Coordination chemistry and applications of versatile 4,5-diazafluorene derivatives

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This perspective review will examine the coordination chemistry and applications of metal complexes of 4,5-diazafluorene derivatives. The versatile derivatives of 4,5-diazafluorene can serve multiple roles, and display a number of coordination modes. The ambidentate derivatives with multiple coordination sites can allow for the syntheses of coordination polymers, multimetallic, and macrocyclic complexes. In addition, certain 4,5-diazafluorene derivatives can serve as spectator ligands to support reactivity at the metal centre, or as reactive actor ligands engaging in atypical reactivity patterns. The applications of metal complexes of 4,5-diazafluorene derivatives in catalysis, photochemistry and photophysics, as well as in bioinorganic chemistry are also surveyed.

I. Introduction

4,5-Diazafluorene (dafH) was first reported in the late 1970s,1,2 and synthesized in two steps from 1,10-phenanthroline (phen). The first step is an oxidative ring contraction of phen with permanganate in basic aqueous media giving 4,5-diazafluoren-9-one (dafo),3 and the second step is a Wolff-Kishner reduction of dafo with hydrazine monohydrate at high temperature (Scheme 1).4,5 The contraction of the middle ring of phen increases the distance between the two N-donors, i.e., 2.72 Å for phen6 and 3.05 Å for dafo7 and dafH.8 In coordination chemistry, the dafo ligand has been conventionally viewed as a 2,2′-bipyridine (bpy) derivative with a methylene linker tethering the two pyridine rings (Fig. 1). The methylene group effectively ties back the two pyridine rings, resulting in a longer N–N distance in dafo (2.82(3) Å) compared to bpy (2.63(4) Å) in complexes. Consequentially, the overlap between the nitrogen lone pairs and the metal orbitals is less effective for dafo compared to bpy (Fig. 1).9–11 The dafo ligand has an even longer N–N distance (2.96(7) Å) since C9 is

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sp$^3$ hybridized in dafo. Although dafH derivatives were considered merely as bpy analogues in the late 1970s, they have recently gained more attention in many areas. Ono and Wong previously reviewed the synthesis and coordination chemistry of several dafH derivatives. The purpose of this perspective review is to highlight the versatile nature of dafH derivatives as ligands, and also to detail some of the recent advances made using this ligand family.

II. Fundamental coordination chemistry of dafH derivatives

II.1. Coordination chemistry of the parent dafH and daf$^-$ ligands

Although being conventionally viewed as a bpy derivative, the dafH ligand can also be viewed as two pyridine rings fused onto a central cyclopentadiene (CpH) ring in a syn fashion. The methylene group of dafH is acidic, analogously the $pK_a$ of CpH is 18, and that of fluorene is 22.6 in DMSO. The methylene linker of dafH may be deprotonated to form the mono-anionic 4,5-diazafluorene (daf$^-$) (Scheme 2A).

Ambidentate ligands containing multiple potential coordination sites of different nature can be used to construct linkage isomers, homo- and heterometallic complexes, and complex molecular architectures through coordination-driven self-assembly. Several 4,5-diazafluorene derivatives possess multiple coordination sites, especially those derivatives that are functionalized at the C9-position discussed later. The daf$^-$ ligand is potentially an ambidentate ligand with two types of metal binding sites, an $\eta^1$-$\eta^1$-chelate site, and the $\eta^2$-$\eta^2$-chelate site, and the C-donors of the central cyclopentadienyl-like moiety. However in most examples daf$^-$ binds metals with its nitrogen donors, without utilizing the C-donors. In addition the daf$^-$ ligand is able to form zwitterionic complexes when only two N-donors are bound to the metal centre with a −1 charge localized onto the ligand backbone. A recurring theme in this review is the reactivity of the ligand backbone in a zwitterionic setup.

