred Treibs [3], who first synthesized the BF_2 complex now known as BODIPY [4]. Since then, the coordination chemistry of this ligand has flourished as a result of significant contributions from several research groups including Jack Fergusson [5], Yukito Murakami [6,7], David Dolphin [8,9], Seth Cohen [10], and Shane Telfer [11]. In the past decade, Ted Betley and co-workers have pioneered the use of transition metal dipyrryn complexes as catalysts [12–15], which has spurred a surge in dipyrryn chemistry that has led to their applications in mediating a wide variety of chemical reactions [16,17].

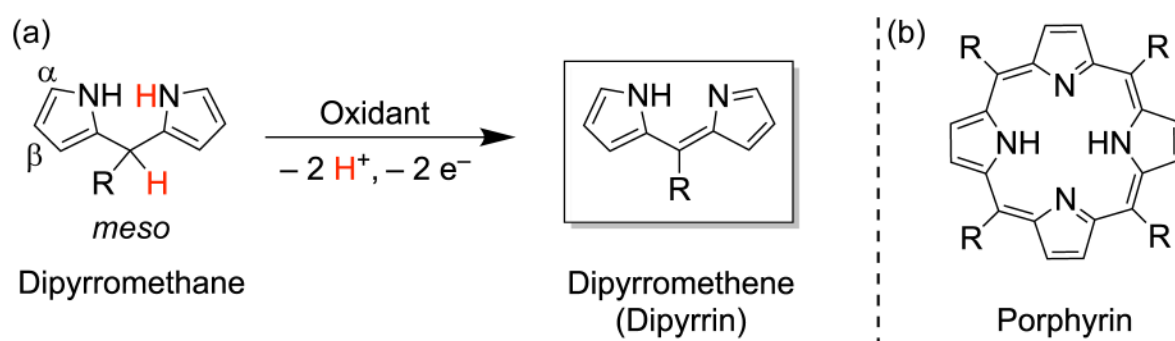


Figure 1. (a) Dipyrromethane precursors are oxidized to the corresponding dipyrromethene or dipyrryn, which is structurally similar to a half-porphyrin (b).

The most common synthetic precursors to dipyrrens are dipyrromethanes, which are comprised of two α -linked pyrrole units bridged by an sp^3 hybridized carbon (Figure 1a). These compounds are synthesized from the acid-catalyzed condensation of pyrrole and an aldehyde. The two-electron, two-proton oxidation of dipyrromethane results in the formation of the fully conjugated dipyrromethene (or dipyrryn) chromophore. Dipyrrens are often synthesized with a *meso*-aryl substituent because these molecules are generally more stable than the unsubstituted analogs [18]. The α , β , and *meso* positions can be functionalized with a wide variety of substituents (e.g., halogens, alkanes, alkynes, aryl rings, carbonyl groups, etc.) to readily tune and diversify the properties of dipyrrens,

highlighting the versatility of the ligand core. Since the electron density of the dipyrryn HOMO often resides primarily on the pyrrole units (Figure 2) [19–21], substituents on the α and β positions largely dictate the electronic properties of the ligand. Additionally, the inclusion of bulky aryl substituents (*e.g.*, mesityl, 2,4,6-tri-isopropyl, 2,4,6-triphenyl) at the α -positions protects the metal center, preventing bimolecular reactions and enabling the stabilization of transient intermediates [14,22]. This approach has led to the widespread use of transition metal dipyrryns as catalysts for a vast array of chemical transformations [16,17]. Fundamental understanding of the interplay between the peripheral substituents and molecular properties is essential to tailor dipyrryn complexes for subsequent applications.

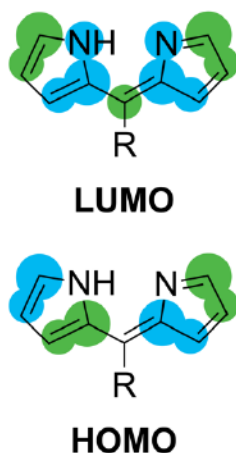


Figure 2. The canonical HOMO and LUMO orbitals of the dipyrryn ligand.

Since dipyrryns are often described as half porphyrins, relevant comparisons can be drawn between these two ligands. Porphyrins are tetrapyrrole macrocycles where the pyrrole units are linked at the α positions with bridging sp^2 carbon atoms, resulting in an aromatic system with 18 π -electrons in the main conjugation pathway (Figure 1b) [23]. Analogous to dipyrryn, dipyrromethanes can be used as synthons for the preparation of porphyrins [24]. However, the synthesis of dipyrryns is generally more facile than analogous porphyrins, requiring fewer synthetic steps and less chromatography with higher product yields. Dipyrryns offer more versatility than porphyrins, enabling substrates to bind at either an equatorial or axial position, whereas porphyrins are restricted to axial

substrate binding. Since dipyrins are not macrocyclic, the primary coordination sphere is readily diversified, enabling the isolation of both homoleptic and heteroleptic complexes. Together, these properties make dipyrin ligands versatile platforms for catalyst development.

In addition to their roles in catalysis, dipyrins are intense chromophores. Boron dipyrin or BODIPY, where a BF_2 unit is coordinated to the ligand, is a popular class of fluorophores that have been widely used as labels, sensors, photosensitizers, and photocatalysts [4]. These dyes have high quantum yields and narrow emission profiles, making them attractive for biomedical applications [25]. In order to maximize the quantum yield of these fluorophores, two primary strategies have been employed: the inclusion of bulky aryl groups (e.g., mesityl) at the *meso* position or the absence of a *meso*-substituent [26]. Functionalization of the *meso*-aryl group at the 2 and 6 positions restricts ring rotation, thereby suppressing non-radiative deactivation that leads to an increased lifetime of the excited state and higher quantum yield. While the BODIPY core emits green light, peripheral functionalization of the dipyrin can tune the optical properties across the visible spectrum. Structural modifications include aryl substitution, rigidification with pyrrole fused rings, dimerization of BODIPY units, and extension of the aromatic π -system [27]. These molecular design strategies have led to numerous applications of BODIPY chromophores. One biomedical example is the photosensitization of singlet oxygen for photodynamic therapy (PDT) [28]. Other applications include *in vivo* bioimaging [29] and biosensing [30]. These examples highlight the diverse applications of BODIPY fluorophores that leverage the unique photophysical properties of these molecules.

Given the prevalence of BODIPY dyes and their ubiquity across the biosciences, there are potential advantages of extending this chemistry to heavier p-block elements (i.e., periods 3 through 6). The use of larger atoms increases the extent of spin-orbit coupling, resulting in more efficient intersystem crossing to access long-lived triplet states. In principle, this heavy atom effect will result in more efficient triplet photosensitizers relative to typical BODIPY fluorophores [31]. However, the potential of enhanced optical properties has been hampered by the dearth of examples of heavy p-block dipyrin complexes. Except for a brief study on the NMR characterization of thallium dipyrins in 1976 [32], the first report of heavy p-block dipyrin complexes with

comprehensive and complete characterization was published in 2006 [10]. This represents a significant lag in development relative to BODIPY, which was first synthesized in 1968 by Triebs and Kreuzer [3]. Research on non-boron dipyrrens began to expand in the mid-2010's. Since then, contributions to this field have been steadily increasing (Figure 3). Indeed, 66% of studies on p-block dipyrrens have been reported in the last decade. There has not yet been a comprehensive review of heavy p-block dipyrren complexes. Given the recent surge in reports of main-group dipyrrens in the past three years (accounting for 24% of all studies in this area, Figure 3), a review of this field is timely.

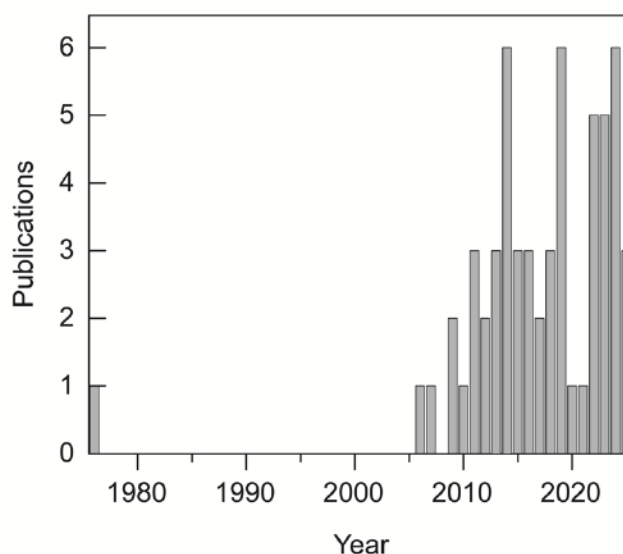


Figure 3. Bar graph illustrating the number of publications on heavy p-block dipyrrens over time.

Here, we present a focused review of main-group p-block dipyrren complexes, providing an overview of the synthesis, structure, and spectroscopic properties of these molecules. These complexes range from tris-homoleptic derivatives to heteroleptic species with one or two dipyrren ligands and diverse primary coordination spheres. Examples with a single dipyrren and ancillary halide ligands represent true heavy-atom congeners of BODIPY and have been termed ALDIPY, GADIPY, PODIPY, etc. The inclusion of intramolecular ligands (*e.g.*, phenol, pyrrole) at the α -positions has led to the development of chelating tri- and tetradentate dipyrren ligands. All varieties of these

complexes exhibit unique photophysical properties, which have been utilized for a range of applications, such as photosensitizers for PDT and fluorescent labels for bioimaging. Other biomedical applications of p-block dipyrin complexes include cytotoxic agents that exhibit antimicrobial activity or inhibit cancer cell proliferation. With established routes to synthesize p-block dipyrins with diverse primary coordination spheres, these molecules can now potentially be leveraged for novel applications. Given the recent surge in the use of main-group complexes for catalysts [33–35], perhaps these dipyrins can now begin to rival their transition metal analogs.

2. Homoleptic Dipyrin Complexes

The synthesis of tris-homoleptic dipyrin complexes with simple, bidentate dipyrin ligands is perhaps more straightforward than the preparation of heteroleptic complexes. This is because the reaction does not require precise control of speciation, which is necessary to preferentially favor the formation of heteroleptic complexes. Tris-homoleptic dipyrin complexes are synthesized using an excess of the dipyrin relative to the metal salt, ensuring that the metal is coordinatively saturated. Excess ligand mitigates variable speciation that results in heteroleptic, mixed-ligand complexes [8]. Generally, the free-base dipyrin ligand is treated with nitrate or chloride metal salts in methanol under ambient (or refluxing) conditions. When a polar aprotic solvent is utilized, diisopropylethylamine (DIPEA) or lithium hexamethyldisilazide (to form the Li dipyrin salt *in situ*) is used to deprotonate the ligand prior to metalation. To the best of our knowledge, aluminum, gallium, and indium are the only examples of p-block tris-homoleptic dipyrins that have been reported (Chart 1).

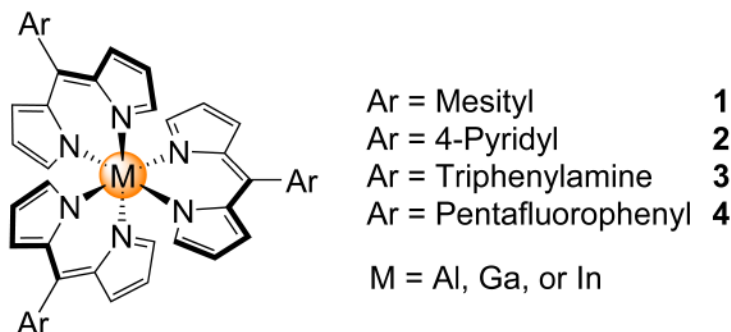


Chart 1. Tris-homoleptic dipyrin complexes.

A 2004 patent reported organic electroluminescent devices that utilized thin films of aluminum dipyrins as the light-emitting layer. The aluminum tris dipyrin complexes with *meso*-aryl groups (phenyl, 4-cyanophenyl) featured various α and β substituents (H, methyl) [36]. In 2025, the first research article to report Al(III) tris dipyrin complexes was published [37], over 20 years after the initial patent on these complexes. Several derivatives were synthesized, functionalizing the *meso*-aryl group with various substituents including bromo, methoxy, alkynyl, naphthyl, and anthryl groups, as well as several esters. These complexes exhibited long-lived triplet states under ambient air (290–390 ns). Anaerobic samples have significantly longer lifetimes of ~80–200 μ s, demonstrating that the excited state is readily quenched by oxygen and substantiating the assignment of a triplet state. Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations revealed that the frontier molecular orbitals are localized on the dipyrin ligand, and the main absorption bands are $\pi \rightarrow \pi^*$ transitions [37]. The solid-state structure of Al-1 was reported (Figure 4a), exhibiting an average Al–N bond length of 2.001 Å.

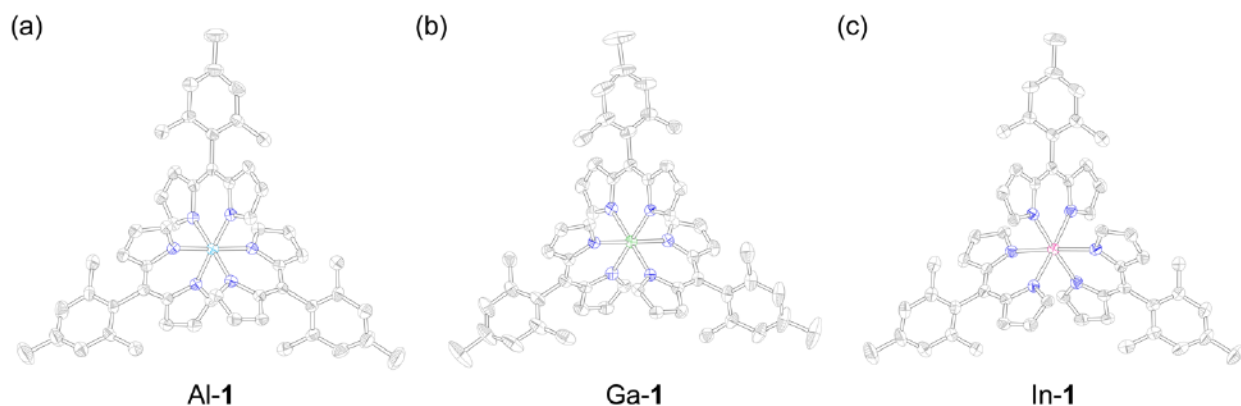


Figure 4. X-ray crystal structures of (a) Al-1 (CCDC 2401898), (b) Ga-1 (CCDC 617591), and (c) In-1 (CCDC 617592). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecules have been removed for clarity.

In 2006, Cohen and co-workers reported the first gallium and indium tris dipyrin complexes: Ga-1 and In-1 [10]. Similar to the Al complexes, the UV–vis absorption spectra exhibited a doublet feature (Figure 5) with bands around 450 and 500 nm. TD-DFT calculations indicated that the absorption features arise from dipyrin-centered $\pi \rightarrow$

π^* transitions. The authors assigned the split transition to excitonic coupling of the dipyrin units [38]. Flash photolysis experiments demonstrated that the excited state lifetime was oxygen-dependent, consistent with the assignment of a triplet state. Under air, the complexes displayed lifetimes of 300–320 ns. The lifetime was further quenched by 1 atm of O₂ to 56–62 ns and extended to 45–80 μ s under argon. The solid-state structures of Ga-1 and In-1 (Figure 4b and 4c) exhibit average Ga–N and In–N bond lengths of 2.054 Å and 2.215 Å, respectively. The 0.161 Å longer In–N bond reflects the increase in ionic radius of the metal: 94 pm for In(III) vs. 76 pm for Ga(III) [39]. Cohen and coworkers then synthesized In-2 and Ga-2 with *meso*-4-pyridyl substituents to utilize these complexes as building blocks for metal-organic frameworks (MOFs) [40]. The average M–N bond lengths are 2.057 Å and 2.222 Å for Ga-2 and In-2, respectively, which are nearly identical to the M-1 derivatives. The addition of Ag(I) salts to In-2 or Ga-2 resulted in the formation of regular MOFs. It was found that the topology of the MOF could be controlled by the size of the anion. For example, AgPF₆ exhibited little preference for a particular network topology, while AgOTf and AgSbF₆ favored three-dimensional and two-dimensional topologies, respectively. Beyond structural studies, Das and Gupta synthesized In-3 and examined the electrochemistry of this complex [41]. Only a quasi-reversible oxidation was observed in the cyclic voltammogram (CV) of In-3 at 1.09 V vs. SCE (0.69 V vs. Fc⁺/Fc).

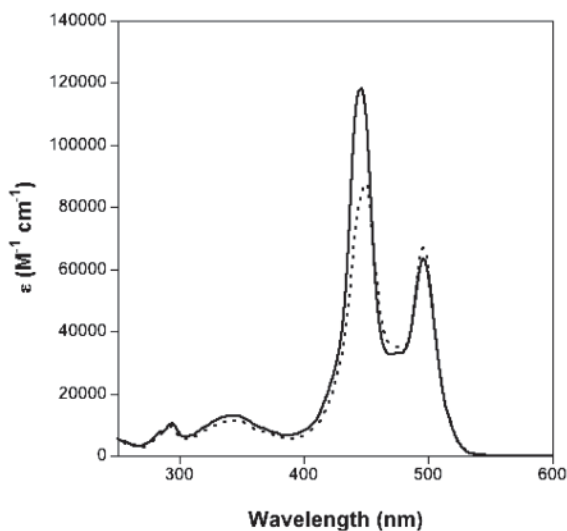


Figure 5. UV–vis absorption spectra of Ga-1 (dotted line) and In-1 (solid line). Reprinted with permission from [10]. Copyright 2006 American Chemical Society.

Wiehe and colleagues synthesized dipyrin complexes **Ga-4** and **In-4** [42]. The average M–N bond lengths are 2.062 Å and 2.220 Å for **Ga-4** and **In-4**, respectively. The UV–vis absorption spectra of **Ga-4** and **In-4** showed bands at ~450 nm and ~515 nm, exhibiting a doublet pattern consistent with **In-1** and **Ga-1**. The authors then leveraged nucleophilic aromatic substitution (S_NAr) to selectively modify the *para* position of the –C₆F₅ group on the dipyrin ligand, generating a family of compounds with substituents that range from butoxy groups to thiol carbohydrates (Chart 2). The S_NAr reactions were performed directly on **Ga-4** or **In-4** rather than the free-base ligand. Modification of the dipyrin ligand by S_NAr resulted in nominal changes in the bond lengths, where the average M–N bond lengths are 2.054 Å and 2.220 Å for **Ga-5b** and **In-5b**, respectively.

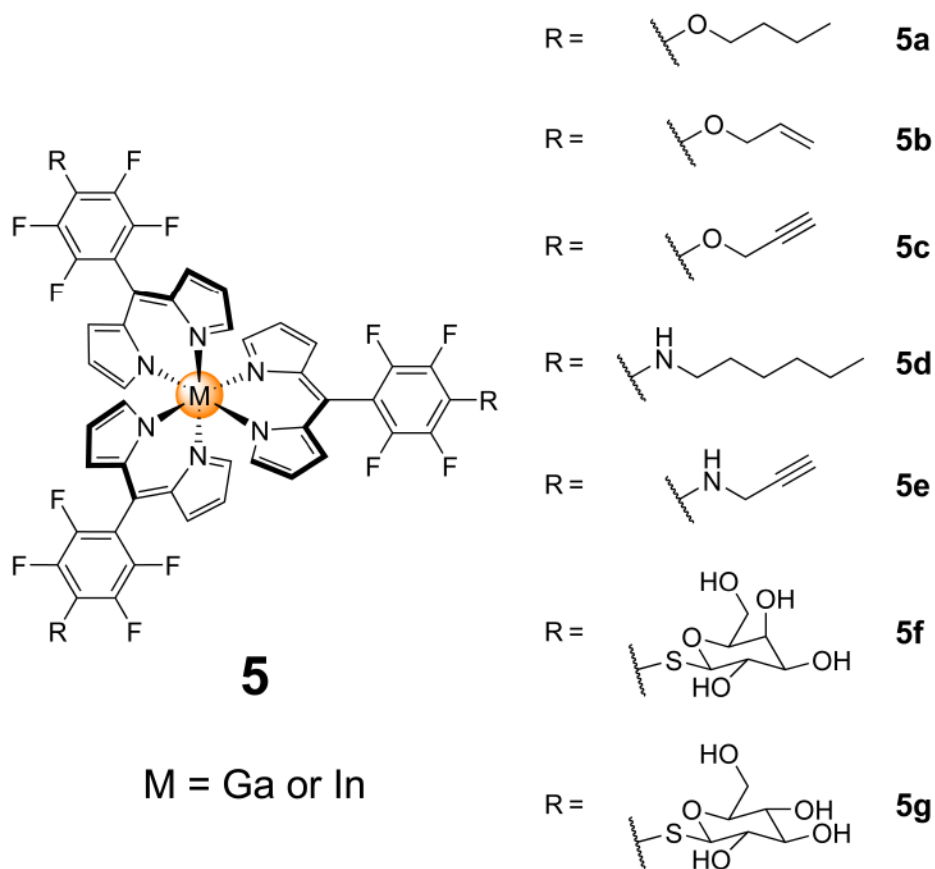


Chart 2. Homoleptic dipyrin complexes prepared by S_NAr derivatization of **M-4**.

Nishihara and co-workers synthesized a series of indium complexes with a variety of β -substituents (Chart 3). DFT calculations of In-**6a** and In-**6b** indicated that the frontier molecular orbitals are centered on the dipyrin ligands, which is consistent with other homoleptic Al(III), Ga(III), and In(III) dipyrin complexes. The UV-vis absorption spectrum of In-**6c** showed a doublet pattern identical to that of In-**1** [43].