Our group’s initial investigations into the coordination chemistry of the 4,5-diazafluorene (daf$^-$) ligand were reported in 2008. The reaction of Na[daf] with $[\text{Pd}(PPh_3)_2\text{Cl}_2]$ gave a dinuclear Pd complex $[\text{Pd}[\text{daf}](PPh_3)_2\text{Cl}]$, in this exceptional case the daf$^-$ ligand was bound to Pd through one of the N-donors and the anionic C-donor of the ligand backbone in an $\eta^1$-$\eta^1$-fashion (Scheme 2B). A zwitterionic Rh(i) complex $[\text{Rh}[\text{daf}](\text{COD})]$ can also be straightforwardly prepared by reacting Na[daf] with 0.5 equiv. of [Rh(COD)Cl]$_2$ (Scheme 2B).

An extension of the work with Rh 4,5-diazafluorene derivatives involved the syntheses of complexes with PPh$_3$ as an auxiliary ligand (see Scheme 2C). The Rh(i) complex $[\text{Rh}[\text{daf}](PPh_3)_2]$ can be synthesized from the reaction of Na[daf] and Wilkinson’s catalyst. Complex $[\text{Rh}[\text{daf}](PPh_3)_2]$ reacts with H$_2$ to give a Rh$^{\text{II}}$ dihydride complex $[\text{Rh}[\text{dafo}](PPh_3)_2\text{H}_2]$, which reacts with HCl to give $[\text{Rh}[\text{dafo}](PPh_3)_2\text{H}_2]\text{Cl}$ (Scheme 2C). Alternatively, $[\text{Rh}[\text{dafo}](PPh_3)_2\text{H}_2]\text{Cl}$ can also be synthesized by reacting dafoH with Wilkinson’s catalyst under a H$_2$ atmosphere, and subsequent deprotonation with NaH gives $[\text{Rh}[\text{dafo}](PPh_3)_2\text{H}_2]$ cleanly.

Parts of Scheme 3 highlight the ambidentate nature of daf$^-$ in its coordination chemistry with a [RuCp*$^+$] fragment. The addition of neutral dafoH to 0.25 equiv. of $[\text{RuCp}*\{\mu_3-\text{Cl}\}]$, starting material gave $[\text{RuCp}*([\text{dafoH}])\text{Cl}]$ where the dafoH ligand coordinates through the nitrogen chelate (Scheme 3). However the addition of Na[dafH] to 0.25 equiv. of $[\text{RuCp}*\{\mu_3-\text{Cl}\}]$, starting material gave a monomeric sandwich complex $[\text{RuCp}*([\text{dafoH}])]$ where the dafoH ligand coordinates through the central cyclopentadienyl-like ring in an $\eta^5$-fashion leaving the nitrogen chelate vacant (Scheme 3). Surprisingly when the $[\text{RuCp}*\{\mu_3-\text{Cl}\}]$, starting material is treated with K[dafH], or if the coordinated 4,5-diazafluorene ligand of $[\text{RuCp}*\text{Cl}(\text{dafoH})]$ is deprotonated.

## Scheme 1
Synthesis of dafoH from 1,10-phenanthroline with numbering scheme of dafoH ligand is shown.

## Scheme 2
(A) Deprotonation of dafoH to give dafo$^-$ (B) Synthesis of $[\text{Rh}[\text{daf}](\text{COD})]$ and $[\text{Pd}[\text{dafo}](PPh_3)_2\text{Cl}]$. (C) Interconversion between Rh 4,5-diazafluorene complexes.
with K[HBE₃] the self-assembly of a tetraruthenamacrocycle [RuCp*(daf)]₄ occurred where the daf⁻ ligand coordinated through both the N-donors and the C-donor of the ligand backbone in an η¹(σ)-fashion (Scheme 3). The different coordination behaviours of daf⁻ in [RuCp*(daf)]ₙ (n = 1 or 4), a monomeric sandwich complex and a tetraruthenamacrocycle, demonstrate its ambidentate nature.

We have used 4,5-diazafluorenide derivatives to synthesize heterobimetallic complexes. When the salt [Na(dme)₃][Pt(daf)(Ph)₂] is treated with [Cu(IPr)Cl], a Pt(II)–Cu(I) heterobimetallic complex [(IPr)Cu(daf)Pt(Ph)₂] was obtained where C9 of daf⁻ is coordinated to the {Cu(IPr)}⁺ fragment in an η¹(π) fashion (Scheme 4). Surprisingly when the metallation sequence is reversed and the [Cu(daf)(IPr)] complex is treated with [Pt(Ph)₂(μ-SMe₂)]ₙ (n = 2 or 3), the exact same Pt(II)–Cu(I) heterobimetallic complex (as opposed to an isomer) was obtained. In the process of generating [(IPr)Cu(daf)Pt(Ph)₂] from [Cu(daf)(IPr)] the {Cu(IPr)}⁺ fragment was replaced by the Pt(Ph)₂ unit at the NₙN-chelate site and migrated to the backbone C-donor. The built-in self-correction featured in the synthesis of the [(IPr)Cu(daf)Pt(Ph)₂] system allowed for a one pot synthesis to be successfully carried out (Scheme 4).

Scheme 3  Coordination chemistry of ambidentate 4,5-diazafluorene derivatives with a RuCp* synthon.  

Scheme 4  Three synthetic routes to [(IPr)Cu(daf)Pt(Ph)₂].
II.2. Coordination chemistry of the aryl substituted dafMes\textsuperscript{H} and dafMes\textsuperscript{−} ligands

A 3,6-dimesityl substituted 4,5-diazafluorene ligand (dafMes\textsuperscript{H}) has been synthesized, which can also be deprotonated to give dafMes\textsuperscript{−}.\textsuperscript{25} These bulkier 4,5-diazafluorene derivatives are also ambidentate. The dafMes\textsuperscript{−} ligand has an \(N_2N\)-chelate site and the \(C\)-donors of the central cyclopentadienyl moiety; in addition, there is also the possibility of the mesityl substituent to participate in bonding. The coordination chemistry of neutral dafMes\textsuperscript{H} and monoanionic dafMes\textsuperscript{−} ligands toward the \({\text{RuCp}^*}\)\textsuperscript{+} fragment was examined (Scheme 3). When K[dafMes] was added to 0.25 equiv. of \([\text{RuCp}^*\text{(µ-Cl)}]\)\textsubscript{4}, a sandwich complex \([\text{RuCp}^*\text{(dafMes})]\) formed where the nitrogen chelate is vacant and the dafMes\textsuperscript{−} ligand is coordinated through the central \(C\)-ring in an \(η^2\)-fashion (Scheme 3).\textsuperscript{25} However upon adding the neutral dafMes\textsuperscript{H} ligand to 0.25 equiv. \([\text{RuCp}^*\text{(µ-Cl)}]\)\textsubscript{4}, \([\text{RuCp}^*\text{(dafMesH})]\)\textsubscript{Cl} was obtained. Since the mesityl groups prevent the \(N\)-donors from coordinating to the \([\text{RuCp}^*\text{(µ-Cl)}]\)\textsubscript{4} fragment, the \([\text{RuCp}^*\text{(µ-Cl)}]\)\textsubscript{4} fragment coordinates to the arene (Scheme 3).\textsuperscript{25} Interestingly two different linkage isomers of \([\text{RuCp}^*\text{(dafMes})]\) were formed, where the \(Ru\)\textsubscript{II} remains coordinated to the arene (Scheme 3).\textsuperscript{25} Interestingly two different linkage isomers of \([\text{RuCp}^*\text{(dafMes})]\), a sandwich complex and a zwitterionic complex, were formed depending on the reaction sequence.