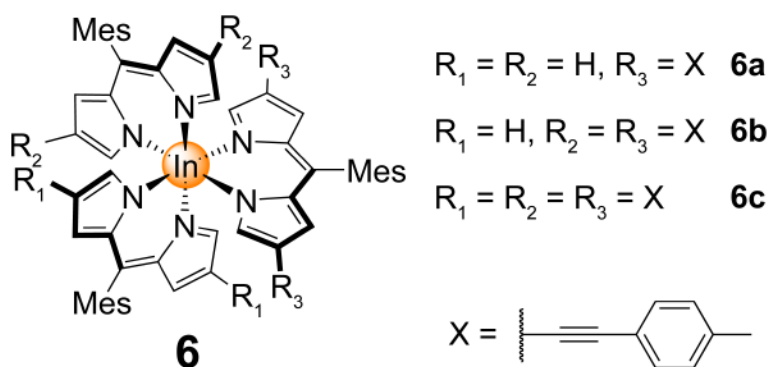


Chart 3. Tris heteroleptic In(III) dipyrin complexes.

Dolphin and co-workers synthesized a family of α -free bis(dipyrromethene) ligands that are β, β' -linked via a CH_2 bridge (*i.e.*, *a,c*-biladienes). The gallium and indium complexes of these ligands were prepared to furnish helicates and mesocates [44]. The X-ray crystal structure of the binuclear gallium bis(dipyrromethene) complex (Figure 6) exhibits an average Ga–N bond length of 2.059 Å, which closely matches Ga-**1**. While the helicates and mesocates did not interconvert, the diastereoselectivity of the product distribution increased when elevated temperatures were used during complex formation. The authors subsequently synthesized a ligand derivative with *gem*-dimethyl groups on the methylene bridge. The dimethyl groups rigidified the bis(dipyrromethene) via the Thorpe–Ingold effect, preferentially forming helicates at room temperature [45]. Ksenofontov and co-workers utilized UV-vis absorption to confirm that these binuclear triple-helix helicates formed through successive mono- and binuclear heteroligand intermediates [46]. The helicate and mesocate complexes exhibit a single broad absorption band at $\sim 490\text{--}520$ nm ($2.0 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$), with a weaker shoulder at ~ 530 nm ($\sim 6.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). This observation contrasts the mononuclear tris-homoleptic

complexes, which exhibit a signature doublet pattern that is attributed to excitonic coupling [10].

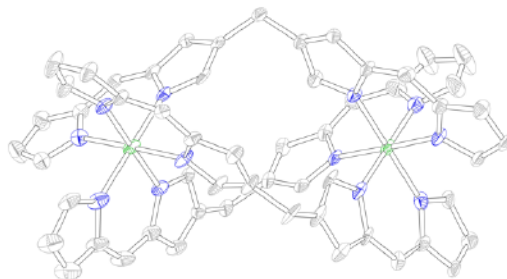


Figure 6. Crystal structure of a binuclear gallium bis(dipyrromethene) complex (CCDC 840436). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, solvent molecules, and *meso*-phenyl substituents have been removed for clarity.

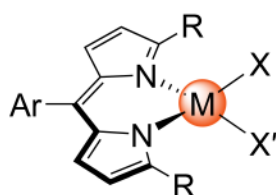
The *a,c*-biladiene ligand used to prepare the helicate complexes can be oxidized to form fully conjugated *a,b,c*-bilatriene, which is a derivative of biliverdin. Antina and co-workers explored metal chelation with the bilatriene ligand, utilizing a variety of first-row transition metals as well as Pb(II) [47]. UV–vis titrations indicated the formation of a 2:1 bilatriene:Pb(II) complex, whereas all of the transition metals formed 1:1 adducts. It should be noted that this homoleptic complex was not isolated, but only observed in solution by absorption spectroscopy. This is similar to the formation of Pb(II) and Pb(IV) corroles, which have been observed spectroscopically, but could not be isolated from the reaction mixture [48]. Lead dipyrins and corroles have remained elusive and stable complexes of both ligands have yet to be isolated and fully characterized.

The optical properties of homoleptic aluminum, gallium, and indium dipyrin complexes are summarized in Table 1. For the series of complexes with dipyrin ligand **1**, the fluorescence lifetimes follow the expected trend, where the lifetime decreases as the mass of the central atom increases. The increased spin–orbit coupling with larger atoms enhances intersystem crossing, resulting in a shorter lifetime of the singlet excited state. Surprisingly, the quantum yields of both Al-**1** and In-**1** are quite similar, despite the significant difference in size, and are larger than that of Ga-**1**. It should be noted that the values were measured in different solvents, which could partially account for this unexpected observation. Extension of the dipyrin π system (In-**6a** to In-**6c**) results in a

red-shift of the emission profile and a substantial increase in fluorescence quantum yield relative to In-1 and In-2. The enhanced quantum yield is likely due to the *meso*-mesityl substituents, which are known to restrict ring rotation, mitigating non-radiative decay of the excited state [4]. This contention is supported by the longer lifetime of In-6a to In-6c compared to other In(III) dipyrroin complexes. The high quantum yield of 41% for In-6a is a noteworthy development in fluorescent p-block dipyrroin complexes, making this compound competitive with BODIPY fluorophores.

3. Heteroleptic Dipyrroin Complexes

Unlike the few examples of tris-homoleptic dipyrroin complexes, there are numerous studies on heteroleptic dipyrromethenes with group 13, 14, and 15 elements, ranging from aluminum to bismuth. By using an excess of the metal salt relative to the ligand (or sometimes a 1:1 ratio), a single dipyrroin is bound to the metal. These heteroleptic complexes are typically synthesized by first preparing the lithium salt of the dipyrroin *in situ*, followed by the immediate addition of a metal chloride salt [49]. Other approaches include the use of a metal hydride [50] or an organometallic reagent (e.g., AlMe₃) [51], resulting in the release of a gaseous byproduct upon deprotonation of the ligand.



M = Al, Ga, or In

Ar = Ph (**7**) or Mes (**8**)

R = Mes (**a**), Trip (**b**), ^tBu (**c**),
DIPP (**d**), or ⁱPr-Anth (**e**)

X, X' = Cl, I, Me, Et, NMe₂, O^tBu,
^tBu, ⁱBu, Ph, or H

Chart 4. Heteroleptic group 13 dipyrroin complexes with various *meso* groups (Ar), α substituents (R), and ancillary anionic ligands (X, X').

3.1 Group 13: Icosagens

The first example of an Al(III) analog of BODIPY, which has been dubbed “ALDIPY”, was reported by Mason and co-workers in 2014 [50]. The authors synthesized numerous derivatives with *meso*-phenyl substituents (**7**) and anionic X-type ligands ranging from hydride to iodide (Chart 4) [50,52]. For Al-**7a**-Me₂, the average Al–N and Al–C bond lengths are 1.936 Å and 1.962 Å, respectively, and the N–Al–N bond angle is 92.2°. The Hänisch group then extended this approach to derivatives with *meso*-mesityl groups (**8**) with X = X' = Me or Et (Chart 4). X-ray structures of Al-**8a**-Me₂ (Figure 7a) and Al-**8a**-Et₂ revealed that the Al centers exhibit tetrahedral geometry with $\tau_4 = 0.94$ and 0.92, respectively, where $\tau_4 = 0$ for square planar and $\tau_4 = 1$ for tetrahedral. The structural metrics of both Al-**8a**-Me₂ and Al-**8a**-Et₂ (Table 2) closely match those of Al-**7a**-Me₂ [51]. In addition to monometallic complexes, Mason and co-workers synthesized a bimetallic oxo-bridged aluminum hydride complex (Figure 8) [50]. The ALDIPY oxo-dimer has slightly shorter Al–N bonds (1.926 Å) relative to the monomeric derivatives. The Al–O bond length of 1.689 Å is shorter than the average Al–C bond distance of 1.962 Å for Al-**8a**-Me₂ and Al-**8a**-Et₂, which reflects the ionic character of the Al–O bond. While typical metal hydrides are moisture-sensitive and quite reactive, this hydride complex was isolable due to the steric bulk of the α -mesityl groups.

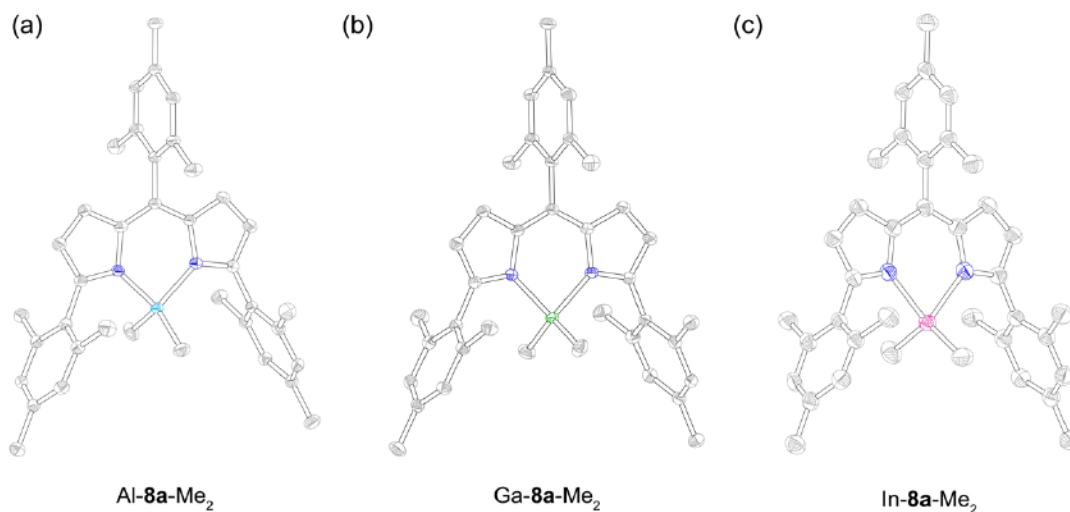


Figure 7. Crystal structures of heteroleptic dipyrin complexes (a) Al-**8a**-Me₂ (CCDC 2261604), (b) Ga-**8a**-Me₂ (CCDC 2261602), and (c) In-**8a**-Me₂ (CCDC 2261606). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecules have been removed for clarity.

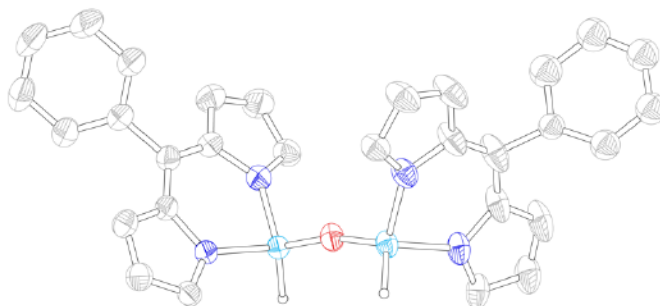


Figure 8. Crystal structure of the aluminum hydride μ -oxo-dimer (CCDC 1032114). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, solvent molecules, and α -mesityl substituents have been removed for clarity.

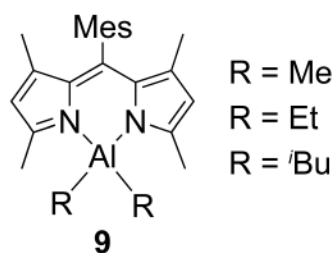


Chart 5. ALDIPYs reported by Li and co-workers [53].

Li and co-workers synthesized a series of three novel ALDIPYs (**9**, Chart 5) [53]. X-ray crystal structures of these complexes exhibited average Al–N bond distances of 1.906 Å (Me), 1.910 Å (Et), and 1.909 Å (*i*Bu) and N–Al–N bond angles of 94.1° (Me), 94.4° (Et), and 93.9° (*i*Bu); these parameters are consistent with Al-**8a**-Me₂ and Al-**8a**-Et₂ (Table 2). For this series of compounds, nominal differences (2–4 nm) in the absorption and emission maxima were observed, with average values of 495 nm and 509 nm, respectively.

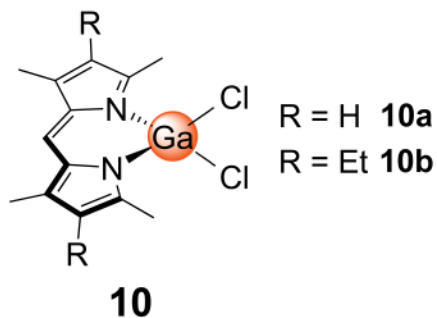


Chart 6. Meso-unsubstituted GADIPYs.

Smith and co-workers reported the first heteroleptic gallium dipyrins, coined GADIPYs, where the ligand was *meso*-unsubstituted with methyl groups at the α and β positions (**10a** and **10b**, Chart 6) [54]. Complex **10a** exhibits an average Ga–N bond length of 1.896 Å with a N–Ga–N bond angle of 98.8°. The shorter bond lengths of **10a** relative to the ALDIPYs are likely due to an inductive, electron-withdrawing effect of the electronegative chloride ligands relative to the alkyl groups. The CV of **10a** displays a quasi-reversible oxidation at 1.30 V vs. SCE (0.90 V vs. Fc⁺/Fc) and reduction at –1.10 V vs. SCE (–1.50 V vs. Fc⁺/Fc). These potentials closely match a related BODIPY analog [55], suggesting that the redox processes are ligand-based. Recently, *meso*-mesityl GADIPYs have been reported with dimethyl (Ga-**8a**-Me₂) or diethyl (Ga-**8a**-Et₂) ligands (Chart 4). Structural metrics of Ga-**8a**-Me₂ and Ga-**8a**-Et₂ (Table 2) are consistent with periodic trends, exhibiting longer M–N bonds relative to the Al(III) derivatives, which reflects an increase in ionic radius [51]: 76 pm for Ga(III) vs. 68 pm for Al(III) [39].

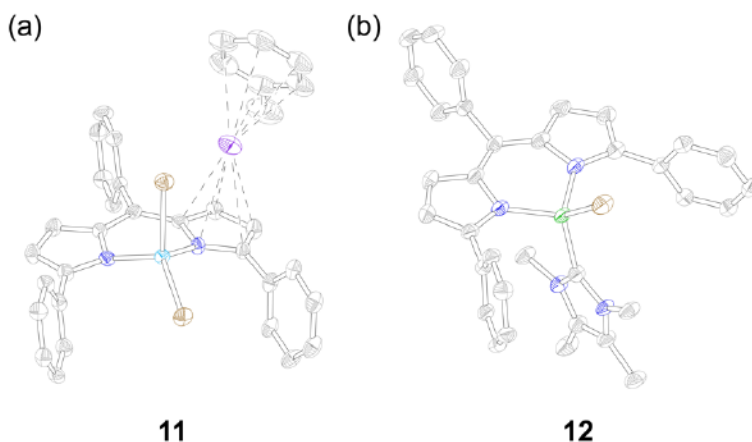


Figure 9. Crystal structures of (a) ALDIPY **11** (CCDC 2241371) and (b) GADIPY **12** (CCDC 2241372). Thermal ellipsoids are drawn at the 50% probability level. For clarity, H atoms and the substituents at the 2, 4, and 6 positions of the α -aryl groups have been removed, as well as the substituents on the NHC ligand of **12**.

Treatment of α -Trip (2,4,6-*tri*-isopropylbenzene) substituted dipyrin **8b** with ⁿBuLi followed by the addition of AlI₃ or GaI₃ led to the formation of Al-**8b**-I₂ or Ga-**8b**-I₂ (Chart 4) [56]. For these Al(III) and Ga(III) complexes, the average M–N bond lengths are 1.883 Å and 1.936 Å, respectively, while the N–M–N bond angles are 96.6° and 94.9°,

respectively. The average M–I bond lengths are 2.508 Å (Al) and 2.512 Å (Ga). The CVs of both Al-**8b**-I₂ and Ga-**8b**-I₂ exhibited a reversible one-electron reduction at –1.82 V Fc⁺/Fc and –1.74 V Fc⁺/Fc, respectively. Reduction of Al-**8b**-I₂ with KC₈ resulted in the formation of the dipyrromethene-centered radical **11** (Figure 9a). While reduced Ga-**8b**-I₂ could not be directly crystallized, the complex was stabilized by the addition of an *N*-heterocyclic carbene ligand (*ipr*NHC), and the adduct (**12**) was characterized by X-ray crystallography (Figure 9b). While radicals **11** and **12** are moisture and oxygen sensitive, they are stable under nitrogen for several weeks. The M–I bond lengths are 2.554 Å and 2.552 Å for **11** and **12**, respectively. The average M–N bond lengths are 1.854 Å (**11**) and 1.902 Å (**12**), which are slightly contracted relative to the parent complexes (M-**8b**-I₂). Notably, the N–M–N bond angles are larger than those of related complexes (Table 2): 99.6° for **11** and 100.4° for **12**. These structural changes could be attributed to delocalization of the radical onto the dipyrromethene core. In the solid-state structure of **11**, the potassium counterion is coordinated to one the pyrrole rings in an η⁵ fashion, as well as a toluene solvent molecule in an η⁶ binding mode. While the EPR spectrum of **11** exhibited a complicated signal, it could be readily simulated and closely matched the experimental spectrum. Despite the similarity to **11**, complex **12** exhibited a less complex EPR spectrum. Computational analysis of simplified derivatives of **11** and **12** revealed that the spin density was primarily localized on the dipyririn core of both complexes (88% for **11** and 92% for **12**), even though the EPR spectra are distinct. It should be noted that neither **11** nor **12** exhibited luminescence. This result is not surprising, given the radical nature of these complexes that results in rapid, non-radiative relaxation of the excited state.

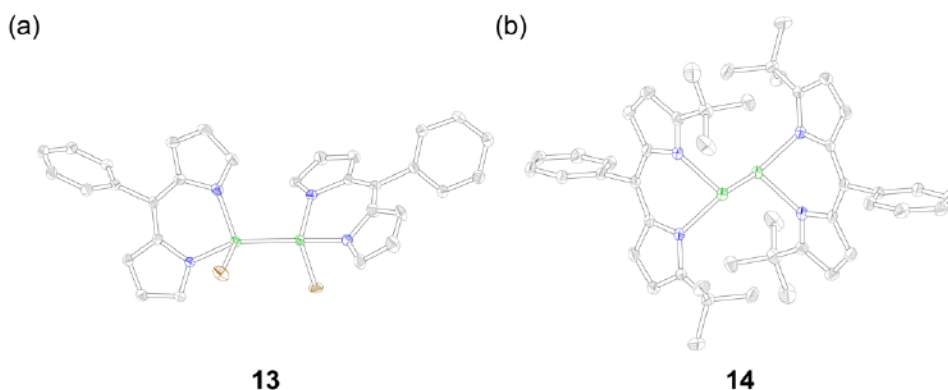


Figure 10. Crystal structures of dimeric low-valent GADIPY complexes (a) Ga(II) **13** (CCDC 2343807) and (b) Ga(I) **14** (CCDC 2343808). Thermal ellipsoids are drawn at the 50% probability level. For clarity, H atoms and solvent molecules have been removed, as well as the α -^tBu groups of **13** and the substituents at the 2, 4, and 6 positions of the *meso*-aryl groups of both structures.

Inspired by a low-valent Ga(I) β -diketiminato complex with bulky aryl groups [57], Harder and co-workers synthesized low-valent Ga(I) dipyrroin complexes with α -^tBu substituents [58]. First, the sodium salt of the ligand was prepared by adding NaN(SiMe₃)₂ to **8c**, followed by transmetallation with GaI₃ to afford Ga-**8c**-I₂. Reduction with potassium metal formed the Ga(II) digallane **13** (Figure 10a). A two-electron reduction of Ga-**8c**-I₂ was achieved after one week, yielding the low-valent Ga(I) digallene **14** (Figure 10b). Complex **14** could be selectively prepared using mechanochemical ball milling, which reduced the reaction time to 30 minutes. It should be noted that analogous reductions of Al-**8c**-I₂ resulted in unselective reactions. For Ga-**8c**-I₂, the average Ga–N and Ga–I bond distances were 1.955 Å and 2.537 Å, respectively, with a Ga–N bond angle of 101.7°. The Ga(II) digallane **13** exhibited slightly longer Ga–N (2.005 Å) and Ga–I (2.613 Å) bonds relative to the Ga(III) precursor, as expected from a decrease in oxidation state. The Ga–Ga bond distance of 2.589 Å is unusually long relative to other digallane complexes. This may be attributed to the orientation of the bulky aryl substituents, which form a tighter pocket around the dipyrroin metal center relative to the β -diketiminato derivatives. Indeed, the interplanar angles between aryl substituents are 45° and 125°, respectively [58]. The Ga–Ga bond in the Ga(I) digallene **14** is slightly lengthened (2.637 Å) upon reduction, and the N–Ga–N angle of 87.9° is significantly more acute than that of **13** (98.9°). The bonding in **13** and **14** was analyzed by DFT and Natural Bond Orbital (NBO) calculations. The natural charges on the Ga centers of **13** were calculated to be +0.92 and +0.93, and a Wiberg Bond Index (WBI) of 0.83 was calculated between the metals, consistent with a formally Ga(II) complex. In the case of **14**, the NBO analysis did not identify a direct Ga–Ga interaction, although a WBI of 0.99 was calculated between the metal centers. The NBO analysis indicated that the Ga–Ga interaction is formed by the donation of a lone pair on one Ga (which resides in an orbital with 90% s-character) into an empty orbital with 98% p-character on the other Ga center in a dative interaction. Treatment of **14** with trimethylsilyl azide (Me₃SiN₃) resulted in the selective formation of the tetrazagallole

Ga(III) product **15a** (Chart 7). Typically, reactions involving low-valent (Ga) complexes with Me_3SiN_3 are not selective, resulting in both the tetrazagallole and a mixed ligand amide/azide complex (**15c**) [59]. The authors hypothesized that selective tetrazagallole formation is due to the small pocket around the metal center formed by the bulky α -substituents. DFT calculations were used to interrogate the mechanism of this reaction, which indicated that imido complexes are key intermediates along the reaction trajectory.