A variety of heterobimetallic complexes can also be synthesized where the central cyclopentadienyl ring of 4,5-diazafluorene is coordinated to one metal centre and the nitrogen chelate is coordinated to a second metal centre, and the ligand displays either \(η^5,η^2-N_2N\) or \(η^5,κ^1-N\) coordination modes.\textsuperscript{27} For example, \([\text{PtPh}_2\text{(daf})]\) and \([\text{PtPh}_2\text{(dafMes})]\) can be metallated successfully with the \([\text{RuCp}^*\text{(µ-Cl)}]\)\textsubscript{4} to obtain \(Ru\)\textsubscript{II}–\(Pt\)\textsubscript{II} heterobimetallic complexes \([\text{RuCp}^*\text{(daf})\text{Pt(Ph)}_2]\) and \([\text{RuCp}^*\text{(dafMes})\text{Pt(Ph)}_2]\) (Scheme 5). These \(Ru\)\textsubscript{II}–\(Pt\)\textsubscript{II} heterobimetallic complexes can also be synthesized from the Ru sandwich complexes, \([\text{RuCp}^*\text{(daf})]\) and \([\text{RuCp}^*\text{(dafMes})]\) (Scheme 5).\textsuperscript{27} The \([\text{RuCp}^*\text{(dafMes})]\) sandwich isomer with a vacant \(N,N\)-chelate site and \(N\)-donor coordination can also serve as a metalloligand for the complexation with metal halides such as \(\text{CuCl}, \text{FeCl}_2(\text{THF})\)\textsubscript{1.5} and \(\text{CoCl}_2(\text{THF})\)\textsubscript{1.5} (Scheme 5).\textsuperscript{27}

II.3. Coordination chemistry of the phosphine donor functionalized dafp\textsuperscript{H} and dafp\textsuperscript{−} ligands

Our group also installed a phosphine arm at the C9-position of 4,5-diazafluorene to give the dafp\textsuperscript{H} ligand, which can also be deprotonated to form the dafp\textsuperscript{−} ligand. Both dafp\textsuperscript{H} and dafp\textsuperscript{−} have been used to assemble head-to-tail macrocycles with \({\text{RuCp}^*}\)\textsuperscript{+} (Scheme 3).\textsuperscript{25} We further demonstrated the transfer of dafp\textsuperscript{−} from \([\text{Cu(IPr)}\text{(dafp})]\)\textsubscript{n} (\(n = 1\) or 2) to either \(Rh\)\textsubscript{II} or \(Au\)\textsubscript{II} resulted in macrocyclic complexes (Scheme 6).\textsuperscript{28} There are a few benefits of constructing these macrocyclic \(Rh\)\textsubscript{II} and \(Au\)\textsubscript{II} complexes through ligand transfer from a \([\text{Cu(IPr)}]\)\textsuperscript{+} fragment, compared to the conventional synthesis by directly reacting the dafp\textsuperscript{−} salt with metal chloride starting materials. The benefits include improved yields, shortened reaction time, and simplified isolation of the product as the soluble \([\text{Cu(IPr)Cl}]\) byproduct can easily be removed by filtration. In addition, dafp\textsuperscript{H} and dafp\textsuperscript{−} are also ambidentate ligands with phosphine and \(N\)-donor coordination sites, while dafp\textsuperscript{−} can also anchor a metal in the P,C-coordination site. The dafp\textsuperscript{−} ligand displayed several coordination modes, where the diazafluorenyle moiety coordinates through one or both \(N\)-donors and the \(P\)-donor with or without the participation of the \(C\)-donor of the cyclopentadienyl-like moiety.

We also have demonstrated that in the heterodinuclear complex \([\text{NHC})\text{Cu(dafp)Pt(Ph)}_2]\) the tethered phosphine of dafp\textsuperscript{−} helps anchor the Pt\textsubscript{II} center onto the carbon site, and

![Scheme 5](image)

**Scheme 5** Synthesis of heterodinuclear Ru\textsubscript{II}–M complexes where the daf\textsuperscript{−} or dafMes\textsuperscript{−} ligand displayed \(η^5,κ^1\)-[\(N,N\)] or \(η^5,κ^1\)-[\(N\)] coordination modes.\textsuperscript{27}

![Scheme 6](image)

**Scheme 6** Synthesis of \([\text{Cu(NHC)}\text{(dafp})]\) from K[dafp], and the synthesis of macrocyclic complexes \([\text{Audp}(dafp)]_2\), \([\text{Rh(dafp)}(\text{COD})]_2\) through salt metathesis, and dafp\textsuperscript{−} ligand transfer from a \([\text{Cu(NHC)}]\) complex.\textsuperscript{28} In addition, the selective syntheses of Pt\textsubscript{II}–Cu\textsubscript{I} heterobimetallic complexes is shown.\textsuperscript{26}
the Cu(I) center is bound to the $N,N$-chelate site (Scheme 6).26