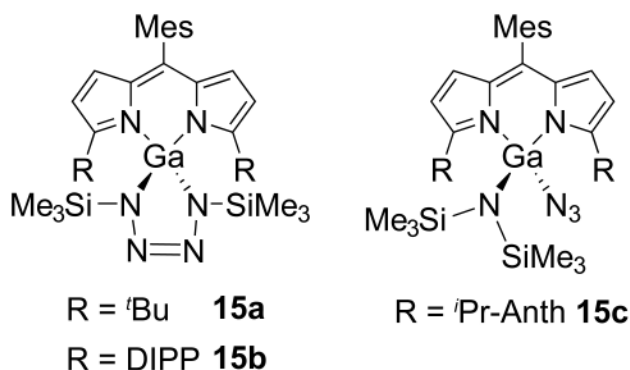


Chart 7. Ga(III) tetrazagallole dipyrin and mixed amide/azide products.

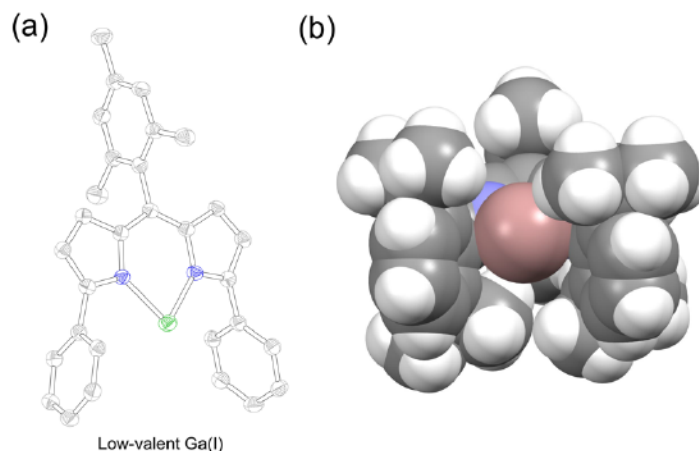


Figure 11. (a) Crystal structure (CCDC 2360739) and (b) corresponding space-filing model of a low-valent mononuclear GADIPY. Thermal ellipsoids are drawn at the 50% probability level. For clarity, H atoms and the substituents at the 2, 4, and 6 positions of the α -aryl groups have been removed.

The synthesis of low-valent gallium dipyrin complexes was then extended to derivatives with 2,6-diisopropylphenyl (DIPP) and 10-isopropyl-9-anthracenyl (*i*Pr-Anth)

substituents at the α -positions (Chart 4) [60]. Upon reduction of Ga-**8d**-I₂ or Ga-**8e**-I₂ with KC₈, mononuclear low-valent GADIPY complexes were isolated (Figure 11a), contrasting the dinuclear complexes **13** and **14** with α -^tBu substituents. The formation of the mononuclear reduced GADIPY complex was attributed to the dispersion forces imposed by the bulky DIPP and ⁱPr-Anth α -substituents. It should be noted that similar reactivity was not observed for the α -mesityl derivative (Ga-**8a**-I₂). The isolation of low-valent mononuclear GADIPYs correlates with the N–Ga–N bite angles of the Ga(III) precursors, and this structural parameter reflects the size of the α -substituents: 101.8° for ^tBu (Ga-**8c**-I₂), 96.4° for Mes (Ga-**8a**-I₂), 95.5° for ⁱPr-Anth (Ga-**8e**-I₂), and 94.7° for DIPP (Ga-**8d**-I₂). This effect is readily visualized with a space-filling model (Figure 11b), where the DIPP derivative exhibits a buried volume of 58% at 3.5 Å and 62.2% at 4.5 Å. Together, this data suggests that an increase in steric bulk shields the Ga center, preventing bimolecular reactions and preferentially forming the mononuclear derivative. Treatment of the reduced DIPP derivative with Me₃SiN₃ yielded **15b**, while the ⁱPr-Anth analog selectively formed the mixed amide/azide product **15c** (Chart 7). DFT calculations suggest that the tetrazagallole products (**15a** and **15b**) are kinetically favored. It is noteworthy that the reactivity of the reduced GADIPYs with Me₃SiN₃ is more selective than the related β -diketiminato complexes [61].

To date, there has been only one report of heteroleptic indium dipyrin complexes [51]. The In(III) center binds alkyl ancillary ligands (Chart 4), completing the group 13 series (Figure 7c). In-**8a**-Me₂ exhibits a distorted tetrahedral geometry ($\tau_4 = 0.87$). The In–N and In–C bond lengths are longer than the corresponding Ga derivative, while the N–In–N and C–In–C bond angles are smaller and larger, respectively. These structural metrics correlate with the larger ionic radius of In(III), exhibiting a regular trend for the group 13 derivatives (Table 2).

In 1976, both Tl(I) and Tl(III) dipyrin complexes were reported (Chart 8), where the *meso*-unsubstituted ligand has α and β alkyl substituents (R = CO₂Et) [32]. First, the free-base dipyrin was treated with thallium(I) ethoxide to afford the proposed Tl(I) complex **16a**. Then, dimethylthallium iodide was added to **16a** to generate the Tl(III) derivative **16b**. To date, these molecules represent the only reported examples of thallium dipyrins. However, the characterization of these first examples of heavy p-block dipyrins

is incomplete. Indeed, **16a** was only characterized by mass spectrometry and elemental analysis, while **16b** was also analyzed by IR and NMR spectroscopy, which exhibited $J(^{203,205}\text{Ti}-^1\text{H})$ coupling. Unfortunately, there have not been any subsequent studies to provide a more holistic understanding of the molecular or electronic structure of thallium dipyrins, perhaps due to concerns of toxicity.

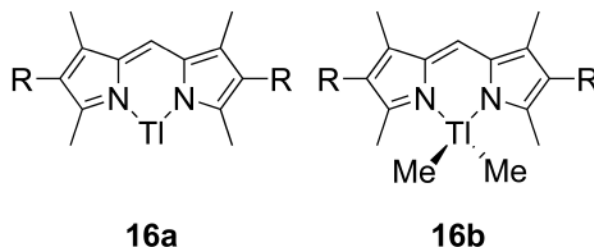
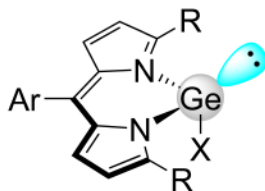


Chart 8. Tl(I) and Tl(III) dipyrins, where R = CO₂Et.

The photophysical properties of the group 13 dipyrin complexes is summarized in Table 3. Mason and co-workers noted that the aluminum hydride complex (Figure 8) exhibited green emission under UV irradiation, but no other photophysical characterization of this molecule was reported [50]. The series of complexes with dipyrin **8** exhibit similar absorption maxima, extinction coefficients, and emission maxima. However, there is a stark difference in the quantum yield of the methyl and ethyl derivatives, where the longer alkyl chain results in a significant decrease [51]. This is presumably due to the increased molecular dynamics of the ethyl group relative to the methyl substituent, which quenches the excited state through non-radiative decay. For complexes of **8**, the quantum yield does not decrease down the group, as would be expected for increasing spin–orbit coupling. Instead, the Ga(III) complexes have higher quantum yields than the Al(III) analogs. Similarly, the quantum yield of **10a** is an impressive 91%, outperforming the Al(III) complexes in Table 3 despite the increased spin–orbit coupling due to the larger Ga(III) center [54]. These results suggest that the optical properties cannot necessarily be predicted from periodic trends. The superior optical properties of **10a** are likely attributed to the lack of a *meso*-aryl substituent, mitigating molecular motions that deactivate the excited state. This example illustrates

that judicious molecular design can produce heavy p-block dipyrin complexes that are competitive with typical BODIPY fluorophores.



Ar = Mes (**17**) or Ph (**18**)

R = Mes (**a**) or Trip (**b**)

X = OEt, OMe, F, Cl, OⁱPr, OH, C₄H₅N, Ph, SPh, N(SiMe₃)₂, or [(OH)B(C₆F₅)₃]⁻

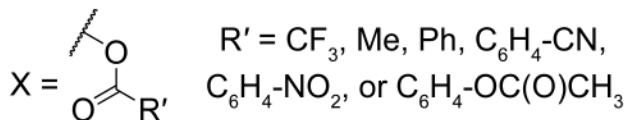


Chart 9. Heteroleptic germanium dipyrin complexes.

3.2 Group 14: Crystallogens

Germanium dipyrins were first synthesized by Nagendran and colleagues, utilizing ligands with α -mesityl substituents and halide X groups: **17a**-Cl and **17a**-F (Chart 9). Complex **17a**-F was prepared by adding excess CsF to **17a**-Cl, and both germylenes are water stable. The X-ray crystal structure of **17a**-Cl exhibits the following structural metrics: average Ge–N bond length of 1.980 Å, Ge–Cl bond length of 2.299 Å, N–Ge–N bond angle of 86.6°, and N–Ge–Cl bond angle of 92.3° [62]. Nagendran and co-workers later extended these germanium complexes to dipyrin ligand **18a** with a *meso*-phenyl substituent and various anionic ligands (X = Cl, OMe, OEt, OⁱPr, and OH, Chart 9) [63]. Only the photophysical properties of **18a**-OH and **18a**-Cl were reported, which exhibited absorption maxima of 511 nm (21,000 M⁻¹ cm⁻¹) and 521 nm (30,800 M⁻¹ cm⁻¹), respectively. For the family of **18a**-X complexes (X = Cl, OH, OMe), the average Ge–N bond length is 1.999 Å and N–Ge–N bond angle is 86.5°. While the Ge–X bond lengths vary with the X ligand (2.261 Å for Cl, 1.736 Å for OH, and 1.813 Å for OMe), the average N–Ge–X bond angles are quite similar across the series: 96.3° for Cl, 96.2° for OH, and

93.1° for OMe. Interestingly, complex **18a**-OH was both water and air stable. DFT analysis of **18a**-OH revealed that the electron density of the Ge center is primarily in the HOMO–1 orbital rather than the HOMO, which may account for the stability of the complex. Nagendran and coworkers synthesized a related library of germanium complexes derived from dipyrin **18a** with a variety of anionic ligands including chloride, pyrrolide, and numerous substituted carboxylates (Chart 9) [64]. For the carboxylate and pyrrolide derivatives, the average Ge–N bond length is 1.992 Å with an average N–Ge–N angle of 86.8°, consistent with other Ge(II) dipyrins. Oxidation of the Ge(II) center in **18a**-Cl (Figure 12b) was achieved using MeOTf to yield a cationic Ge(IV) complex **19c** (Figure 12d). Upon oxidation, the bond length decreased and the bond angle increased (Table 4) [63].

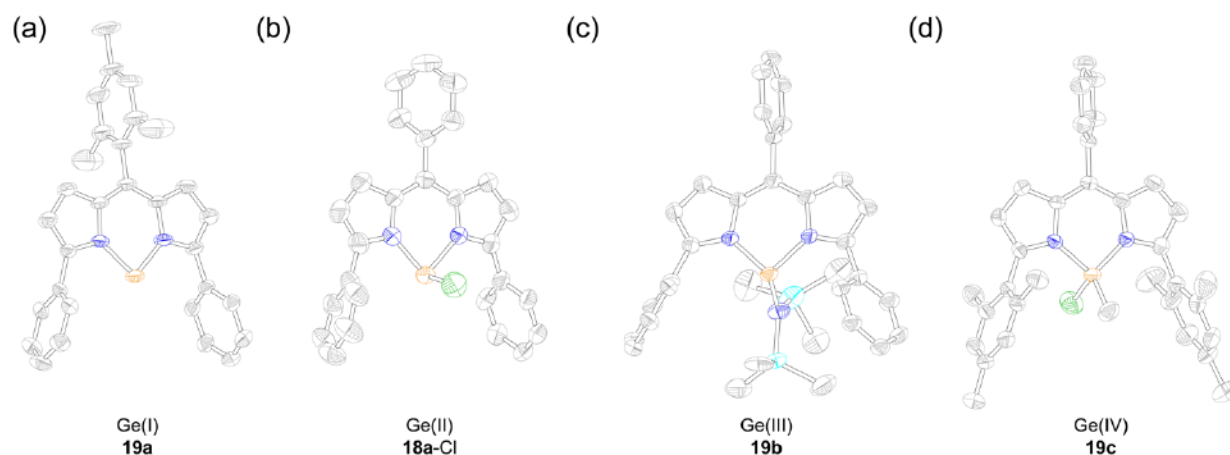


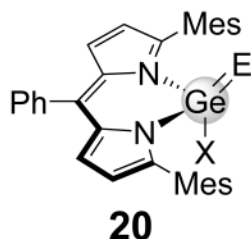
Figure 12. Germanium dipyrins in various formal oxidation states: (a) **19a** (CCDC 2144194), (b) **18a**-Cl (CCDC 1982260), (c) **19b** (CCDC 2144197), and (d) **19c** (CCDC 1982263). Thermal ellipsoids are drawn at the 50% probability level. For clarity, H atoms and counter anions have been removed. To better illustrate the coordination environment of the Ge center, the substituents at the 2, 4, and 6 positions of the α -aryl groups have been removed for **19a**, **18a**-Cl, and **19b**, as well as the substituents at the 2, 4, and 6 positions of the *meso*-aryl group of **19b**.

Nagendran and coworkers synthesized a cationic Ge(II) dipyrin by treating **18a**-OH with tris(pentafluorophenyl)borane to afford [**18a**][(OH)B(C₆F₅)₃] [65]. The Ge–N and Ge–O bond lengths are 1.971 Å and 2.019 Å, respectively, with a N–Ge–N bite angle of 86.7°. The Ge–O bond length is longer than that of **18a**-OH (1.736 Å) suggesting a weakly coordinated borane complex. This cationic complex exhibited greater stability (1 month in

air and 20 days in water) relative to the parent compound **18a**-OH (10 days in air and 5 days in water). DFT analysis of the frontier orbitals revealed that the HOMO–1 (with Ge lone pair character) was significantly stabilized for the cationic Ge(II) complex (62.5 kJ/mol) compared to **18a**-OH (20.7 kJ/mol). The empty Ge p-orbitals are delocalized due to interactions with $[(\text{OH})\text{B}(\text{C}_6\text{F}_5)_3]^-$, and the bulky anion shields the germanium center. Together, these features potentially explain the limited reactivity of the complex with small molecules such as water and oxygen.

Su and colleagues reported a series of Ge(II) complexes using a derivative of ligand **17b** with α -Trip substituents and several anionic ligands ($\text{X} = \text{Cl}$, $\text{N}(\text{TMS})_2$, and SPh, Chart 9) [66]. The Ge(II) complex **17b**-Cl was reduced using sodium metal to form a neutral Ge(I) radical (**19a**) that was localized on the ligand. The EPR spectrum at 120 K displayed a well-resolved, yet complicated pattern arising from ligand hyperfine coupling to two nitrogen atoms and two protons. DFT calculations on a simplified model of **19a** suggest that the spin density of the radical is evenly distributed over both the dipyrin core and germanium center. The lack of hyperfine coupling to the ^{73}Ge in the EPR spectrum was attributed to the low natural abundance of this isotope (7.8%). The crystal structure of the Ge(I) complex (Figure 12a) illustrates that the bond lengths decrease upon reduction, which is counter to the expectation that the bond lengths would increase for the reduced complex. This suggests that the reduction may be predominantly ligand-centered rather than Ge-centered. The low-valent germanium complex was treated with diphenyl disulfide (PhS-SPh) to synthesize the Ge(II) derivative **17b**-SPh. The photophysical properties of the **17b**-X series ($\text{X} = \text{SPh}$, $\text{N}(\text{TMS})_2$, and Cl) is limited to absorption spectroscopy, and the complexes exhibit an average maximum wavelength of 524 nm. The average Ge–N bond lengths and N–Ge–N bond angles for the Ge(II) complexes are 2.011 Å and 87.6°, respectively, consistent with other heteroleptic Ge(II) dipyrins (Chart 9). The CV of both **17b**- $\text{N}(\text{TMS})_2$ and **17b**-SPh exhibited a one-electron reduction at –1.9 V vs. Fc^+/Fc , illustrating the electrochemical generation of the Ge(I) complex. Silver polyfluoroalkoxyaluminate was used to oxidize **17b**- $\text{N}(\text{TMS})_2$, providing the first example of a cationic, formally Ge(III) dipyrin complex (**19b**) (Figure 12c). The EPR spectrum exhibited a broad, featureless signal at $g = 2.0004$, suggestive of a metal-based oxidation; the lack of hyperfine coupling to ^{73}Ge is attributed to the low natural

abundance of this isotope. DFT calculations substantiated that the radical is primarily localized on the germanium center. The bond lengths and angles of **19b** are intermediate to those of the Ge(II) and Ge(IV) derivatives, corroborating the Ge(III) assignment. The steric hinderance of the bulky α -Trip substituents likely enables the stabilization of both the Ge(I) and Ge(III) radical species.



X = Ph	E = S 20a	E = Se 20b
X = OH	E = S 20c	E = Se 20d
X = OEt	E = S 20e	E = Se 20f
X = N(TMS) ₂	E = S 20g	E = Se 20h

Chart 10. Ge(IV) germacarbonyl dipyrin complexes.

Ge(IV) germacarbonyl (Ge=S and Ge=Se) dipyrins (**20**) have been reported by Nagendran and co-workers (Chart 10) [67]. To synthesize these compounds, Ge(II) precursors **18a**-OH, **18a**-OEt, or **18a**-N(TMS)₂ (Chart 9) were treated with elemental sulfur or selenium to form the corresponding germacarbonyls. A novel Ge(II) complex **18a**-Ph was prepared by treating **18a**-Cl with PhLi, and the germacarbonyl derivatives were synthesized from elemental S or Se. These complexes are air and water stable, presumably due to the bulky α -mesityl groups that protect the Ge(IV) center. The germacarbonyl complexes **20a**, **20b**, **20e**, **20g**, and **20h** exhibit an average Ge–N bond length of 1.941 Å, which is slightly shorter than the Ge(II) **18a**-X derivatives (1.999 Å) due to the increase in metal oxidation state. It should be noted that the bonds are not as short as those observed for cationic **19c** (1.855 Å), suggesting that charge may contribute to the difference in bond lengths. The average germanium–chalcogen bond lengths are 2.057 Å for the Ge=S bonds (**20a**, **20e**, **20g**) and 2.195 Å for the Ge=Se bonds (**20b**, **20h**). The N–Ge–X bond angles vary with the identity of the anionic ligand: 102.8° for Ph,

101.7° for OEt, and 106.5° for N(TMS)₂. The average N–Ge=E bond angles appear to correlate with the bulkiness of the anionic ligand X rather than the size of the chalcogen: 116.2° for X = Ph, OEt (**20a**, **20b**, **20e**) vs. 111.8° for X = N(TMS)₂ (**20g**, **20h**). These germacarbonyl complexes were then used as ligands for CuX salts (X = Cl, Br, I), where the terminal sulfide or selenide coordinates to the Cu(I) center, forming dimeric Cu₂X₂ diamond core structures for X = Br, I (Figure 13) or monomeric CuCl adducts. Dimer **21** exhibits a 2.349 Å Se–Cu bond, while the sulfur analog has a S–Cu bond length of 2.241 Å.

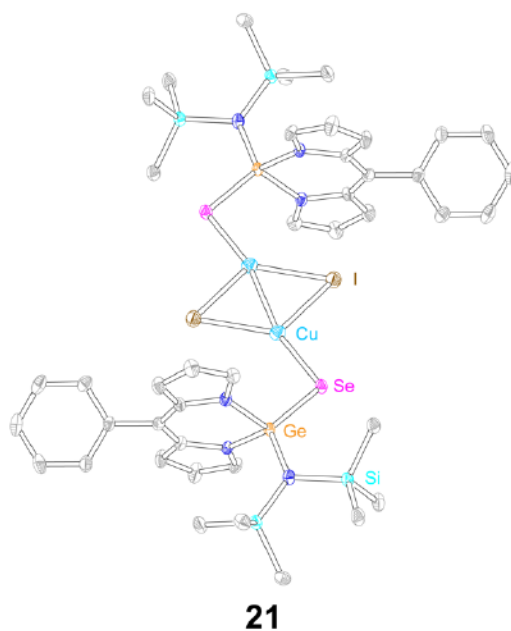
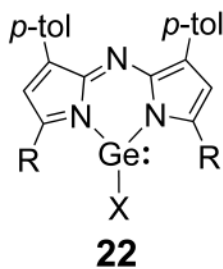


Figure 13. Crystal structure (CCDC 2117003) of the selenido germacarbonyl **20h** coordinated to CuI, forming a dimeric Cu₂I₂ diamond core (**21**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and α -mesityl substituents have been removed for clarity.



R = *p*-tol X = Cl **22a**

R = naph X = Cl **22b**

R = naph X = N(TMS)₂ **22c**

Chart 11. Germanium aza-dipyrrins.