The synthesis of these Pt$^{II}$–Cu$^{I}$ heterobimetallics is highly regioselective, and can also be performed in one-pot (Scheme 6).26

II.4. Coordination chemistry of sulfur donor functionalized 4,5-diazafluorene derivatives

Baudron, Hosseini, and co-workers have created ambidentate ligands with sulfur donors and demonstrated their use in the stepwise synthesis of multimetallic complexes and coordination polymers.29–32 Both 4,5-diazafluoren-9-dithiolene ($L^1$) ligands30,32 and 4,5-diazafluoren-9-dithiolate ($L^2$)29,31,32 are generated in situ by the removal of propionitrile S-protecting groups using NR$_4$OH (Scheme 7). Both ambidentate dianionic ligands provide different chelates, a dithiolate or dithiolene chelate and the 4,5-diazafluorene moiety. The homoleptic mononuclear complexes of the generic form $[ML^1]_2$+[Ni$_4$Bu$_4$]$_2$ (where $M$ = Ni(II) or Hg(II)),30 and $[ML^2]_2$+[NEt$_4$]$_2$ (M = Ni(II), Pd(II), Zn(II), or Hg(II))31 can be synthesized (Scheme 7). The homoleptic complexes all have a central metal which is coordinated by the dithiolate or dithiolene moiety of the ligands, leaving the 4,5-diazafluorene chelate sites vacant. These mononuclear complexes form one-dimensional coordination polymers in the presence of Na$^+$ ions (Scheme 7).30,31 The heterotrimetallic complex $[(\text{cyclen})\text{Ni}]_2\text{Pd}[L^2]_2$[(BF$_4$)$_2$]$_2$ can be prepared where the $[(\text{cyclen})\text{Ni}]^{2+}$ fragment is coordinated to the 4,5-diazafluorenyl moiety via the $N,N$-chelate (Scheme 7).31 The 4,5-diazafluoren-9-dithiolate ligand can serve as a bridging ligand through the two anionic S-donors to assemble an octanuclear Cu complex $[\text{Cu}_8(L^2)_6]$$_4$ where the eight Cu centres occupy the vertices of a cube and on the periphery of the complex are the potentially chelating 4,5-diazafluorenyl moieties (Fig. 2).29

Heteronuclear metallamacrocycles can be constructed from $L^1$ and $L^2$ ligands (Scheme 8).32 The dianionic ligands are first metallated with (dppp)M$^1$Cl$_2$ (where M$^1$ = Pd, Pt, and dppp = 1,2-bis(diphenylphosphino)propane) which bears a diphosphine capping ligand allowing for a discrete neutral species of the general form $[(\text{dppp})\text{M}^1(L)]$ or $[(\text{dppp})\text{M}^1(L^2)]$ to be isolated, where both $L^1$ and $L^2$ ligands coordinate to M$^1$ through
II.5. Coordination chemistry of 9-hydroxy-9-alkynyl functionalized dafoH derivatives

The coordination chemistry of 9-hydroxy-9-alkynyl-4,5-diazafluorene derivatives which possess several potential sites of coordination has been explored.7,41,42 The 9-hydroxy-9-ethynyl-4,5-diazafluorene ligand can be dehydrated upon binding with a 16-electron coordinatively unsaturated species such as in situ generated [M(diphosphine)Cl]⁺ (M = Ru, Os)11 and [Ru(dppe)Cl]OTf precursor42 (Scheme 9). The resulting Ru and Os allenylidene complexes feature a vacant N₅-chelate which is a potential site for further coordination. Indeed this N₅-chelate moiety can be coordinated to a second metal centre to form Ru(II)-Ru(II) and Ru(II)-Re(I) multimetallic complexes.72

When the 9-hydroxy-9-phenylethynyl-4,5-diazafluorene ligand is reacted with K₂PtCl₄ or ZnI₂, the corresponding mononuclear complex forms with the metal bound to the N₅-chelate (Scheme 9).7 However the reaction of 9-hydroxy-9-phenylethynyl-4,5-diazafluorene with Co₂(CO)₈ led to a (μ-alkyne)-hexacarbonyldicobalt complex where the N₅-chelate remains unoccupied (Scheme 9).7