Recently, Ge(II) aza-dipyrins, where the *meso* carbon is replaced by a nitrogen atom, were reported with *p*-tolyl or naphthyl groups at the α or β positions and Cl or N(TMS)₂ anionic ligands (Chart 11) (**22**) [68]. The average Ge–N bond length in **22a** and **22c** is 2.044 Å, which is slightly longer than that of Ge(II) *meso*-aryl dipyrins (1.999 Å for **18a-X** derivatives). The CVs of the aza-dipyrins exhibited sequential irreversible and quasireversible ligand-based oxidations: +0.453 and 0.735 V for **22a**, +0.612 and +0.804 V for **22b**, +0.404 and +0.740 V for **22c** (relative to Fc⁺/Fc). DFT calculations demonstrated that the electron density of the HOMO and LUMO are centered on the ligand, and the absorption features are due to $\pi \rightarrow \pi^*$ transitions. The average HOMO–LUMO gap of these Ge(II) aza-dipyrins was calculated to be 1.72 eV, whereas the gap for the dipyrin analogs was 2.96 eV. This result accounts for the significant red-shift in the absorption profiles of aza-dipyrin complexes.

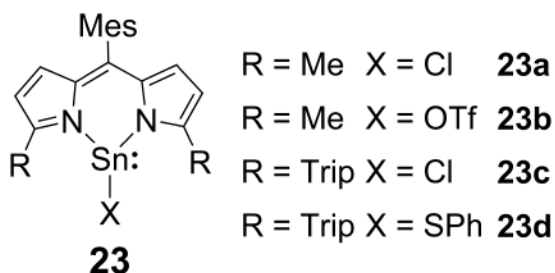


Chart 12. Sn(II) dipyrin complexes.

In 2009, Kawashima and colleagues published the first report of a heteroleptic tin dipyrin [19]. Compound **23a** was synthesized by lithiation of the dipyrin followed by the addition of SnCl₂ (Chart 12). The chloride ligand could be substituted with triflate upon treatment of AgOTf to afford **23b** *via* salt metathesis. Computational analysis of a simplified version of **23a** confirmed that the main absorption features are $\pi \rightarrow \pi^*$ transitions, and the electron density is centered on the dipyrromethene ligand. The average Sn–N bond lengths are 2.189 Å (**23a**) and 2.158 Å (**23b**), and the N–Sn–N bond angles are 82.8° (**23a**) and 84.9° (**23b**). These bond lengths are longer than the Ge(II) congeners (1.999 Å for **18a-X** derivatives), consistent with the increase in ionic radius down the group. Recently, Su and co-workers synthesized a similar Sn(II) **23c** with bulky

α -Trip substituents [49]. Reduction of the complex with sodium metal resulted in a dipyrin-centered radical, which reacts with PhS–SPh to afford **23d**. This reactivity is analogous to the Ge(II) complexes (*vide supra*). DFT calculations revealed that the electron density of the reduced complex is centered on the dipyrin core rather than on the tin center. The CV of **23c** exhibits a reversible ligand-based reduction at -1.9 V vs. Fc^+/Fc , consistent with the computational results.

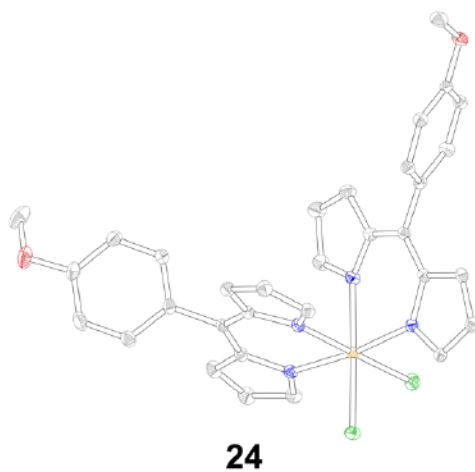


Figure 14. Crystal structure (CCDC 917693) of the heteroleptic Sn(IV) bis-dipyrin complex **24**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been removed for clarity.

Only one report of heteroleptic Sn(IV) bis-dipyrins (**24**) has been published (Figure 14) [69]. These complexes were synthesized from the free-base ligand and Sn_2Cl_2 in pyridine. The dipyrin ligands featured *meso*-aryl groups with a variety of *para*-substituents: $-\text{H}$, $-\text{CH}_3$, and $-\text{Br}$. The average Sn–N bond length of 2.148 Å was slightly shorter than that of Sn(II) dipyrins (2.174 Å: average of **23a** and **23b**), while the average N–Sn–N bond angle of 85.8° was larger than the Sn(II) derivatives (83.9° : average of **23a** and **23b**). The average absorption maximum of the Sn(IV) complexes was observed at 462 nm ($78,570$ $\text{M}^{-1} \text{cm}^{-1}$), which is blue-shifted (2190 cm^{-1}) relative to the Sn(II) derivatives. The CVs exhibited an irreversible reduction at -1.145 V vs. SCE (-1.545 V vs. Fc^+/Fc), which could be consistent with a metal-based reduction. Indeed, the reduction of Sn(IV) to Sn(II) would necessitate ligand loss, resulting in an electrochemically irreversible reduction.

The photophysical properties of group 14 heteroleptic dipyrin complexes are outlined in Table 5. Carboxylated germanium dipyrins (**17** and **18** with X = CO₂R', Chart 9) are emissive both in solution and the solid-state, exhibiting an average red-shift of 1,417 cm⁻¹ relative to solution emission. In general, the fluorescence quantum yields for the germanium and tin complexes are quite low ($\phi < 4\%$). The exception is **23b** ($\phi = 42\%$), which has a triflate anion rather than chloride. Perhaps the greater electron withdrawing effect of the triflate anion rigidifies the tin dipyrin, mitigating non-radiative deactivation of the excited state. Tin dipyrins have longer fluorescence lifetimes (4.95 ns for **23c** and 3.22 ns for **23d**) than germanium dipyrins (1.23 ns for **17a-Cl** and 1.94 ns for **17a-F**). These results are somewhat counterintuitive, as the heavier Sn center would be expected to have a shorter lifetime due to enhanced spin-orbit coupling that increases the rate of intersystem crossing. Germanium aza-dipyrins (**22**) exhibit an average absorption maximum at 642 nm, which is significantly red-shifted relative to *meso*-aryl dipyrins. It should be noted that emission data for complexes **22** were not reported. Indeed, the presence of a lone pair on the metal center might be responsible for fluorescence quenching via photo-induced electron transfer (PET).

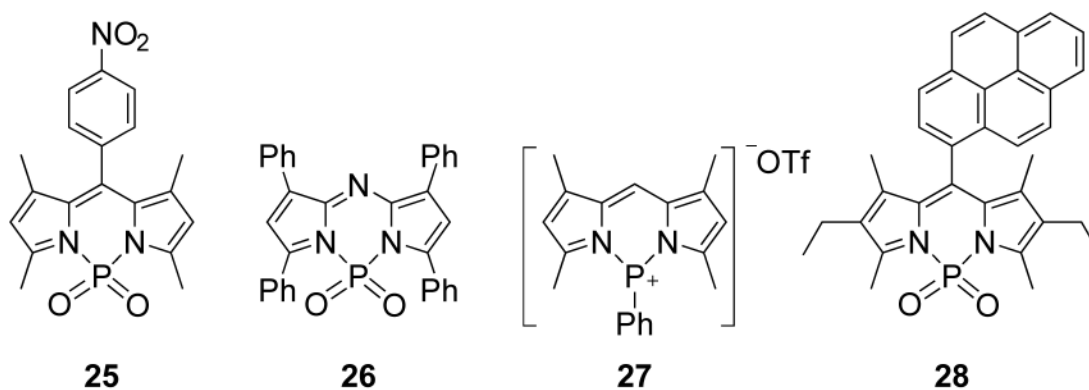


Chart 13. Phosphorus dipyrin complexes.

3.3 Group 15: Pnictogens

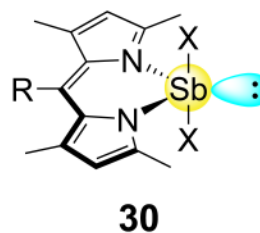
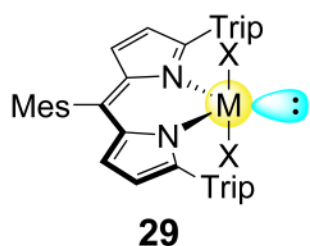
In 2015, the first examples of phosphorus analogs of BODIPY (*i.e.*, PODIPY) were reported. These P(V) di-oxo complexes utilized either a dipyrin (**25**) or aza-dipyrin (**26**) ligand (Chart 13) [70]. The PODIPY complexes were synthesized by treating the free-base dipyrin with phosphorus oxychloride in the presence of NEt₃. DFT calculations of

26 revealed a HOMO–LUMO gap of 2.7 eV, which is larger than the 2.21 eV gap for the aza-BODIPY analog. These results are consistent with experimental observations, where the 625 nm absorption maximum of **26** is blue-shifted relative to the BODIPY (640 nm). Later, a cationic P(III) PODIPY (**27**) was synthesized by treating the lithiated dipyrin with PCl_2Ph and TMS-OTf [54]. However, complex **27** could not be completely purified and was isolated with 19% of a decomposition product, as demonstrated by spectroscopic analysis. The authors attributed impurity to the lability of the PODIPY. Despite the cationic nature of **27**, DFT calculations indicated that the electron density of the HOMO and LUMO was centralized on the dipyrin core, resembling neutral GADIPY and BODIPY analogs.

In 2019, a novel PODIPY compound with a *meso*-pyrene group (**28**) was reported (Chart 13) [71]. The absorption and emission spectra of this complex were measured in ten solvents, and the largest Stokes shift (1944 cm^{-1}) was observed in cyclohexane. In certain solvents, the absorption spectra displayed a second peak. The authors attributed this to an acid–base interaction, where the two oxo groups could serve as a potential binding site for solvent molecules. Mono- and multi-layer films of PODIPY **28** were prepared on glass slides using the Langmuir–Schaeffer method. Since absorption spectra could not be recorded, excitation spectra were measured as a proxy for the absorption profile. Fluorescence quenching was observed with increasing numbers of molecular layers in the film, which is distinct from the analogous BODIPY derivative. The authors then extended this approach to the study of derivatives of **28** with various *meso*-substituents, examining the solvent-dependent optical properties and aggregation behavior of these PODIPY derivatives [72]. Aggregate formation was detected, even at low concentrations, as demonstrated by a bathochromic shift in the emission band. The authors attribute this behavior to the amphiphilic nature of the PODIPY complexes, which are comprised of a hydrophilic PO_2 moiety and hydrophobic α , β , and *meso*-substituents.

A computational study examined PODIPY complexes **25** and **26**, as well as numerous derivatives with a variety of α and β substituents on both the dipyrin and aza-dipyrin ligands [73]. It was found that that these PODIPYs exhibited larger complexation and solvation energies with water molecules relative to the BODIPY analogs, suggesting that the phosphorus complexes are more water stable than the corresponding boron complex. A survey of various ligand architectures indicated that aza-PODIPY derivatives

with fused aromatic rings would exhibit near-infrared (NIR) ($\lambda > 895$ nm) absorption and emission. Another computational study was conducted that surveyed the speciation and coordination environment of the phosphorus center on an unsubstituted dipyrryn ligand [74]. It was found that hydration of the P(V) center (*i.e.*, formation of 5- and 6-coordinate intermediates) resulted in a blue-shift of the absorption profile and an increase in the Stokes shift. The formation of weak hydrogen bonds enables the stabilization of different phosphorus species. This study provides molecular insight into the effect of phosphorous speciation on the optical properties, as well as the solvatochromic behavior of PODIPY fluorophores.



M = As X = Cl **29a**

M = Sb X = Cl **29b**

M = Sb X = S-Ph **29c**

M = Sb X = Se-Ph **29d**

M = Bi X = Cl **29e**

R = H X = F **30a**

R = H X = Cl **30b**

R = H X = Br **30c**

R = Ph X = Cl **30d**

R = Mes X = Cl **30e**

Chart 14. Pnictogen dipyrryn complexes.

Recently, the first and only example of an arsenic dipyrryn (ASDIPY) was reported [49]. For complex **29a** (Chart 14), the As–N and As–Cl bond lengths are 1.895 Å and 2.426 Å, respectively, and the N–As–N angle is 93.7°. The CV of **29a** exhibited a quasi-reversible reduction at –1.72 V vs. Fc⁺/Fc and an irreversible reduction at –2.32 V. TD-DFT calculations indicated that the main absorption transition was primarily HOMO to LUMO, exhibiting an energy gap of 2.76 eV, which is comparable to that calculated for aza-PODIPY **26** (2.7 eV). This similar value would suggest that the effect of switching the P center for As is comparable to the change in going from dipyrryn to aza-dipyrryn. However, this prediction does not match experimental observations (*vide infra*, Table 6),

highlighting the fact that computational methods are often unable to accurately predict spectroscopic properties.

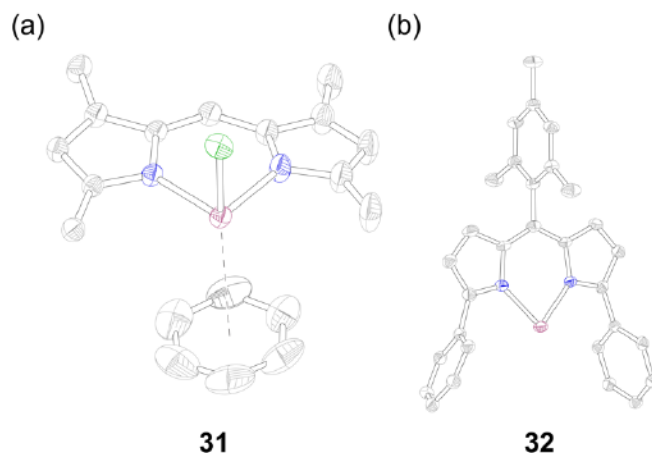


Figure 15. Crystal structures of (a) cationic Sb(III) complex **31** (CCDC 2241589) and (b) low-valent Sb(I) complex **32** (CCDC 2214167). Thermal ellipsoids are drawn at the 50% probability level. For clarity, H atoms, solvent molecules, and the BArF counter anion of **31** were removed, as well as the substituents at the 2, 4, and 6 positions of the α -aryl groups of **32**.

In 2023, the first examples of antimony dipyrrole complexes were reported [20,21]. These complexes were synthesized by treating the lithium salt of the dipyrrole ligand with SbCl_3 [20]. Several derivatives were prepared that varied both the *meso*-substituent and the anionic ligands (Chart 14). Complexes **30b**, **30d**, **30e**, and **29b** have average Sb–N bond lengths that range from 2.059 Å (**30e**) to 2.111 Å (**29b**), with an average N–Sb–N angle of 88.1°. The Sb–N bonds are longer and the N–Sb–N angles are smaller than ASDIPY **29a**, consistent with the increase in ionic radius: 72 pm for As(III) vs. 90 pm for Sb(III) [39]. To date, **30c** is the only example of a pnictogen dipyrrole with bromide ligands, exhibiting a Sb–Br bond that is 0.182 Å longer than the chloride derivative. Interestingly, **30a** crystallized as a dimeric species with two bridging fluorides, adopting distorted pseudo-octahedral geometry with average Sb–F bond lengths of 1.968 Å. It was found that the stability of the complex increased with larger halide ligands, as monitored by absorption spectroscopy. The cationic Sb(III) dipyrrole complex **31** (Figure 15a) was synthesized by performing halogen exchange on compound **30b** with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BArF), a weakly-coordinating anion. The Sb center in

the cationic complex coordinates to a benzene solvent molecule, with a Sb to C₆ centroid distance of 3.211 Å [20]. Su and co-workers synthesized Sb(III) dipyrin complexes with anionic –SPh or –SePh ligands (**29c**, **29d**). The chloride complex **29b** was reduced with sodium metal to prepare the formally Sb(I) dipyrin complex **32** (Figure 15b), which exhibits an average Sb–N bond length of 2.092 Å that is slightly shorter than the parent Sb(III) complex (2.111 Å). DFT calculations revealed that the HOMO and HOMO–1 of **32** exhibit 5s and 5p lone pair character on the metal center, consistent with the Sb(I) assignment. Treatment of the Sb(I) complex with diphenyl dichalcogenides (e.g., PhS–SPh) afforded **29c** and **29d**.

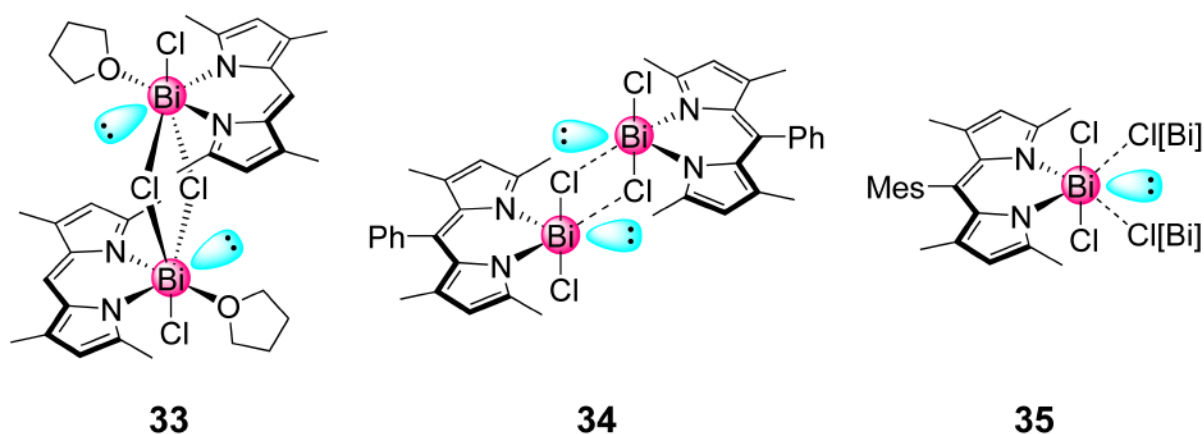


Chart 15. Illustration of diverse bismuth dipyrin structures that have been observed in the solid state.

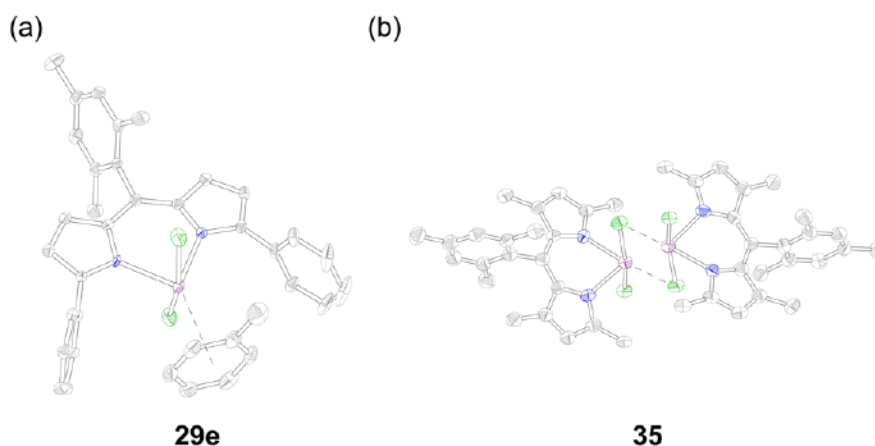


Figure 16. Crystal structures of Bi(III) dipyrin complexes (a) **29e** (CCDC 2214166) and (b) **35** (CCDC 2241587). Thermal ellipsoids are drawn at the 50% probability level. For clarity, H atoms and solvent molecules were removed, as well as the substituents at the 2, 4, and 6 positions of the α -aryl groups of **29e**.

The first bismuth dipyrrens were also reported in 2023 [20,21]. Unlike the antimony derivatives, the sodium dipyrren salt was required for Bi(III) metalation [20]. Like antimony dipyrrens, the bismuth derivatives exhibit an array of structures, including solvent adducts, as well as dimeric and tetrameric species in the solid-state (Chart 15, **33–35**). Bi(III) complexes have been synthesized with both *meso*-unsubstituted and *meso*-aryl (phenyl and mesityl) dipyrren ligands. Unlike the Sb(III) fluoride complex, **29e** (Figure 16a) was isolated as a monomeric species, presumably due to the bulky Trip substituents at the α positions. The distorted trigonal bipyramidal geometry exhibited average Bi–N bond lengths of 2.222 Å, which are 0.163 Å longer the Sb–N bonds in **30e**, while the N–Bi–N angle of **29e** (85.7°) is smaller than that of **30e** (87.4°). These structural metrics are consistent with the increase in ionic radius: 110 pm for Bi(III) vs. 90 pm for Sb(III) [39]. The distance from the centroid of the toluene molecule to the Bi(III) center is 3.196 Å, which is comparable to bismuth sandwich complexes, which exhibit Bi–arene distances of 3.263 Å [75]. The differences in the solid-state intermolecular interactions of bismuth dipyrrens (**33–35**, Chart 15) is reflected in the Bi–Cl bond lengths. For the bridging chlorides in **33** and **34**, the average Bi–Cl distance is 2.833 Å and 3.070 Å, respectively, whereas the Bi–Cl interactions are asymmetric in **35**: 2.683 Å and 3.133 Å (Figure 16b). Consequently, **35** does not exhibit a typical Bi₂Cl₂ diamond core, as has been observed in Bi(III) porphyrin dimers, where the Bi–Cl bonds are 3.042 Å and 3.064 Å [76]. In all cases, the Bi–Cl distances are longer than those observed in the monomeric complex **29e** (2.627 Å), suggesting that these dimeric and polymeric structures reflect weak crystal packing effects rather than true bonding interactions. It was found that these bismuth dipyrrens were less stable than the antimony congeners, which may be due to the longer Bi–N bonds. Theoretical calculations for both the antimony and bismuth complexes indicated that the absorption transitions are primary $\pi \rightarrow \pi^*$, as the electron density of both the HOMO and LUMO are centered on the dipyrren core. While the calculations did not predict a change in the HOMO–LUMO gap, the experimental absorption data demonstrated a 676 cm^{–1} red-shift for **29e** relative to **29b**, which may be expected due to the larger Bi(III) center.