II.6. Coordination chemistry of the dafo ligand

Dafo has been used as a ligand for metals across the periodic table: Mn,43 Co,44,45 Ni,46-48 Cu,44,48-62 Zn,7 Mo,63 Ru,9,64-73 Pd,17,44,74-87 Ag,88-90 Cd,17,91,92 Re,93 Ir,93 Pt,17,81 Hg,48 and the lanthanides.50,94

II.7. Coordination polymers containing dafoH derivatives

Recently metal–organic frameworks (MOFs) have received substantial attention due to the wide variety of potential architectures arising from different metal–ligand combinations, and the possibility of creating materials with intriguing applications. A variety of MOFs with different architectures were constructed from Zn(II) ions, a variety of aromatic polycarboxylic acid ligands and a 4,5-diazafluoren-9-oxime ligand.98

The polynuclear Zn secondary building units (SBUs) comprising the various MOFs were modulated by the 4,5-diazafluoren-9-oxime ligand, which can coordinate to Zn either in a chelating or monodentate fashion.98

Azide containing MOFs can potentially be used as molecule-based magnets. A three-fold interpenetrating MOF of the general formula [Mn₉(μ₃-N₃)₈(μ₁-N₃)₉(L)₄] where L is the bis(bidentate) Schiff base ligand 4,5-diazafluoren-9-one azine exhibited spin-canted long-range ferromagnetic ordering.99

The L⁴ ligand served as the long link in the 3D structure while the chain of Mn₉(μ₃-N₃)₈(μ₁-N₃)₉ served as the SBU.99 A series of isostructural tetranuclear clusters [M₄(dafo)₄(N₃)₂][μ₁,1-N₃]₄-[μ₁,1,N₃]₂ have been synthesized with azido ligands bridging the four M²⁺ ions, and the dafo coordinated in a chelating fashion to the metal vertices of the clusters, where the metal can be Co,43,106 Mn,43 Cd,91 or Cu.49

A luminescent Ag(I) one-dimensional polymer chain of the generic formula [Ag₂(L⁵)₂(ClO₄)₃]ₔ where L⁵ = 4,5-diaza-9,9'-spirobiﬂuorene was structurally characterized.100 Both of the L⁵ ligands adopt a bis-monodentate bridging mode between the two crystallographically independent Ag(I) centres where the Ag–Ag distance is 2.776(1) Å, and one of ClO₄⁻ligands also bridges two adjacent Ag centres to construct the polymer chain (Fig. 3).101
The fullerene C₆₀ with four peripheral malonate groups can be functionalized with two 4,5-diazafluorenone moieties in the trans-1 positions, since 4,5-diazafluorenone is planar the N,N-chelates can be situated 180° relative to each other. The reaction between AgOTf and this large ditopic bis(4,5-diazafluorenone)tetrakis(malonate) substituted fullerene ligand (L⁶) gives a 1-D coordination polymer [Ag₂(L⁶)(OTf)₂], where each Ag(i) centre is four-coordinate and is bound to the Cd centres through both the N and S termini.

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III. Applications of 4,5-diazafluorenone derivatives

III.1. As actor ligands in reactivity chemistry

Most of inorganic and organometallic chemistry is dominated by metal centred reactivity where the ligand is a spectator, hence the term “spectator ligand”. There are emerging examples of ligand-centred, or metal–ligand cooperative reactivity where reactions with incoming substrates occur at the “actor ligands”. The use of multifunctional actor ligands in small molecule activation and catalysis has gained significant interest in the chemistry community and there are few recent reviews on this topic. There are several examples where 4,5-diazafluorenone derivatives behave as actor ligands, where the majority of the ligand-based reactions occur at the reactive C₉.