A computational study predicted the two-photon absorption (2PA) properties of **10a** (GADIPY), **30a–30e**, **33–35**, and other pnictogen dipyrren complexes with a variety of α ,

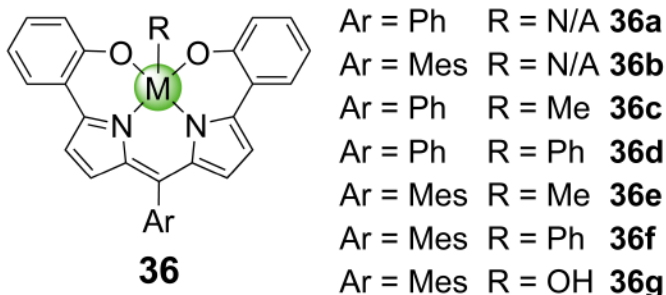
β , and *meso*-substituents [77]. These results demonstrated that there are small, negligible changes in 2PA with the identity of the central atom for the parent, unsubstituted dipyrin. The nature of the ligand was predicted to have a significantly greater effect on the 2PA, with larger cross-sections calculated for dipyrin derivatives with aryl substituents at the α and β positions of the ligand, independent of the level of theory used for the computations. In the case of the substituted dipyrins, the identity of the metal had a more significant effect on the 2PA properties. However, the trends across the series of complexes were irregular, indicating that the effects are not additive. This study suggests that the inherent 2PA of a given dipyrin ligand may not necessarily be retained when the central metal is substituted.

The photophysical properties of the pnictogen dipyrin complexes are summarized in Table 6. For the PODIPY series, there is a significant difference in quantum yield for **25** (17%) and **27** (80%). This disparity is likely due to the *meso*-aryl substituent of **25**, which can freely rotate and deactivate the excited state [4], whereas **27** is *meso*-unsubstituted. The high quantum yield of **27** is a noteworthy achievement for heavy p-block dipyrin complexes. However, **27** was not isolated as a pure substance, containing ~20% of an impurity. This complicates the interpretation of the photophysical properties, as the impurity may have a higher quantum yield than the PODIPY itself. Notwithstanding, the difference in oxidation state (5+ vs. 3+) and charge (neutral vs. cationic) may contribute to the differences in quantum yield. Indeed, phosphorus speciation (*i.e.*, P(OH)₂ vs. P=O) modulates the fluorescence quantum yields of P(V) corroles [78]. The low quantum yield of the P(V) aza-dipyrin **26** (8%) is likely due to the rotation of the α and β phenyl substituents. The red-shift in the absorption and emission profiles for aza-dipyrin **26** relative to phosphorus dipyrins is significant (661 nm vs. 524 nm). Complex **26** was inspired by an aza-BODIPY with a quantum yield of 0.77 [79], but this property did not translate to the aza-PODIPY analog. ASDIPY **29a** has a quantum yield of 5.6% (higher than Bi complexes and most Sb derivatives) and lifetime of 3.04 ns. The antimony and bismuth dipyrins exhibit a main absorption transition in the 451 to 514 nm range, comparable to the phosphorous complexes **25** and **26**, but have lower quantum yields ($\phi < 3\%$). The increase in size of the pnictogen down the group correlates with lower fluorescence quantum yields due to the increased spin-orbit coupling, populating excited

triplet states at the expense of the singlet state. The exception is **29b**, which has a quantum yield of 6.6%, which is higher than ASDIPY **29a** and comparable to aza-PODIPY **26**. The combination of the bulky *meso*-mesityl and α -Trip substituents on the dipyrin likely increases the radiative lifetime of the excited state. This result suggests that judicious molecular design can modulate and enhance the photophysical properties of heavy p-block dipyrin complexes.

4. Dipyrin Complexes with Intramolecular Chelating Substituents

Since the dipyrin ligand provides only two donor atoms, additional dipyrin ligands or other ancillary ligands are required to complete the primary coordination sphere of the metal. An alternative approach is to incorporate intramolecular ligands, such as phenol, aniline, or pyrrole, to furnish tri- or tetradentate ligands. These complexes are analogous to porphyrins, and the π -extended system of the ligand can serve as a non-innocent ligand, particularly for first-row transition metals such as Co [80] and Cu [81]. Consequently, these N₂O₂ chelating dipyrin complexes have led to analogies with transition metal corroles [82], which are prototypical examples of ligand non-innocence [83,84]. Like simple bidentate dipyrins, these ligands possess promising optical properties, but have remained underexplored. However, in the past five years, there has been an increase in the number of reports of tetradentate dipyrins with main-group elements. While there have been several general reviews on dipyrins [17,85,86] most have primarily focused on boron due to the popularity and extensive studies on BODIPYs. Though some reviews include non-boron examples with intramolecular dipyrin chelates, none have been specifically dedicated to p-block elements.



M = Al, Ga, In, Si, Ge, or Sn

Chart 16. Bis-phenolate dipyrin complexes with an N₂O₂ primary coordination sphere.

4.1 Tetradentate Dipyrromethene Complexes

Four-coordinate dipyrins with *ortho*-phenol substituents at the α positions have been termed “bisphenol” or “bisphenolate” dipyrins. These tri-anionic ligands bind to metals through two nitrogen and two oxygen atoms, giving an N_2O_2 primary coordination sphere. The first example of this ligand and the corresponding boron complex were reported in 1999 by Burgess and co-workers [87,88]. These complexes (Chart 16) are generally synthesized in a $CHCl_3/MeOH$ mixture with added NEt_3 to deprotonate the ligand, followed by the addition of a metal source. Boron chelates (**BODIPY**, Figure 17a) are commonly synthesized using either trimethyl borate or tri-isopropyl borate as the boron source [89,90]. The resultant complex exhibits tetrahedral geometry at the boron, where the two phenol rings are not coplanar with the dipyrin plane. **BODIPY** has a B–N distance of 1.516 Å and a N–B–N bond angle of 105.4° [90]. While transition metal complexes of this ligand architecture have been extensively studied, particularly for Au, Pt, and Co [82,91,92], examples with heavy p-block elements are rare.

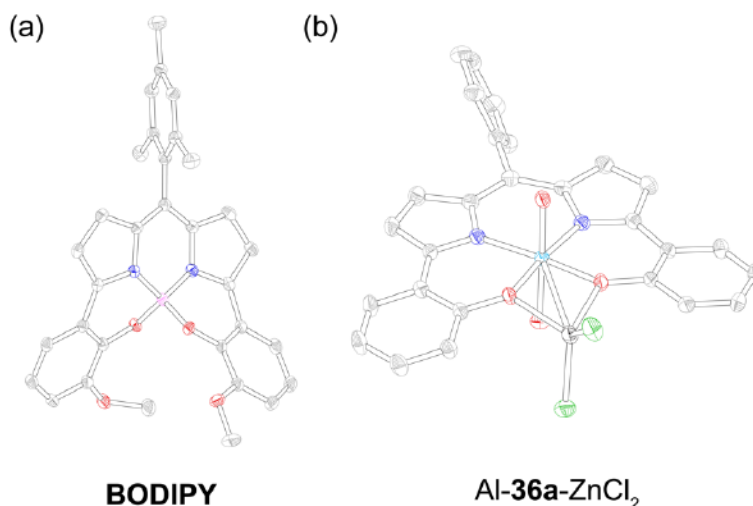


Figure 17. Crystal structures of N_2O_2 dipyrin complexes (a) **BODIPY** (CCDC 1446111) and (b) **Al-36a-ZnCl₂** (CCDC 708972). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecules have been removed for clarity.

The first report of Al(III) N_2O_2 dipyrin complexes was published in 2009 by Nabeshima and co-workers [89]. Both **Al-36a** and **Al-36b** were synthesized in high yields (98%) using $Al(O^iPr)_3$ as the metal source. The aluminum chelates exhibited octahedral

geometry, with a nearly planar N₂O₂ core and axial water ligands. The phenol oxygen atoms of these complexes can serve as donor atoms, enabling the preparation of heterobimetallic systems. Treatment of Al-**36a** or Al-**36b** with ZnCl₂ or ZnBr₂ resulted in the formation of a 1:1 complex. Conversely, treatment with Zn(OAc)₂ resulted in the formation of a dimeric species where the Zn(OAc)₂ unit bridged two dipyrin complexes, and the acetate ligands coordinated to both the Zn(II) and Al(III) centers. The ZnCl₂ adduct (Al-**36a**-ZnCl₂, Figure 17b) exhibited an Al–N distance of 1.936 Å and N–Al–N angle of 93.63°. Despite the tetradentate nature of the N₂O₂ ligand, these structural metrics are similar to Al-**8a**-Me₂. The inclusion of methoxy groups *ortho* to the phenol oxygen atoms (**37d**, Chart 17) expanded the scope of metal recognition. Both B-**37d** and Al-**37d** served as ionophores for alkaline earth cations (Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺) [90].

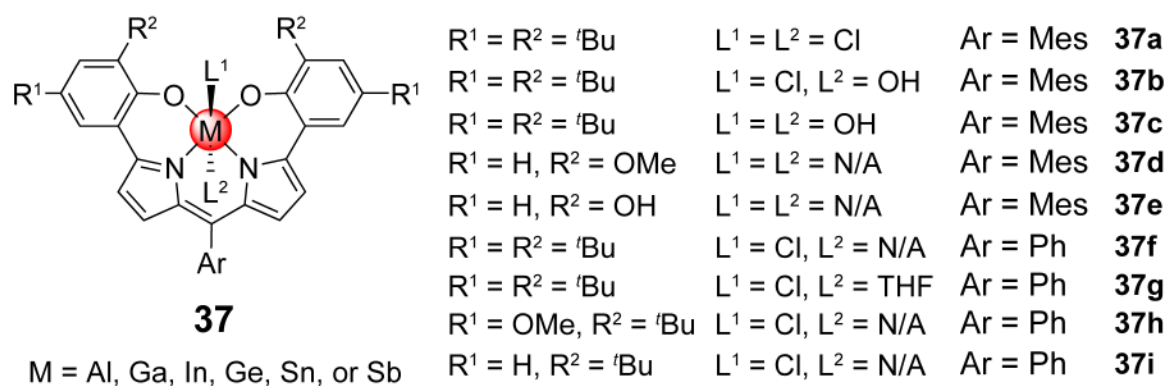


Chart 17. Bis-phenolate dipyrin complexes with various functional groups on the α -phenol substituents.

It was not until 10 years later that this chemistry was extended to the heavier group 13 elements of gallium and indium [93]. A standard N₂O₂ ligand with an unsubstituted phenol ring (**36b**) was employed, as well as a derivative with a methoxy group *ortho* to the hydroxy group (**37d**, Chart 17) that was then deprotected to the corresponding alcohol (**37e**) [90]. The functionalized phenol could enable cation sensing and/or enhance the emission properties upon metal binding, akin to the Al(III) derivatives. The In(III) and Ga(III) complexes were synthesized using acetylacetonate (acac) metal salts and isolated in moderate to high yields (50–95%). The complexes exhibited octahedral geometry with axial solvent ligands, displaying a slight distortion in the phenol rings, which are tilted 2.5–

13.3° out of the dipyrin plane. Interestingly, the crystal structure of Ga-**36b** showed that the complex dimerizes through the phenol oxygens with the two dipyrin units retaining their octahedral geometry, albeit with a slight distortion. However, the dimer was not observed by mass spectrometry, suggesting that dimer formation may be an artifact of crystallization. Ga-**36b** has an average Ga–N bond distance of 1.975 Å and N–Ga–N angle of 91.0°. While the bond distance is comparable to GADIPY **10a**, the bite angle is more acute than that of **10a** (98.8°), which could be due to the tetradentate nature of the N₂O₂ ligand.

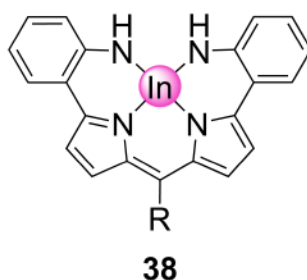


Chart 18. In(III) bis-aniline dipyrin complex with an N₄ primary coordination sphere.

In 2021, Kilina and co-workers published a computational study on chelating In(III) dipyrins with α -*o*-phenol or α -*o*-aniline (**38**, Chart 18) substituents, surveying the effect of peripheral functional groups on the optical properties of the complex [94]. The authors selected five *para*-substituted *meso*-aryl groups, as well and two additional substituents (2-(1,3-benzothiazole), 2-benzoxazole) that extended the π conjugation of the ligand. The optimized geometries of the N₄ chelates were more tetrahedral than the N₂O₂ motif, which generally exhibited a more planar geometry for the ligand. The N₂O₂ complexes had two axial acetonitrile molecules to complete the overall octahedral coordination sphere of the In(III) center. For the N₄ chelates, it was found that electron withdrawing *meso*-substituents and an extended π -system resulted in the greatest red-shift of the calculated spectra, with emission maxima in the 900–950 nm range. However, these substituents resulted in weak oscillator strengths, suggesting that the quantum yield may be low. A similar study examined the rigidity between the pyrrole units and phenol rings at the α -position of In(III) N₂O₂ complexes [95]. It was found that increasing the structural rigidity

enhanced the calculated quantum yields by decreasing vibrational modes that contribute to non-radiative deactivation of the excited state. Additionally, the presence of electron donating *meso*-substituents enhanced the quantum yield. Together, these computational studies serve to guide synthetic chemists in designing In(III) dipyrin complexes with enhanced optical properties, which could then be used for PDT or other biological applications (*vide infra*).

The spectroscopic data for group 13 N₂O₂ dipyrin complexes is summarized in Table 7. Complexes Al-**36a** and Al-**36b** exhibited emission maxima ~650 nm with quantum yields of 0.23 and 0.72, respectively. The higher quantum yield of Al-**36b** is due to the *meso*-mesityl substituent, which restricts ring rotation that would otherwise non-radiatively deactivate the excited state. Zinc binding to these Al(III) complexes resulted in a blue-shift of the emission maximum from 650 nm to 620 nm. Interestingly, the ZnBr₂ and ZnCl₂ adducts exhibited an increase in quantum yield: 0.56 for Al-**36a**-ZnBr₂, 0.55 for Al-**36a**-ZnCl₂, and 0.83 for Al-**36b**-ZnCl₂. This enhancement may be due to rigidification of the α -aryl substituents upon Zn(II) binding, mitigating molecular motions that quench the excited state. In general, the unsubstituted phenol groups (**36b**) exhibit higher quantum yields. Indeed, the addition of a non-chelating –OH substituent on the aryl ring (**37e**) leads to a significant decrease: $\phi = 0.53$ for Ga-**36b** vs. $\phi = 0.025$ for Ga-**37e**. For dipyrin **37e**, the quantum yield decreases down the group, as expected from increased spin–orbit coupling with heavier atoms. However, the trend is not followed for **36b**, where the In(III) complex displays a higher quantum yield than the Ga(III) analog. Similar deviations have been observed for homoleptic and heteroleptic group 13 dipyrin complexes (Table 1 and Table 3). Overall, these complexes exhibit red emission ($\lambda > 640$ nm) with high quantum yields, indicating that these heavy p-block dipyrins are competitive with BODIPY fluorophores.

In 2013, the first report of group 14 complexes of tetradentate N₂O₂ dipyrin ligands was published by Nabeshima and co-workers, extending this chemistry to Si(IV), Ge(IV), and Sn(IV) [96,97]. The free-base ligand **36d** was treated with diisopropylethylamine in THF to deprotonate the ligand, followed by the addition of MCl₃Ph as the metal source. The complexes were isolated in high yield: 67% for Si-**36d**, 73% for Ge-**20d**, and 80% for Sn-**36d**. In contrast to the Al(III) analogs, these M(IV) complexes require an additional

anionic ligand (e.g., methyl, phenyl) to give neutral, five-coordinate complexes with approximately trigonal bipyramidal geometry for Si-**36d** ($\tau_5 = 0.82$) and Ge-**20d** ($\tau_5 = 0.67$), where $\tau_5 = 0$ for square pyramidal and $\tau_5 = 1$ for trigonal bipyramidal. This significant difference in the τ_5 parameter indicates that Ge-**20d** deviates more from idealized trigonal bipyramidal geometry than Si-**36d**. Conversely, Sn-**36d** forms a dimeric structure in the solid state where one phenol serves as a bridging ligand between metal centers, resulting in octahedral geometry for both Sn(IV) centers. Nozaki and co-workers later synthesized tin and germanium N₂O₂ dipyrins as polymerization catalysts [98,99]. The complexes were prepared by deprotonating the ligand with sodium hydride followed by the addition of the metal tetrachloride (MCl₄), and the complexes were isolated in high yields (> 90%). The Ge(IV) complex (Ge-**37f**) is a five-coordinate complex with an axial chloride ligand, whereas the Sn(IV) complex (Sn-**37g**) is six-coordinate with axial Cl and THF ligands. A series of M(IV) chloride complexes were synthesized with substituents (^tBu or OMe) on the α -aryl ring *para* to the oxygen donor (**37h** and **37i**, Chart 17). Similar to the other chloride structures, the germanium complex exhibited distorted trigonal bipyramidal geometry ($\tau_5 = 0.81$), while the tin complex displayed octahedral geometry with a planar N₂O₂ ligand. It should be noted that the photophysical properties of these complexes were not reported.

The optical properties of these group 14 complexes are summarized in Table 8. Phenyl substituents at the *meso* position greatly decrease the quantum yield relative to the *meso*-mesityl derivative: 1.2% for Si-**36d** vs. 76% for Si-**36e**. For the **36d** complexes, the emission maxima are element-dependent: Si emission at 650 nm, Sn emission at 664 nm, and Ge emission at 675 nm. Despite the *meso*-phenyl substituents, the quantum yields of Ge-**36d** and Sn-**36d** are significantly higher than Si-**36d**. This series of complexes represents a rare example where the quantum yield increases down the group, countering the expectations based on the heavy atom effect and enhanced spin-orbit coupling. This observation may be attributed to structural differences, where the germanium and tin complexes have a larger N–M–O bite angle (126.5° for Ge-**36d** and 123.2° for Sn-**36d**) compared to Si-**36d** (120.8°), thereby restricting the rotation of the *meso*-phenyl group and increasing the quantum yield.

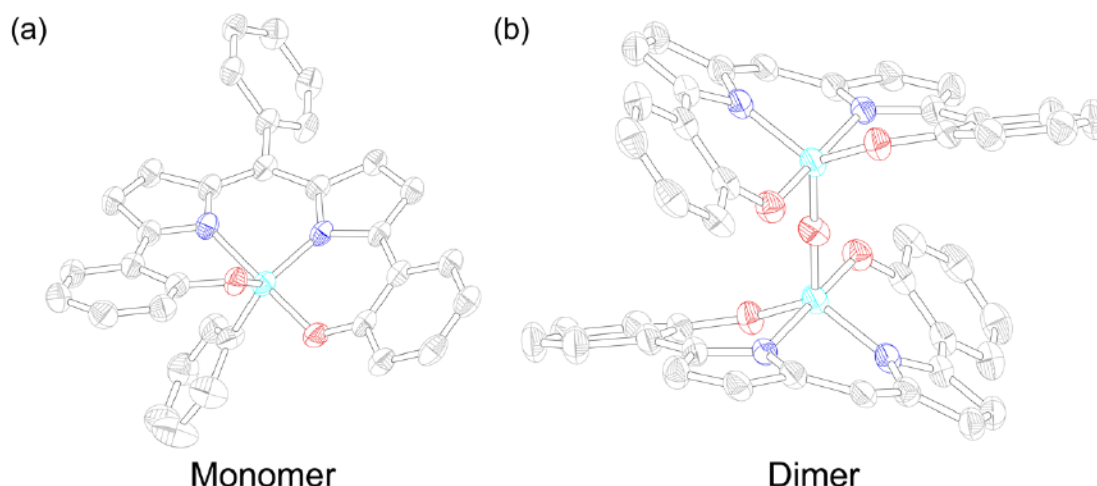
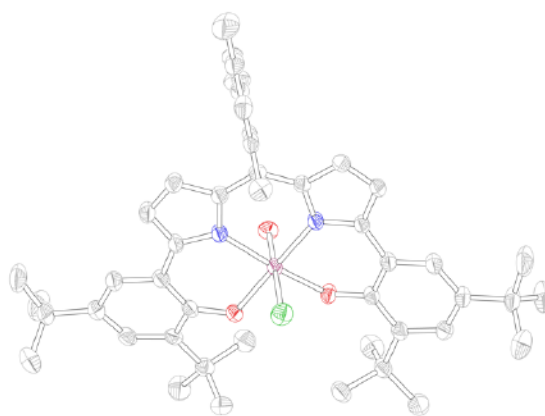


Figure 18. Crystal structures of (a) the monomeric Si(IV) N₂O₂ dipyrin complex **Si-36d** (CCDC 806888) and (b) the corresponding μ -oxo-dimer (CCDC 806889). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecules have been removed for clarity.