Rillema and co-workers have uncovered divergent chemical behaviour for coordinated dafo ligand and free dafo in reactions with nucleophiles. Free dafo reacts with 2-aminopyridine in ethanol to give a Schiff-base product (Scheme 10A), however under the same reaction conditions the coordinated dafo ligand of [Ru(bpy)₂(dafo)]⁺ reacts with 2-aminopyridine to give a ring-opened product possessing a coordinated esterified 2,2'-bipyridine ligand (Scheme 10B). In another example no reaction occurs between free dafo and DBU in wet dichloromethane (Scheme 10A), while coordinated dafo in [Ru(bpy)₂(dafo)]⁺ reacts with DBU to give another ring-opened product (Scheme 10B). The spectator metal centre plays a major role in altering the reaction pathways of dafo with nucleophiles; the driving force to form a coordinated 2,2'-bipyridine ligand from a coordinated dafo is the release of coordination-induced ring strain and the formation of shorter, stronger Ru–N bonds. There are two potential nucleophilic
sites in 2-aminopyridine, the amine and the pyridyl ring nitrogen atoms; the spectator metal ion increases the electron density on the carbonyl carbon atom of dafo thus hindering the reaction with the amine nitrogen and the formation of the Schiff-base product.71 Free dafo does not react with ethylene glycol, meanwhile coordinated dafo of [Ru(bpy)₃(dafo)₃]⁺ (n = 1 and m = 2, or, n = 0, and m = 3) reacts to give the corresponding ketal ligand coordinated to Ru(n) which is resistant to hydrolysis with HCl(aq) – a highly unusual feature compared with most organic ketals.72 Siemeling and co-workers synthesized the sandwich complex [Cp*Co(η⁴-dafo)], where the dafo ligand is coordinated through the π system leaving the [N,N]-chelate vacant.45 The {Cp*Co} fragment coordinates η² to each of the two six-membered de aromatized rings of dafo; this results in cyclopentadienone-like behaviour where the nucleophilicity of the oxygen atom is increased substantially versus free dafo.45 The nucleophilic, coordinated, cyclopentadienone-like dafo of [Cp*Co(η⁴-dafo)] reacts with electrophiles such as acetyl chloride to give the O-acylated cobaltocenium species (Scheme 10C); in contrast free dafo does not react with acetyl chloride (Scheme 10A).45

Our group discovered a surprising example of ligand-based reactivity: free 4,5-diazafluorene is air-stable but the coordinated 4,5-diazafluorene ligand in [Ru(dafo)(PPh₃)₂(H)(N₂)] can selectively undergo an aerobic oxidation reaction giving a coordinated dafo ligand (Scheme 11).66 The selectivity of this ligand-based oxidation reaction is surprising since the typically oxygen-sensitive phosphine ligands are left intact.

Our group also previously demonstrated an interesting example of metal–ligand cooperativity. The Ru(n) 4,5-diazafluorenide complex, [Ru(dafo)(PPh₃)₂(H)(N₂)], can be synthesized where the dafo⁻ ligand possesses a central negatively charged cyclopentadienyl like moiety that remains uncoordinated and thus has unquenched basicity (Scheme 12).21
Scheme 13  Two studies involving the formation of H2 from a co-ordinated dafH ligand. (A) Isolation of [Ti(Cp*)2(dafH)]2.23 (B) Synthesis of [Yb(Cp*)2(dafH)] from the stabilized biradical, [Yb(Cp*)2(dafH)], or the dinuclear complex, [(Yb(Cp*)3)2(bdafH2)].24

LUMO+1 of 2b1 symmetry has unpaired spin density at the 9-position carbon, this orbital is possibly responsible for the chemistry observed.24 The unpaired spin density at the 9-position aids in the cleavage of the C–H bond to give the dinuclear Yb complex.

Our group also investigated the reactivity of the zwitterionic Ru(ii) diazafluorenide complex [Ru(def)(PPh3)2(H)2[N2]] toward CO2 and uncovered an interesting example of ligand-based reactivity.115 At room temperature [Ru(def)(PPh3)2(H)2[N2]] selectively and reversibly undergoes a formal insertion of CO2 into a remote ligand C–H bond to generate a monoanionic 4,5-diazafluorenyl-9-carboxylic acid ligand (dafCO2H−) on Ru(ii) (Scheme 12).115 The activation of CO2 in our system occurs at the ligand backbone remote from the metal centre where the metal’s role is to adjust the nucleophilicity of the ligand-based carbanion, the acidity of the C–H bond involved in proton migration, as well as the strength of the newly formed C–C bond. Given the unusual situation of having an actor ligand and a spectator metal centre, a variety of spectator metal centres were used to tune the reactivity and electronics of the actor def− ligand for tandem CO2 and C–H activation.24 Since Rh(III) is isoelectronic with Ru(ii), the complex [Rh(def)(PPh3)2(H)2] also reacts with CO2 in an analogous way where CO2 reversibly inserts into the C–H bond of the ligand backbone (Scheme 14).22