Both the silicon [96] and germanium [100] complexes can form μ -oxo dimers. The **Si-36d** monomer (Figure 18a) exhibits an average Si–N bond length of 1.856 Å and a N–Si–N bond angle of 88.2°, and the corresponding dimer (Figure 18b) adopts nearly identical structural metrics (Si–N = 1.852 Å and $\angle$ N–Si–N = 88.2° with Si–O = 1.700 Å). The quantum yield of the Si dimer ($\phi = 0.4$) is approximately half that of the monomer **Si-36d**. Interestingly, the dimer exhibited two absorption transitions at 573 nm and 601 nm, each with a distinct emission transition at 664 nm and 671 nm, respectively. The authors suggested that the two bands may arise from interactions between the Si dipyrin units. The absorption and emission profiles of the dimer are red-shifted relative to the monomer, which has also been observed for Si(IV) corroles [101,102]. In the case of the Ge dimer (of monomer **Ge-36b**), the two Ge(IV) centers adopt distorted trigonal-bipyramidal geometry with $\tau_5 = 0.89$ and 0.77. The average Ge–N and Ge–O bond lengths are 1.923 Å and 1.825 Å respectively, which are longer than those of the Si dimer. It was found that the Ge dimer hydrolyzed into **Ge-36g**, precluding measurement of the dimer's optical properties.

In 2024, the coordination chemistry of N₂O₂ tetradentate dipyrins was extended to antimony [103]. Nabeshima and co-workers synthesized dipyrin ligands with ^tBu groups *ortho* and *para* to the phenol oxygen (**37a**) (Chart 17). The corresponding

octahedral Sb(V) complexes were prepared by treating the free-base ligand with SbCl₃ in pyridine under an O₂ atmosphere with white LED irradiation. A mixture of three complexes was isolated with different anionic axial ligands: dichloride (Sb-**37a**), dihydroxide (Sb-**37c**), and mixed chloride/hydroxide (Sb-**37b**). The dichloride Sb-**37a** was converted to Sb-**37c** upon refluxing the complex in a mixture of H₂O and pyridine. All three complexes were characterized by X-ray crystallography. Sb-**37b** displayed average Sb–N, Sb–Cl, and Sb–O bond lengths of 2.076 Å, 2.370 Å, and 1.911 Å, respectively, and a N–Sb–N bond angle of 88.3° (Figure 19). While Sb-**37a** was non-emissive, Sb-**37c** exhibited emission with a maximum at 657 nm and quantum yield of 0.68. The mixed axial ligand complex Sb-**37b** displayed very weak emission ($\phi = 0.003$) at 658 nm. Perhaps the lack of emission in Sb-**37a** is due to the heavier chloride ligands (relative to hydroxide), thereby promoting intersystem crossing via enhanced spin–orbit coupling. This explanation seems to be substantiated by the very weak emission of Sb-**37b** with only one axial chloride ligand.



Sb-37b

Figure 19. Crystal structure of the Sb(V) dipyrin Sb-**37b** (CCDC 2323628). Thermal ellipsoids are drawn at the 50% probability level. For clarity, hydrogen atoms and solvent molecules have been removed.

Dimeric N₂O₂ dipyrins (**39**, Chart 19) analogous to **37e** have been synthesized. These ligands contain a core of six oxygen atoms that bridges the two dipyrin units, which can serve as a receptor for metal cations [90]. The dimeric aluminum complex **39a** was characterized by X-ray crystallography and was found to bind a Na⁺ cation in the core

(**39a**-Na⁺ Figure 20a). Presumably, the source of the sodium was the glassware used for recrystallization. The ligand core in **39a**-Na⁺ is twisted, exhibiting an interplanar angle of 54.4° between the two dipyrin units. Each aluminum center exhibits octahedral geometry with axial methanol ligands, and the sodium cation has an axial aqua ligand. The average Al–N bond distance is 1.949 Å with an average N–Al–N bond angle of 91.1°, and these structural metrics are comparable to Al-**36a**-ZnCl₂. The binding affinity of **39a** for alkaline earth cations (Ca²⁺, Sr²⁺, and Ba²⁺) was higher than that of the corresponding monomer (Al-**37d**), except in the case of Mg²⁺, where **39a** and Al-**37d** exhibited similar affinity [90]. This macrocyclic ligand (**39**) was then utilized to synthesize heterobimetallic complexes (Chart 19) [104]. The introduction of boron and a second group 13 element (Al, Ga, In) induced a significant twist between the two dipyrin units due to the tetrahedral geometry of the boron center. In the case of **39b** (Figure 20b), the interplanar angle between the two dipyrin units is 86.1°, which precludes cation binding in the O₆ pocket. The structural metrics of the boron site in **39b** (B–N = 1.519 Å and ∠ N–B–N = 105.5°) are consistent with those of **BODIPY**. The Ga site has an average Ga–N distance of 1.996 Å and N–Ga–N angle of 90.7°. A red-shift (380 cm⁻¹) in the absorption maximum was observed for the heterobimetallic boron and aluminum complex **39c** relative to the homobimetallic aluminum derivative **39a**. The heterobimetallic complexes **39b–39d** exhibit weak emission ($\phi < 0.01$) with a maximum ~650 nm. Based on DFT calculations, the low quantum yields may be due to PET.

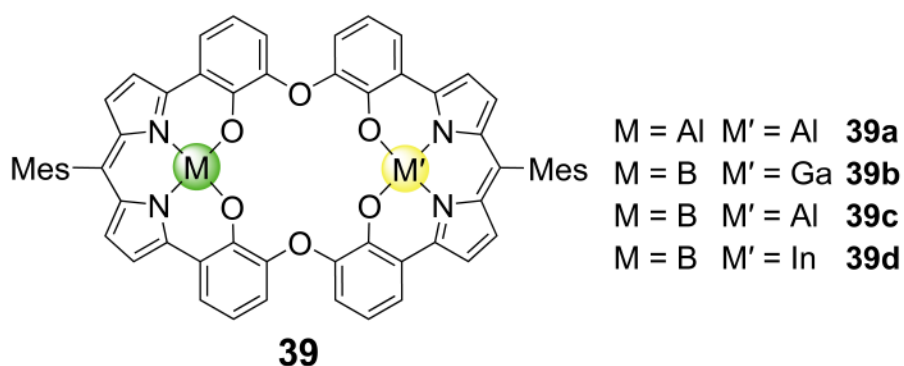


Chart 19. Homo- and hetero-dinuclear macrocyclic N₂O₂ dipyrin complexes.

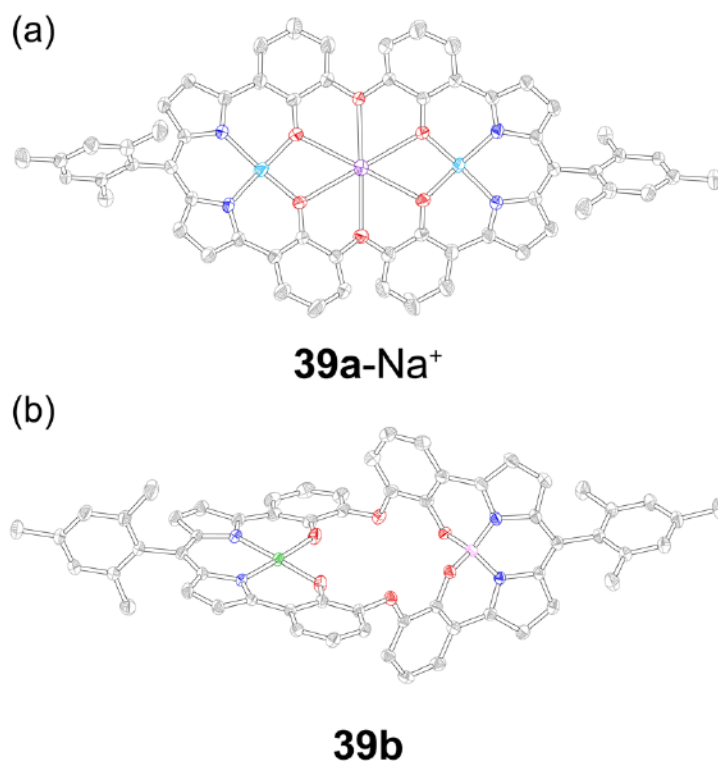


Figure 20. Crystal structures of the macrocyclic dipyrin complexes (a) **39a-Na⁺** (CCDC 1446112) (b) **39b** (CCDC 1848533). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, axial ligands, and solvent molecules have been removed for clarity.

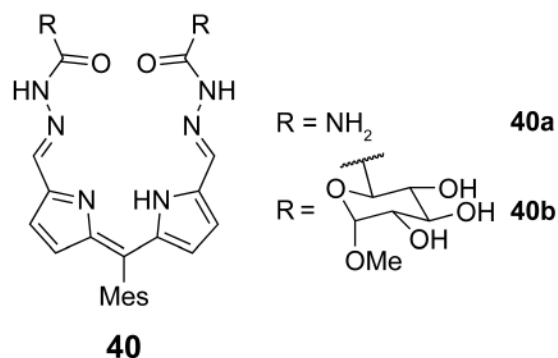


Chart 20. Acyclic polydentate dipyrin ligand **40**.

In addition to macrocyclic dipyrin ligands (**39**), acyclic polydentate dipyrin ligands (**40**, Chart 20) have been reported. This ligand platform was synthesized by Rissanen and co-workers with the goal of developing photometric metal sensors [105]. Dipyrin **40** has 6 possible donor atoms: two dipyrin nitrogen atoms, two α -substituent nitrogen atoms, and two carbonyl oxygen atoms. While the authors examined complexation of this

ligand with a wide range of transition metals, only two main-group metals were tested: In(III) and Sn(IV). While the UV–vis spectra indicated possible metal complexation, the products were not isolated or characterized by any other technique, similar to the purported Pb(II) *a,b,c*-bilatriene complexes [47].

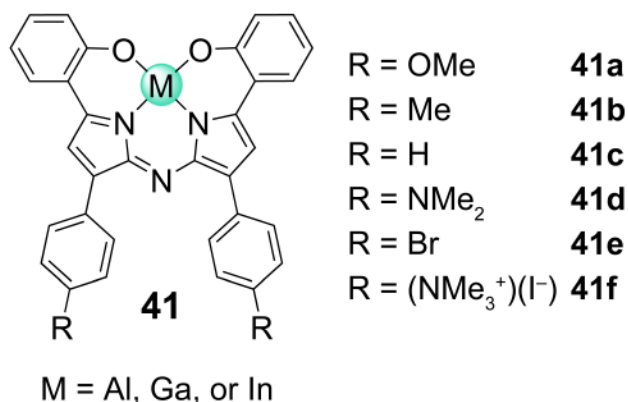


Chart 21. Tetradentate aza-dipyrin complexes with β -aryl substituents.

4.2 Tetradentate Aza-Dipyrromethene Complexes

Aza-dipyrins are dipyrromethene analogs with a *meso*-nitrogen atom, and derivatives with α -*ortho*-phenol substituents have been synthesized to furnish tetradentate ligands with an N₂O₂ primary coordination sphere. While this ligand design has been primarily explored with boron [106], this approach has only recently been extended to the heavier p-block elements Al, Ga, and In [107–109]. The first example of a non-boron N₂O₂ aza-dipyrin was published in 2022 by Chase and co-workers [107]. The ligand core was derivatized by installing *para*-substituted aryl groups at the β -positions adjacent to the *meso*-nitrogen (Chart 21). The complexes were synthesized by refluxing the ligand and a M(acac)₃ salt in pyridine, and the products were isolated in moderate yield (65–71%). Al-**41b** was crystallized from a mixture of pyridine and toluene, and the solid-state structure exhibited octahedral geometry with two axial pyridine ligands. The N₂O₂ core is slightly distorted from planarity, where the phenol substituents are tilted 3.3° relative to the dipyrin plane. Interestingly, when In-**41b** was crystallized from THF and *n*-decane, a dimeric complex containing an In₂O₂ core was isolated (Figure 21a). The two pyrrole nitrogen donors and one phenol oxygen of the aza-dipyrin ligand are nearly coplanar and

bind to one metal center, while the other phenol serves as a bridging ligand between metal centers. The pseudo-octahedral geometry of the In(III) centers is completed with axial THF ligands. DFT calculations were performed to determine the effect of the aryl substituents ($-\text{Me}$ vs. $-\text{OMe}$) on the optical properties of the complex. The energies of the HOMO and LUMO did not vary significantly across the series of compounds. The smallest HOMO–LUMO gap of 1.78 eV was calculated for B-**41a**, while the largest gap of 1.90 eV was for B-**41b**.

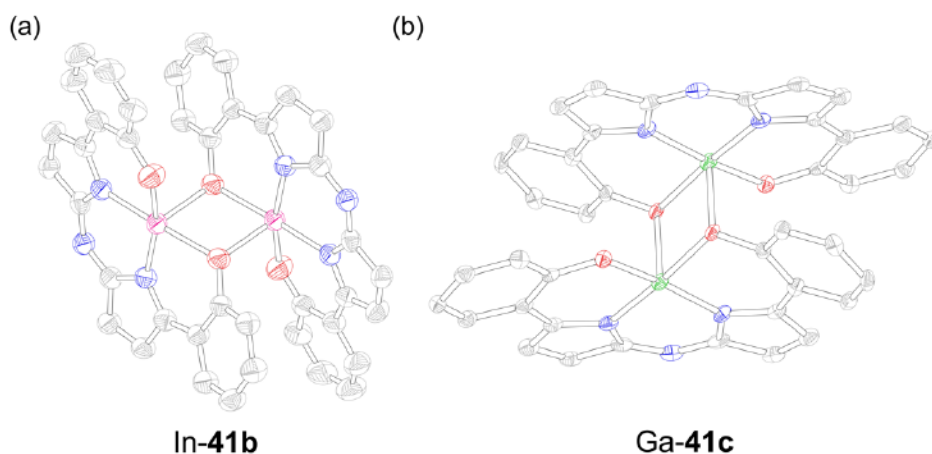


Figure 21. Crystal structures of aza-dipyrin complexes that dimerize in the solid-state: (a) In-**41b** (CCDC 2190931) and (b) Ga-**41c** (CCDC 2178000). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, solvent molecules, and β -aryl substituents have been removed for clarity.

Bodio and co-workers then synthesized a series of aza-dipyrins that further derivatized the *para*-position of the β -aryl ring [108]. The Al(III) complexes were prepared from AlMe_3 , which served as both a base and metal source, whereas the Ga(III) derivatives were prepared by treating the free-base ligand with NaH then GaCl_3 . The gallium complexes were isolated in moderate to high yields (55–85%). The solid-state structure of Ga-**41c** (Figure 21b) exhibited a dimeric structure akin to In-**41b**. The average Ga–N bond length is 1.959 Å and the N–Ga–N bond angle is 89.5° , which is comparable to Ga-**36b**. The CV of B-**41c** exhibits two reversible one-electron reductions, whereas the analogous processes are irreversible for Al-**41c** and Ga-**41c**. Additional ligands were synthesized, where the $-\text{NMe}_2$ derivative (Ga-**41d**) was treated with iodomethane to afford the cationic methylated derivative $-\text{NMe}_3^+$ (Ga-**41f**) [109].

The photophysical properties of the tetradentate group 13 aza-dipyrin complexes is summarized in Table 9. The emission profile of the methyl complexes (**41b**) is red-shifted relative to the methoxy derivatives (**41a**). The boron complex **41c** exhibits an emission maximum at 756 nm with a quantum yield of 0.28. Although the emission profiles of the Al and Ga analogs exhibit red-shifted ($\sim 568\text{ cm}^{-1}$) emission relative to the boron complex, the quantum yields are significantly lower ($\phi < 0.15$). As expected, the quantum yield decreases down the group with the increasing size of the central element, as demonstrated by the **M-41b** complexes: 13.7% for B, 7.5% for Al, 6.1% for Ga, and 0.3% for In. While the substituents on the β -aryl groups modulated the absorption and emission wavelengths, they had a nominal effect on the quantum yield. Conversion of the $-\text{NMe}_2$ group to $-\text{NMe}_3^+$ did not significantly impact the absorption wavelength, but a nominal red-shift (156 cm^{-1}) and increase in quantum yield was observed. The quantum yield of Ga-**41f** decreased in aqueous solvents (relative to organic solvents), although the decrease was less significant in mouse serum.

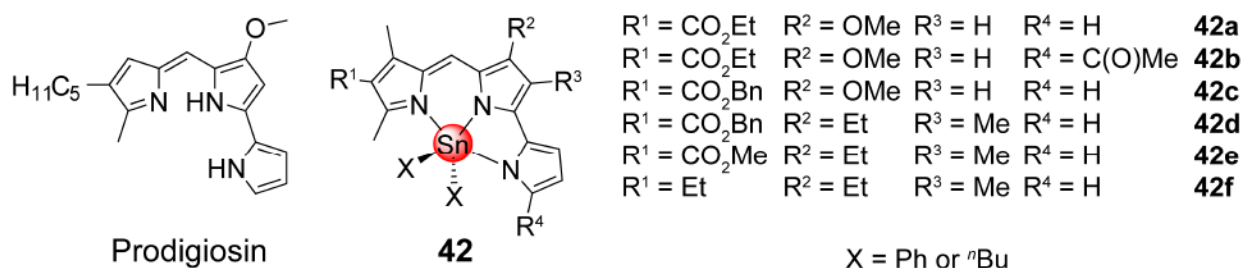


Chart 22. Prodigiosin and related Sn(IV) complexes of α -pyrrolyldipyrins.

4.3 Tridentate Dipyrromethene Complexes

While the tetradentate α -bisphenol-substituted N_2O_2 complexes described in the previous sections are the most widely studied dipyrins with intramolecular ligands, tridentate derivatives have also been explored. There are some examples with one α -phenol substituent, giving a N_2O primary coordination sphere that can be diversified with both axial and equatorial ancillary ligands. However, in terms of main-group chemistry, these tridentate ligands have only been explored for boron coordination [110,111]. While

a variety of donor ligands could be appended to the α -position of dipyrin ligands, tridentate ligands with an α -pyrrolyl substituent have been reported (Chart 22). Such ligands are inspired by the naturally occurring red pigment known as prodigiosin. This natural product exhibits diverse biological activity, which ranges from antibacterial to anticancer effects [112]. The most common method to synthesize these α -pyrrolyl ligands is to halogenate the α -position of a dipyrin and perform a Suzuki cross-coupling reaction with an *N*-Boc protected α -boronic acid pyrrole [113]. To date, boron and tin represent the only p-block complexes of these prodigiosin analogs [113–115].

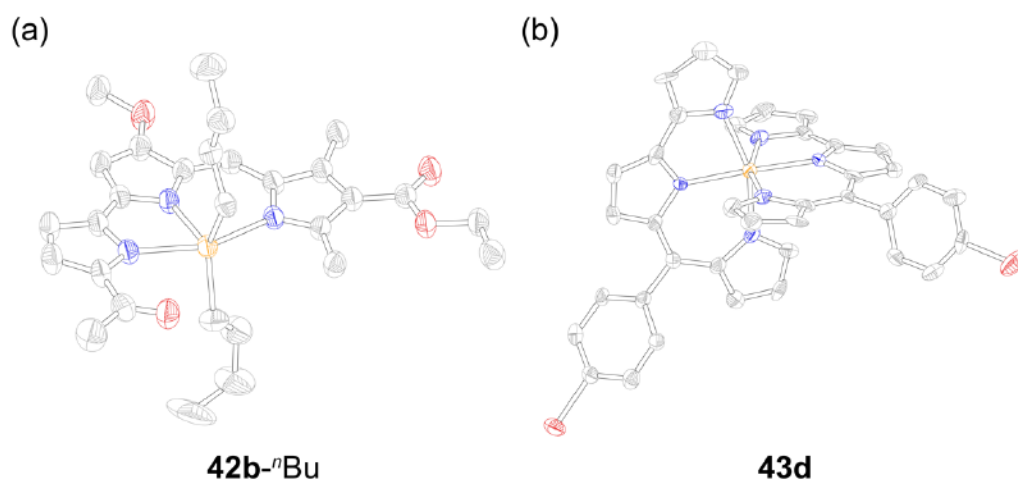


Figure 22. Crystal structures of (a) heteroleptic **42b-ⁿBu** (CCDC 851111) and (b) homoleptic **43d** (CCDC 1447991) Sn(IV) α -pyrrolyldipyrins. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been removed for clarity.

In 2011, Thompson and co-workers synthesized the first tin complexes of α -pyrrolyldipyrins by refluxing the free-base ligand with an alkyltin oxide (Ph or ⁿBu) in methanol [113]. For these pentacoordinate Sn(IV) complexes (Chart 22), the dipyrin occupies the equatorial plane and the two alkyl ligands occupy the axial positions. The metal center in **42b-ⁿBu** exhibits distorted square pyramidal geometry ($\tau_5 = 0.27$, Figure 22a). The average Sn–N (dipyrin) bond length of 2.218 Å and N–Sn–N angle of 81.2° closely match the Sn(IV) heteroleptic complex **24**, which has a Sn–N bond length of 2.148 Å and N–Sn–N bond angle of 85.8°. The spectroscopic data is summarized in Table 10. All complexes exhibit similar quantum yields ($\phi = 0.5$ –0.6) except for the derivatives of

42f, where the quantum yield is nearly half that of the other analogs. This may be due to the incorporation of two β -ethyl substituents, resulting in increased molecular motions that non-radiatively deactivate the excited state. For comparison, the boron analog of **42a** exhibits an emission maximum at 559 nm with a quantum yield of 0.92. The red-shift in the emission profiles and lower quantum yields relative to the boron complex can be attributed to the heavy atom effect. The identity of the ancillary alkyl ligand (n Bu vs. Ph) has little effect on the spectroscopic properties of the complex.

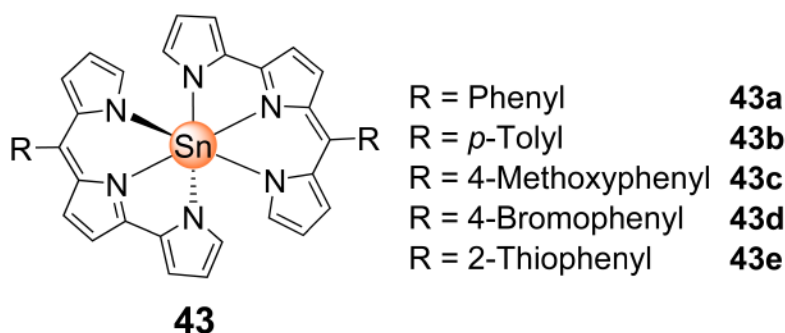


Chart 23. Homoleptic Sn(IV) α -pyrrolyldipyrin complexes.

In 2016, a series of homoleptic, six-coordinate Sn(IV) complexes of α -pyrrolyldipyrins with various *meso*-aryl substituents was reported (Chart 23) [115]. The complexes were prepared by treating the free-base α -pyrrolyldipyrin ligand with SnCl₂ in refluxing chlorobenzene with a catalytic amount of DIPEA. The complexes were isolated in moderate to high yields (50–95%). The X-ray structure of **43d** revealed octahedral geometry of the Sn(IV) center where the two dipyrin units are nearly perpendicular (Figure 22b). The average Sn–N (dipyrin) bond length is 2.130 Å, which is comparable to the heteroleptic Sn(IV) complex **24**. The nature of the *meso*-substituent had a nominal effect on the optical and electrochemical properties of the complex (Table 11). However, the thiophene derivative (**43e**) exhibited the largest bathochromic shift relative to the boron analog and the longest wavelength absorption of the Sn(IV) complexes. In contrast to the heteroleptic derivatives (Chart 22), the homoleptic α -pyrrolyldipyrin complexes were not emissive. The CVs of these complexes exhibited an irreversible oxidation and two reversible reductions, and each of these redox events were attributed to ligand-based processes (Table 11).

5. Applications of Main-Group Dipyrin Complexes

Although the number of publications on p-block dipyrin complexes has been steadily increasing in recent years, these studies have primarily focused on the synthesis, structure, and optical properties of these molecules. Only a small fraction of these reports (~25%) have utilized these molecules for a specific application, typically leveraging the unique photophysical properties of these complexes. To date, p-block dipyrins have been used for five distinct purposes: 1) catalysis, 2) photodynamic therapy (PDT), 3) cytotoxic agents, 4) bioimaging, and 5) cation sensing. Akin to their transition metal congeners [16,17], main-group dipyrin complexes have been explored as catalysts, although the scope of their reactivity is primarily limited to polymerization reactions. The inclusion of heavy atoms enhances intersystem crossing to photoactive triplet states, which can then react with molecular oxygen (a ground-state triplet) to produce singlet oxygen ($^1\text{O}_2$). This photogeneration of $^1\text{O}_2$, a short-lived reactive oxygen species (ROS), serves as the basis for PDT. Since $^1\text{O}_2$ can only be generated in the presence of light and a photosensitizer, selective irradiation of diseased tissue can be performed to minimize damage to healthy cells. Singlet oxygen can interact directly with biological substrates or initiate a cascade of radical reactions to generate other ROS, such as superoxide or hydroxyl radical. Both types of $^1\text{O}_2$ reactivity lead to oxidative cell damage that ultimately results in cell death [116]. In addition to phototoxicity, some dipyrin complexes are inherently cytotoxic, providing an opportunity to explore the medicinal chemistry of these molecules. The favorable fluorescence properties of heavy BODIPY analogs have been utilized for both cellular and *in vivo* bioimaging. Changes in the absorption and/or emission profiles upon analyte binding serve as a platform for biosensing. However, these main-group dipyrin complexes have only been explored as colorimetric cation sensors. The foundational studies outlined in this section serve as a basis for the further development of novel applications of heavy p-block dipyrin complexes.

5.1 Catalysis

The first example of catalysis with heavy p-block dipyrin complexes was reported in 2011 by Nozaki and coworkers [98]. They utilized Ge(IV) and Sn(IV) catalysts with tetradentate N_2O_2 dipyrin ligands to copolymerize carbon dioxide with either propylene

oxide or cyclohexene oxide to form propylene carbonate (PPC) or poly(cyclohexene carbonate) (PCHC), respectively. The tin complex Sn-**37g** exhibited a turnover frequency (TOF) of 12 h⁻¹ for PPC and 17 h⁻¹ for PCHC, whereas the germanium complex Ge-**37f** was more active with TOFs of 8–26 h⁻¹ for PPC and 60 h⁻¹ for PCHC. In 2014, the same group synthesized germanium N₂O₂ dipyrin complexes for the copolymerization of propylene oxide and carbon dioxide [99]. These *meso*-phenyl substituted ligands varied the substituent *para* to the phenol oxygen (Ge-**37h** and Ge-**37i**, Chart 17), exhibiting TOF of 15 h⁻¹ and 8 h⁻¹, respectively. These initial studies demonstrate that main-group tetradentate N₂O₂ complexes can serve as catalysts, providing a starting point to explore additional substrates and discover other reactions that could be catalyzed by these complexes.

Heteroleptic aluminum dipyrins Al-**7a**-NMe₂ and Al-**7a**-(O^tBu)₂ have been utilized as catalysts for the ring-opening polymerization of ϵ -caprolactone [52]. However, these ALDIPY pre-catalysts exhibited poor activity and low turnover numbers persisted, even under forcing conditions. At 60°C and 300–400 equivalents of the monomer per Al complex, low conversions were observed (5–10%) and the polymer products had a large molecular weight distribution, with polydispersity indices ranging from 1.26–2.53. While the α -mesityl substituents enabled the isolation of these aluminum dipyrinato complexes, this bulky group prevented the substrate from accessing the metal center. Although Al-**7a**-NMe₂ and Al-**7a**-(O^tBu)₂ exhibited low conversions for the polymerization of ϵ -caprolactone, the reactivity could potentially be modulated by varying the α -substituents of the ligand. As an example, the reactivity of low-valent Ga(I) complexes with Me₃SiN₃ could be tuned with the size of the α -aryl group, preferentially forming the tetrazagallol with DIPP (**15b**, Chart 7) or the mixed amide/azide product with ⁱPr-Anth (**15c**). This approach could access novel reactivity by adjusting the size of the dipyrin pocket to vary substrate accessibility.

Since ALDIPYs exhibit low polymerization reactivity, Li and co-workers used ALDIPY complexes (**9**) as an *in situ* mechanistic probe to determine the active species in the *cis*-1,4-polymerization of isoprene [53]. This reaction involved a Sc(III) bis-dipyrin complex with a –CH₂SiMe₃ ancillary ligand as the catalyst and a borate activator. Upon the addition of excess AlR₃, the reaction underwent a color change from red to green and

exhibited green emission, consistent with the formation of ALDIPY. This result suggests that a dipyrin ligand was transferred from the Sc(III) to the Al(III) center. *In situ* monitoring of the reaction by ^1H NMR indicated that the dipyrin ligand exchange rate was dependent on the AlR_3 concentration. The authors proposed that a novel trinuclear species $[\text{Sc}((\mu\text{-Me})_2\text{AlMe}_2)_2]^+$ is the active catalyst in the polymerization of isoprene. This intermediate was characterized by absorption and emission spectroscopy, as well as *in situ* ^1H NMR. This study demonstrates that fluorescence can be utilized as a tool to investigate reaction mechanisms.

To date, there has only been one report of a heavy p-block dipyrin complex used to catalyze a transformation beyond polymerization reactions. The heteroleptic complex **[18a]** $[(\text{OH})\text{B}(\text{C}_6\text{F}_5)_3]$ was used for the catalytic hydrosilylation of ketones and aldehydes [65]. Under mild conditions (30–35 °C), this complex could hydrosilylate a multitude of aldehydes and ketones with > 99% conversion in > 91% yield using triethylsilane (Et_3SiH). The highest TOF of 105 h^{-1} was observed when using 1 mol% catalyst. The formation of a 1:1 adduct of the Ge complex and Et_3SiH was observed by ^{29}Si NMR. The potential reaction mechanism and key intermediates were surveyed using computational methods. Upon dissociation of the $(\text{OH})\text{B}(\text{C}_6\text{F}_5)_3^-$ anion (a process that is exothermic by 155.3 kJ/mol), the germanium center reacts with Et_3SiH to form a Ge–H intermediate. The hydride and the cationic triethylsilane (Et_3Si^+) interact with the carbonyl group of the aldehyde or ketone, resulting in substrate hydrosilylation. This example provides a basis for exploring other low-valent main-group complexes, such as **14**, **16a**, and **32**, for potential catalytic applications.

5.2 Photodynamic Therapy

Heavy p-block dipyrin complexes are attractive photosensitizers for PDT due to their greater spin–orbit coupling relative to BODIPY and other typical fluorophores. The enhanced intersystem crossing to triplet excited states in these complexes increases the photogeneration of $^1\text{O}_2$. Despite these favorable photophysical properties, it was not until 2018 that the first study was published that examined the PDT potential of heavy p-block dipyrin complexes. Wiehe and colleagues synthesized a series of tris-homoleptic Ga(III) dipyrin complexes (**5a** to **5g**, Chart 2) and tested the photocytotoxicity against several

tumor cell lines and the bacterium *Staphylococcus aureus* [42]. The S-glycosylated dipyrin derivatives (**5f** and **5g**) were synthesized because S-glycosylated porphyrins are resistant to hydrolysis by glycosidases and exhibit enhanced stability in both basic and acidic media relative to O-glycosylated analogs [117]. Additionally, the Fe(III) analogs were synthesized and tested as a PDT control. Cells were incubated with 2 μM or 10 μM complex and irradiated with a white LED at a dose of $\sim 50 \text{ J cm}^{-2}$ for tumor cells or $\sim 100 \text{ J cm}^{-2}$ for bacteria. At 2 μM , the phototoxicity against tumor cells was significantly enhanced for Ga-**5f** and Ga-**5g** relative to the iron analogs and the non-glycosylated derivative Ga-**5b**. When tested for photodynamic inactivation of *S. aureus*, both Ga-**5f** and Ga-**5g** showed complete inactivation at 1 μM , whereas Ga-**5b** exhibited no inactivation at 100 μM . The metal complexes displayed minimal dark toxicity for both tumor cells and bacteria, indicative of a substantial phototherapeutic index. These results suggest that both the metal center and ligand glycosylation play significant roles in enhancing PDT efficacy.

Recently, Senge and colleagues synthesized a series of tris-homoleptic Al(III) dipyrins and examined their PDT activity against mouse colon carcinoma [37]. The singlet oxygen quantum yields (ϕ_{Δ}) were measured in ethanol ($\phi_{\Delta} = 0.10\text{--}0.35$) and toluene ($\phi_{\Delta} = 0.59\text{--}0.76$). In the absence of light, most complexes displayed no cytotoxic effects up to 20 μM . A broadband LED lamp (400–700 nm) was used to provide a light dose of 2.6 J cm^{-2} for 48 minutes. The best performing complex with a *meso*-2,4,5 trimethoxyphenyl substituent ($\phi_{\Delta} = 0.70$) resulted in 100% cell death at concentrations of 0.62–20 μM with $\text{IC}_{50} = 80 \text{ nM}$. Similar to glycosylated Ga-**5f** and Ga-**5g**, Al(III) complexes with hydrogen bonding functional groups ($-\text{OH}$, $-\text{CO}_2\text{H}$) at the *para* position of the *meso*-aryl group caused complete cell death at 10 μM with $\text{IC}_{50} = 3.5$ and 1.8 μM , respectively. These findings suggest that judicious ligand design, which includes polar functional groups, is essential for cell permeation by increasing the amphiphilicity of the photosensitizer.

5.3 Cytotoxic Agents

In addition to phototoxicity, some heavy p-block dipyrin complexes exhibit inherent toxicity against bacteria and cancer cells. The first such study was reported by Thompson and co-workers in 2013, where they examined the antimicrobial activity Sn(IV) complexes with tridentate α -pyrrolyldipyrin ligands (**42c-Ph** and **42c-ⁿBu**, Chart 22) [118]. They hypothesized that the structural similarity of this ligand to the natural product prodigiosin would yield potent antibiotics. However, the Sn(IV) dipyrins were not as active as the corresponding free-base ligand (**42c**) against Gram-positive bacteria: methicillin-resistant *Staphylococcus aureus* (MRSA), *Staphylococcus warneri*, and vancomycin-resistant *Enterococcus faecium* (VRE). For all strains, ligand **42c** had $IC_{50} = 9.1 \mu M$, whereas the corresponding tin complexes exhibited significantly higher values (95–400 μM). As an example, the IC_{50} values against VRE were 9.1 μM , 95.2 μM , and > 405 μM for **42c**, **42c-Ph**, and **42c-ⁿBu**, respectively. Notably, the complex with axial phenyl ligands exhibited higher toxicity for all three bacterial strains than the ⁿBu derivative. The authors proposed that the lower activity of the tin complexes relative to the free ligand is due to the loss of the pyrrole protons in the complex, which are thought to be essential for the antimicrobial activity of prodigiosins against Gram-positive bacteria. Similarly, the antimalarial activity of a variety of prodigiosin-like ligands and the corresponding Zn(II) and Sn(IV) were tested using the 3D7 strain of *Plasmodium falciparum* [119]. Unlike the antibacterial study, the metal complexes exhibited higher antimalarial activity than the free-base ligands. For example, **42c-ⁿBu** had an IC_{50} of 116 nM, while the free-base ligand had an IC_{50} of 900 nM. Similarly, the tin complex **42a-ⁿBu** exhibited an $IC_{50} = 521$ nM, whereas the ligand alone had an $IC_{50} = 1500$ nM. These studies serve as a starting point to further modify the α -pyrrolyldipyrin core and test the biological activity of these ligands and metal complexes as cytotoxic agents to treat other diseases.

Nagendran and colleagues tested the antiproliferative activity of the heteroleptic Ge(II) dipyrin complex **18a-OH** [63]. Unlike the few examples of hydroxygermylenes that have been reported in the literature [120,121], **18a-OH** is stable in air and water. The activity of **18a-OH** was tested against several cancer cell lines (HeLa, MCF7, and Huh7), comparing the activity to the clinically used chemotherapeutics cisplatin and doxorubicin. Although doxorubicin exhibited the best antiproliferative activity in all three cell lines, **18a-OH** was more active than cisplatin in Huh7 and MCF7 cells. Importantly, **18a-OH** was less

cytotoxic to a normal epithelial cell line than both cisplatin and doxorubicin, indicating that this dipyrin complex has some selectivity for cancer cells over healthy cells.

5.4 Bioimaging

Despite the synthesis of dipyrin derivatives with fluorescent properties that are competitive with BODIPYs, it was not until 2015 that heavy p-block dipyrin complexes were first used for bioimaging applications. Xiao and co-workers utilized the water-soluble aza-PODIPY **26** for fluorescence labeling studies because it exhibits far-red emission at ~660 nm [70]. Hep-2 cells were incubated with complex **26** and live-cell imaging was performed, exciting the cells at 590 nm. It was found that the aza-PODIPY was membrane permeable, and the cell nuclei remained intact, suggesting that the dye was not lethal to the cells. This study highlights that heavy BODIPY analogs are viable fluorophores for fluorescent imaging applications, even if the quantum yields are low ($\phi = 0.08$). The more significant attributes of the complex are water solubility and red emission.

In 2024, Sancey and co-workers published the first report of *in vivo* bioimaging with a heavy p-block dipyrin complex, where a water-soluble Ga(III) tetradentate N₂O₂ aza-dipyrin (Ga-**41f**) was used as the fluorophore [109]. The emission maximum of the dye is ~800 nm, thereby accessing the NIR region I (NIR-I: 700–950 nm). However, the tail of the emission profile extends out to 1150 nm, enabling NIR-II detection (1000–1700 nm) as well. The emission in NIR-I could be detected to a depth of 4 mm, while NIR-II emission was observed up to 6 mm. The complex exhibited low cytotoxicity in three human cell lines: endothelial HUVEC, glioblastoma U87MG, and renal HEK293. For Ga-**41f** concentrations up to 50 μ M, cell viability was > 85%, although some cytotoxicity was observed for HEK293 cells when treated with 100 μ M of the complex. A cell internalization study was performed on U87MG and HEK293 cells, which were incubated with 10 μ M of the complex for 1 hour. Higher cytoplasmic accumulation of Ga-**41f** was observed for U87MG cells than HEK293 cells, as measured by flow cytometry and confocal microscopy. The fluorophore exhibited qualitative photostability in mouse serum and resistance to photobleaching after excitation with an 808 nm laser. *In vivo* studies were performed to image mice with ovarian cancer tumor models. As proof of concept for potential fluorescence-guided surgery, mice were injected with IGROV-1 cells that were

transfected with a luciferase gene, resulting in an intraperitoneal tumor that could be detected by luciferin bioluminescence. In this way, the tumor could be unambiguously identified and the colocalization of luciferin luminescence and aza-dipyrrin emission confirmed tumor uptake. Imaging was conducted in both the NIR-I and NIR-II optical windows. Aza-dipyrrin Ga-**41f** was administered by intravenous injection, and complex accumulation was detected in the liver and tumor 48 hours post-injection (Figure 23). While tumor uptake was not statistically significant in the NIR-II window, a higher NIR-I fluorescence signal was observed in the tumor relative to the surrounding tissue. The complex had a longer serum half-life relative to other small fluorophores, which was attributed to an interaction with blood lipoproteins. The authors proposed that the complex could be synthesized with gallium-68, thereby enabling bimodal positron emission tomography and fluorescence imaging with a single complex. This study serves as a starting point for the further investigation of p-block dipyrrin complexes for *in vivo* bioimaging.

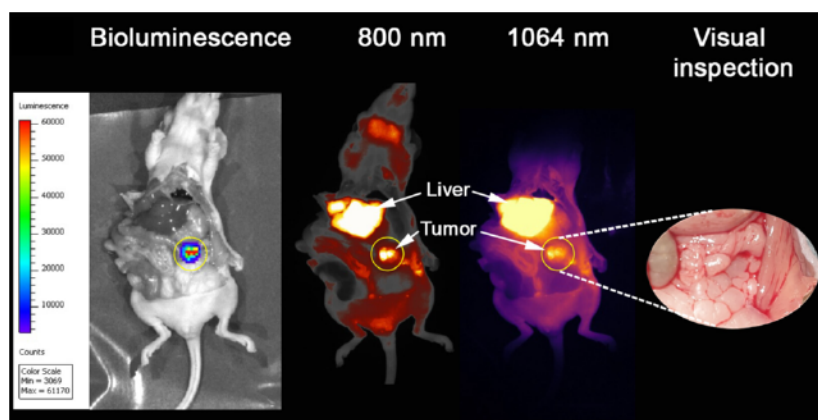


Figure 23. Imaging of a tumor-bearing mouse using Ga-**41f** as the fluorophore. The IGROV-1 tumor expresses luciferase, enabling selective tumor identification with luciferin bioluminescence. After the administration of Ga-**41f**, *in vivo* emission was detected at 800 nm and 1064 nm. This approach could be used for fluorescence-guided surgery to precisely identify the margins of a tumor, which are difficult to discern by visual inspection alone. Reprinted with permission from [109]. Copyright 2024 American Chemical Society.

5.5 Cation Sensing

Changes in the absorption or emission profiles of p-block dipyrrin complexes upon analyte binding serve as a basis for colorimetric or fluorescence sensing. To date, these

dipyrrin complexes have only been explored as cation receptors. In 2015, Xiao and co-workers demonstrated that PODIPY **25** serves as a selective colorimetric sensor for Hg^{2+} , where the sample exhibits a color change from pink to violet/red (Figure 24) [122]. Binding selectivity was tested by adding other cations (Fe^{3+} , Ag^+ , Cr^{3+} , Pb^{2+} , Zn^{2+} , Ni^{2+}) to the sample, and complex **25** remained selective for Hg^{2+} , demonstrating that other metal cations do not interfere with mercury detection. IR spectroscopy indicated that the P=O bond was polarized in the presence of Hg^{2+} , as evidenced by the broadening of a characteristic P=O vibration at 1346 cm^{-1} . DFT calculations revealed that the HOMO–LUMO gap decreases by 0.14 eV when Hg^{2+} was bound, which reflects the experimental red-shift in the absorption spectrum. The limit of Hg^{2+} detection with complex **25** was $0.5\text{ }\mu\text{mol/L}$. Colorimetric test strips were developed as a low-cost and efficient Hg^{2+} test kit. This approach could be extended to detect other toxic cations, such as Pb^{2+} or As^{3+} , by modifying the α or *meso*-substituents to tune the steric and electronic properties of the dipyrin, thereby modulating cation selectivity.



Figure 24. PODIPY **25** is a colorimetric sensor for Hg^{2+} , exhibiting a color change from pink to violet red. Reprinted with permission from [122]. Copyright 2015 Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences. Published by Elsevier B.V.

In order to have greater molecular control for cation binding, Nabeshima and co-workers synthesized macrocyclic dipyrin dimers (**39**) with a pre-organized and well-defined metal binding site, akin to crown ethers [90]. Both **39a** and the corresponding monomer **Al-37d** were treated with metal perchlorate salts (Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}), and metal binding was monitored by UV–vis absorption. In the case of **Al-37d**, the absorption intensity decreased upon cation binding, whereas **39a** exhibited an increase in absorption

with metal binding. Overall, macrocycle **39a** showed a higher binding affinity for each cation relative to Al-**37d**, with the largest difference observed for Sr^{2+} : $\log K_a = 5.80$ for Al-**37d** vs. $\log K_a > 7$ for **39a**. Although the O_6 binding site in the macrocycle is neutral, the high binding affinity is likely attributed to the preorganization of a rigid macrocycle in conjunction with four phenolate oxygen atoms that bear a partial negative charge (due to the polarized Al–O bonds). This approach could be used to develop colorimetric or fluorometric cation sensors. Moreover, this macrocyclic ligand scaffold could be modified to potentially tune the affinity and specificity of these cation receptors.

6. Conclusions and Future Directions

Dipyrrins represent a versatile class of ligands that can be used to synthesize an array of homo- and heteroleptic complexes with diverse primary coordination spheres. Since much of the attention on dipyrrin coordination chemistry has focused on transition metals, main-group complexes of heavy p-block elements (periods 3 to 6) have remained underexplored. However, a recent renaissance in this area has seen a significant increase in the number of publications, with 36% of all reports being published in the past 5 years. While not all studies of these complexes have been complete or compelling (*e.g.*, Tl and Pb), there are published examples of all the heavy group 13, 14, and 15 elements. For these complexes, the ligands range from simple, bidentate dipyrrins, as well as α -linked dimers (*i.e.*, *a,c*-biladiene and *a,b,c*-bilatriene), to tri- and tetra-dentate derivatives with intramolecular ligands (*e.g.*, phenol, pyrrole) at the α -positions. This results in rich coordination chemistry that diversifies the dipyrrin toolbox. One area that could be further explored is the incorporation of alternative α -substituents that contain donor atoms, such as sulfur containing rings, to determine the impact of these groups on the optical properties of the complex. Indeed, a variety of polydentate dipyrrins (similar to **40**) have been synthesized [123,124], but the p-block coordination chemistry of these ligands has not yet been explored.

Given the conjugated π system of the dipyrromethene core, closed-shell main-group dipyrrin complexes are often emissive, accessing wavelengths that are generally red-shifted compared to BODIPY. While the introduction of heavier central atoms often decreases the quantum yield due to enhanced spin–orbit coupling (accessing triplet

states at the expense of the singlet), this is not universally true. Judicious ligand design, particularly when using *meso*-mesityl or *meso*-unsubstituted derivatives, enables heavy p-block dipyrin complexes, such as the Ga(III) complex **10a**, to be competitive with BODIPY fluorophores. The use of aza-dipyrin ligands or extension of the dipyrin π system shifts the absorption and emission profiles of these main-group complexes to far-red and NIR wavelengths. Computational studies have been utilized to predict the optical properties of these complexes, identifying specific ligand architectures that might exhibit NIR emission [73]. However, synthetic chemists have not yet explored these predictions. The use of heavy metals enhances spin–orbit coupling, accessing long-lived ($\sim 10^2$ μ s) triplet states, which can be leveraged for the photogeneration of $^1\text{O}_2$. Indeed, several of these complexes have been utilized for various types of PDT. The foundational studies outlined in this review provide a starting point to further tailor the optical properties of heavy p-block dipyrin complexes for a variety of applications.

Despite the rapid expansion in the field of heavy p-block dipyrin complexes, there are only a few publications that report their applications, representing only 24% of the publications outlined in this review. These complexes have been used as polymerization catalysts, PDT photosensitizers, cytotoxic agents, bioimaging fluorophores, and cation sensors. Like their transition metal congeners, these main-group dipyrins have been most studied as catalysts, namely for polymerization reactions [52,53,98,99]. However, heteroleptic germanium dipyrins can perform catalytic hydrosilylation of ketones and aldehydes [65]. The dearth of examples indicates that the chemical space for catalysis with these complexes has just begun to be explored, suggesting that there likely more reactions yet to be discovered. The inclusion of heavy p-block elements promotes efficient intersystem crossing to triplet states, which is essential for PDT. However, there have only been two such PDT reports, which used tris-homoleptic Al(III) and Ga(III) complexes [37,42]. This implies that there is vast potential for the newly synthesized metal complexes described in this review to be used as photosensitizers for PDT and potentially photocatalysis. In addition to photocytotoxicity, some main-group dipyrins have inherent cytotoxicity that can be leveraged to treat disease. Specifically, Sn(IV) α -pyrrolyldipyrins are toxic to *Plasmodium falciparum* [119], and Ge(II) dipyrins exhibit some selective toxicity to tumor cells over related healthy cell lines [63]. While some examples of p-block

dipyrrin complexes exhibit fluorescent properties that are competitive with BODIPY, there have been only two bioimaging reports [70,109]. A water-soluble Ga(III) aza-dipyrrin showed low cytotoxicity and selective tumor uptake in murine models [109]. This lone *in vivo* study was just reported in 2024, signifying that there is incredible potential for advances in intravital imaging with heavy BODIPY analogs. Finally, the optical properties of main-group dipyrrins can be leveraged for sensing applications. However, only colorimetric metal cation sensing has been reported, as analyte binding was monitored by absorption spectroscopy [122]. Consequently, the emission properties of these complexes have not yet been exploited for sensing applications. This demonstrates that there is a vast opportunity to utilize heavy dipyrrin complexes for the fluorescence-based quantification of biomedical analytes. Given the potential provided by the *in vivo* study, coupling an analyte receptor to these complexes would enable *in vivo* biosensing for the early detection of disease.

Although there have been reports of dipyrrin complexes of all heavy group 13, 14, and 15 elements, the scope of the coordination chemistry with these metals is far from complete. Indeed, the only examples of homoleptic tris-dipyrrins are In(III), Ga(III), and Al(III), with the latter just reported in 2025. It is noteworthy that this chemistry doesn't extend to the crystallogens or pnictogens, perhaps due to the stereochemically-active lone pair (ns^2) on these elements. Indeed, all examples of simple, bidentate dipyrrin complexes with group 14 and 15 metals are heteroleptic. To date, the only examples of tetradentate N_2O_2 aza-dipyrrins are for group 13 elements. Examples of the heaviest elements, namely Tl and Pb, are poorly characterized, lacking solid-state structures, and in the case of lead, the complex was not isolated from the reaction mixture. It is also noteworthy that the coordination chemistry is primarily for the lower oxidation states of these elements. While there are several Ge(IV) and Sn(IV) dipyrrins, there is only one recent report on Sb(V) complexes and no examples of Bi(V). Likewise, it is worth noting that group 16 elements have not been coordinated with dipyrrromethenes, despite literature precedent for tellurium porphyrins [125]. With the ligand design and synthetic strategies outlined in this review, examples of N_2O_2 or traditional dipyrrins with group 16 elements could now be investigated.

The dipyrin complexes presented in this review can readily be tailored for a variety of additional applications. For example, photo-active MOFs have been utilized to detect biomarkers [126]. The foundational work reported by Cohen and coworkers on dipyrin-based 3D architectures [40] can be tailored for biomedical sensing, thereby leveraging the unique photophysical properties of p-block dipyrin complexes. While the Cohen group utilized 4-pyridyl *meso*-substituents, this chemistry can readily be extended to other coordinating functional groups such as thiols, nitriles, or carboxylic acids. Additionally, the nature and identity of the metal that templates the self-assembly process could be varied to control the shape and porosity of dipyrin-based MOFs. Similarly, functionalized dipyrin ligands have been employed to assemble supramolecular structures [127]. For example, some aza-BODIPYs can self-assemble into nanorods [128]. This approach could be extended to heavy p-block dipyrin complexes, providing an inroad to photo-active molecular materials with long-lived triplet states for potential photocatalytic or PDT applications. Some of the reported dipyrin complexes (such as Al-1, Ga-1, In-1) exhibit oxygen-dependent excited state lifetimes, which could be used for optical oxygen sensing in biological systems [129–131].

Recently, there has been a boom in main-group complexes for catalysis [33–35]. The development of synthetic methods to access p-block dipyrin complexes now provides an opportunity to extend this chemistry, perhaps offering advantages over other ligand platforms. In this way, the main-group dipyrin complexes outlined in this review may show promise for both catalytic and biological applications. The use of bulky α -substituents enables the preparation of formally low-valent Ge(I) and Sb(I) complexes, which could provide a starting point to develop catalytic cycles. Indeed, this chemistry would directly emulate the low-valent Bi(I)/Bi(III) [132–134] and potentially Bi(III)/Bi(V) [135] catalytic cycles developed by Cornella and co-workers. Similarly, Radosevich and co-workers have developed P(III)/P(V) catalytic cycles [136–138]. Given the ability to readily access dipyrin complexes in two oxidation states, such chemistry could be extended to dipyrin-based catalytic cycles that utilize P(III)/P(V), Ge(II)/Ge(IV), or Sn(II)/Sn(IV) couples. Another recent example of multi-electron main-group catalysis is the four-electron reduction of O₂ to H₂O using a phosphorus-based catalyst [139]. The extension of this chemistry could provide an inroad to green chemistry and alternative

energy applications with dipyrin complexes. Given the similarities in electronic structure, analogies have been drawn between tetradentate N_2O_2 dipyrin complexes and corroles [82]. Since main-group corroles serve as photosensitizers and perform photochemical reactions [140], perhaps this photochemistry could also extend to p-block N_2O_2 dipyrin complexes. For example, the recently reported Sb(V) dichloride dipyrins [103] could potentially undergo photochemical halogenation elimination akin to Sb(V)X₂ corroles [141]. Given the use of main-group complexes in medicinal chemistry [142,143], p-block dipyrins provide an opportunity for novel therapeutics. Together, heavy p-block dipyrins represent an emerging class of main-group complexes with a wide range of potential applications in photochemistry, catalysis, and biomedicine. The tunability of main-group dipyrin complexes could enable their use as novel catalysts, advanced materials, or chemotherapeutic drugs, potentially surpassing the performance of other ligand platforms.

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Declaration of Competing Interest

The authors report there are no competing interests to declare.

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Table 1. Spectroscopic data of tris-homoleptic dipyrin complexes.

Complex	Solvent	$\lambda_{\text{abs,max}}$ (nm)	ϵ_{max} (M ⁻¹ cm ⁻¹)	$\lambda_{\text{em,max}}$ (nm)	ϕ	τ_f (ns)	Ref.
Al-1	Toluene	454	70,800	535	0.07	4.7	[37]
Ga-1	Hexanes	496	68,000	528	0.024	3.75	[10]
In-1	Hexanes	496	60,100	522	0.074	1.93	[10]
In-3	EtOAc	480	N/A	560	0.014	1.99	[41]
Al-4	Toluene	461	79,400	580	0.01	3.6	[37]
In-6a	Toluene	459 570	118,000 67,300	592	0.41	2.44	[43]
In-6a	DCM	N/A	N/A	N/A	0.053	1.29	[43]
In-6b	Toluene	542(sh.) 564	92,400 (sh.) 113,000	596	0.34	2.53	[43]
In-6b	DCM	N/A	N/A	N/A	0.021	1.42	[43]
In-6c	Toluene	528 572	156,000 140,000	600	0.28	2.49	[43]
In-6c	DCM	N/A	N/A	N/A	0.015	1.48	[43]

Table 2. Structural metrics for group 13 heteroleptic dipyrin complexes [51].

Complex	M–N Bond (Å)	M–C Bond (Å)	N–M–N Angle (°)	C–M–C Angle (°)	τ_4
Al- 8a -Me ₂	1.940	1.964	94.3	114.8	0.94
Al- 8a -Et ₂	1.930	1.959	94.4	114.6	0.92
Ga- 8a -Me ₂	1.998	1.968	92.3	119.0	0.91
Ga- 8a -Et ₂	1.993	1.968	92.1	117.7	0.89
In- 8a -Me ₂	2.196	2.147	85.1	124.5	0.87
In- 8a -Et ₂	2.196	2.154	85.4	123.0	0.87

Table 3. Photophysical properties of group 13 heteroleptic dipyrin complexes.

Complex	Solvent	$\lambda_{\text{abs,max}}$ (nm)	ϵ_{max} (M ⁻¹ cm ⁻¹)	$\lambda_{\text{em,max}}$ (nm)	ϕ	Ref.
B- 8b -F ₂	Hexane	519	N/A	540	0.45	[56]
Al- 8a -Me ₂	Toluene	504	127,000	540	0.44	[51]
Al- 8a -Et ₂	Toluene	505	130,000	551	<0.01	[51]
Al- 8b -I ₂	Hexane	514	N/A	537	0.022	[56]
Ga- 8a -Me ₂	Toluene	500	130,000	539	0.51	[51]
Ga- 8a -Et ₂	Toluene	502	110,000	545	0.02	[51]
Ga- 8b -I ₂	Hexane	516	N/A	550	0.02	[56]
Ga- 8c -I ₂	Toluene	503	162,000	N/A	N/A	[58]
In- 8a -Me ₂	Toluene	499	143,000	540	0.02	[51]
In- 8a -Et ₂	Toluene	505	149,000	547	<0.01	[51]
10a	Toluene	497	N/A	505	0.91	[54]
11	Hexane	513	N/A	N/A	N/A	[56]
12	Hexane	508	N/A	N/A	N/A	[56]
13	Toluene	500	169,000	N/A	N/A	[58]
14	Toluene	500	52,800	N/A	N/A	[58]

Table 4. Structural metrics for germanium dipyrins in different formal oxidation states.

Complex	Formal Oxidation State	Ge–N₁ Bond (Å)	Ge–N₂ Bond (Å)	N₁–Ge–N₂ angle (°)	Ref.
19a	I	1.868(3)	1.868(3)	91.7	[66]
18a-Cl	II	1.977(3)	1.992(3)	86.8	[63]
19b	III	1.885(4)	1.893(4)	95.2	[66]
19c	IV	1.853(2)	1.858(2)	97.6	[63]

Table 5. Photophysical properties of group 14 heteroleptic dipyrin complexes.

Complex	Solvent	$\lambda_{\text{abs,max}}$ (nm)	ϵ_{max} $\text{M}^{-1} \text{cm}^{-1}$	$\lambda_{\text{em,max}}$ (nm)	ϕ	Ref.
17a-Cl	Toluene	524	48,724	555	0.0028	[62]
17a-F	Toluene	517	45,456	538	0.0014	[62]
18a-Me^a	Toluene	517	57,840	598	0.0203 ^b	[64]
18a-CF₃^a	Toluene	520	54,470	589	0.0202 ^b	[64]
18a-C₆H₅^a	Toluene	521	54,201	589	0.0131 ^b	[64]
18a-C₆H₄-CN^a	Toluene	521	54,474	590	0.0187 ^b	[64]
18a-C₆H₄-NO₂^a	Toluene	521	56,690	595	0.0167 ^b	[64]
18a-C₆H₄-OC(O)CH₃^a	Toluene	521	52,880	591	0.0254 ^b	[64]
22a	CHCl ₃	643	49,180	N/A	N/A	[68]
22b	CHCl ₃	640	41,942	N/A	N/A	[68]
22c	CHCl ₃	644	56,100	N/A	N/A	[68]
23a	Benzene	509	85,400	518	0.04	[19]
23b	Benzene	513	64,600	524	0.42	[19]
23c	Toluene	516	N/A	538	0.033	[49]
23d	Toluene	518	N/A	551	0.066	[49]

^aCompound names denote the R' substituent of the anionic ligand X = COOR' (see Chart 9)^bSolid-state quantum yield

Table 6. Photophysical properties of group 15 heteroleptic dipyrin complexes.

Complex	Solvent	$\lambda_{\text{abs,max}}$ (nm)	$\lambda_{\text{em,max}}$ (nm)	ϕ	Stokes Shift (cm ⁻¹)	Ref.
25	DCM	510	524	0.17	523	[70]
26	DCM	625	661	0.08	871	[70]
27	DCM	467	510	0.80	1,805	[54]
29a	Toluene	496	539	0.056	1,608	[49]
29b	Toluene	514	547	0.066	1,173	[21]
29c	Toluene	452	550	N/A	3,942	[21]
29d	Toluene	451	552	N/A	4,057	[21]
29e	Toluene	513	568	0.002	1,887	[21]
30a	DCM	496	522	N/A	1,004	[20]
30b	DCM	501	516	0.025	580	[20]
30c	DCM	504	518	0.004	536	[20]
30d	DCM	501	520	N/A	729	[20]
30e	DCM	501	523	0.011	840	[20]
31	DCM	513	518	N/A	188	[20]
32	Toluene	456	527	0.002	2,955	[21]
35	DCM	506	535	N/A	1,071	[20]

Table 7. Photophysical properties of group 13 N₂O₂ dipyrin complexes.

Complex	Solvent	$\lambda_{\text{abs,max}}$ (nm)	$\lambda_{\text{em,max}}$ (nm)	ϕ	Ref.
B- 36b	Toluene	626	645	0.72	[89]
Al- 36a	Toluene	624	650	0.23	[89]
Al- 36a -ZnCl ₂	Toluene	607	620	0.55	[89]
Al- 36a -ZnBr ₂	Toluene	607	620	0.56	[89]
Al- 36b	Toluene	625	647	0.72	[89]
Al- 36b -ZnCl ₂	Toluene	608	619	0.83	[89]
Al- 37e	CHCl ₃	624	646	0.08	[93]
Ga- 36b	Toluene	629	653	0.53	[93]
Ga- 37e	CHCl ₃	629	652	0.025	[93]
In- 36b	Toluene	613	639	0.67	[93]
In- 37d	CHCl ₃	619	644	0.19	[93]
In- 37e	CHCl ₃	609	636	0.015	[93]

Table 8. Photophysical properties of group 14 N₂O₂ dipyrin complexes in CHCl₃.

Complex	$\lambda_{\text{abs,max}}$ (nm)	ϵ_{max} M ⁻¹ cm ⁻¹	$\lambda_{\text{em,max}}$ (nm)	ϕ	Ref.
Si- 36c	606	N/A	648	0.012	[96]
Si- 36e	606	N/A	649	0.76	[96]
Si- 36f	612	N/A	662	0.72	[96]
Si- 36g	605	N/A	648	0.81	[96]
Si- 36d	612	44,000	650	0.028	[96,97]
Si dimer	601	N/A	671	0.37	[96]
Ge- 36d	620	35,000	675	0.12	[97]
Sn- 36d	637	42,000	664	0.22	[97]

Table 9. Spectroscopic data of N₂O₂ aza-dipyrin complexes.

Complex	Solvent	$\lambda_{\text{abs,max}}$ (nm)	ϵ_{max} M ⁻¹ cm ⁻¹	$\lambda_{\text{em,max}}$ (nm)	ϕ	τ_f (ns)	Ref.
B-41a	MeOH	732	29,500	751	0.088	N/A	[107]
B-41b	MeOH	728	31,600	747	0.137	N/A	[107]
B-41c	DMSO	728	52,000	756	0.28	4.31	[108]
Al-41a	MeOH	728	36,300	762	0.07	N/A	[107]
Al-41b	MeOH	731	30,200	766	0.075	N/A	[107]
Al-41c	DMSO	732	87,000	787	0.13	2.39	[108]
Ga-41a	MeOH	732	51,300	770	0.084	N/A	[107]
Ga-41a	DMSO	734	110,000	782	0.11	N/A	[108]
Ga-41b	MeOH	734	38,000	774	0.061	N/A	[107]
Ga-41c	DMSO	728	81,000	782	0.11	2.22	[108]
Ga-41d	DMSO	754	75,000	796	0.10	N/A	[108]
Ga-41e	DMSO	744	32,000	802	0.08	2.05	[108]
Ga-41f	DMSO	752	48,000	806	0.09	N/A	[109]
Ga-41f	MeCN	748	35,000	808	0.05	N/A	[109]
Ga-41f	Water	715	18,000	785	<0.001	N/A	[109]
Ga-41f	PBS	716	49,000	787	0.007	N/A	[109]
	Buffer						
Ga-41f	Mouse	755	30,000	811	0.06	N/A	[109]
	Serum						
In-41a	MeOH	713	28,200	746	0.007	N/A	[107]
In-41b	MeOH	714	46,800	752	0.003	N/A	[107]

Table 10. Spectroscopic data for heteroleptic Sn(IV) α -pyrrolyldipyrrin complexes in CH₂Cl₂ [113].

Complex	$\lambda_{\text{abs,max}}$ (nm)	ϵ_{max} M ⁻¹ cm ⁻¹	$\lambda_{\text{em,max}}$ (nm)	ϕ
B-42a	543	105,000	559	0.92
42a-ⁿBu	561	87,800	584	0.53
42b-ⁿBu	570	116,000	582	0.61
42c-ⁿBu	561	88,200	584	0.53
42c-Ph	561	74,000	583	0.55
42d-ⁿBu	585	86,900	607	0.52
42e-Ph	587	86,300	609	0.51
42f-ⁿBu	599	116,000	617	0.28
42f-Ph	603	87,000	622	0.32

Table 11. Characterization data for homoleptic Sn(IV) α -pyrrolyldipyrin complexes [115].

Complex	$\lambda_{\text{abs,max}}$	ϵ_{max}	Oxidation ^a	1 st	2 nd
	(nm)	M ⁻¹ cm ⁻¹		Reduction ^a	Reduction ^a
B-43a	578	91,200	0.57	−1.08	N/A
43a	604	83,200	0.54	−1.27	−1.50
43b	604	87,100	0.50	−1.33	−1.56
43c	604	85,100	0.52	−1.32	−1.55
43d	607	74,100	0.56	−1.23	−1.46
43e	620	110,000	0.52	−1.22	−1.42

^a All potentials (in V) are relative to the Fc⁺/Fc couple