In contrast, when the more electron-rich Rh(i) complex [Rh(def)(PPh3)2] is placed under CO2, a dinuclear Rh(i) complex, [[Rh(PPh3)2(defCO2)]], is formed where the two Rh(i) centres are bridged by a dianionic 4,5-diazafluorenyl-9-carboxylate ligand (dafCO2−), along with the formation of free dafH (Scheme 14).22 The result of tuning def− with a more electron rich metal centre is the increased basicity of the ligand-based carbanion which can deprotonate the carboxylic acid initially formed from CO2 insertion into the ligand C–H bond. This proton transfer gives [Rh(defH)(PPh3)2]2+ and [Rh(dafCO2)(PPh3)2]2−; the carboxylate of the latter replaces the dafH ligand of the former to yield the dinuclear product.22 As a result CO2 is trapped by the second metal centre, and also there is no proton on O that can engage in proton transfer necessary for the decarboxylation.22 The dinuclear [[Rh(PPh3)2( defCO2)] complex was reacted with H2 to attempt ligand-based CO2 reduction.116 A series of stepwise stoichiometric reactions with H2, NMR experiments at low temperatures with added PPh3 or CO2, along with 13C-labelling experiments were conducted in an attempt to gain some mechanistic insight.116 Upon the addition of a CO2 and H2 gas mixture to [[Rh(PPh3)2(defCO2)]−], a mixture of the carboxylated Rh(III) complex [Rh(defCO2)(PPh3)2(H)2] and [Rh(PPh3)2(H)2(k2-HCO2)] results (Scheme 14).116

It is worth noting that the carboxylic acid intermediate in the reaction between [Rh(def)(PPh3)2] and CO2 could not be isolated or even observed in NMR experiments, presumably because the highly basic carbanion in [Rh(def)(PPh3)2] is formed from CO2 insertion into the ligand C–H bond and the decarboxylation of [Rh(def)(PPh3)2(H)] under an N2 atmosphere. In both cases, a dinuclear Cu(i) complex [[Cu(IPr)2(defCO2)] and dafH are obtained as thermodynamic products (Scheme 15).22 In both the Cu(i) and Rh(i) cases, the metal 4,5-diazafluorenyl and the metal 4,5-diazafluorenyl-9-
carboxylic acid complexes react with each other in solution, in contrast to the less electron rich Ru(II) and Rh(III) systems.

III.2. 4,5-Diazafluorene derivatives as ligands in catalysis

Nitrogen-donor ligands have been used extensively in oxidative aerobic organic transformations, especially given their robustness versus traditional phosphine ligands under oxidizing reaction conditions. Stahl and co-workers initially explored the use of 4,5-diazafluorene derivatives in oxidative organic reactions where O₂ is the oxidant.⁷⁶ A variety of nitrogen-donor ligands were screened in the Pd-catalyzed aerobic allylic acetoxylation of allylbenzene; most of the ligands screened gave low yields of the cinnamyl acetate product (Table 1).⁷⁴ Conversely, when 9,9-dimethyl-4,5-diazafluorene (Me₂daf) was used as the ligand, a 50% yield of cinnamyl acetate was obtained, the yield was further improved to 81% when dafo was used as the ligand. The structures of 4,5-diazafluorene derivatives seem to have a large impact on the catalytic results obtained relative to the other nitrogen-donor ligands tested. Both the ability of dafo to withdraw electron density through π back-bonding and the unique ligand bite angle may play a role in catalysis. Recently Stahl reported the mechanistic investigations where they suggest that the dafo ligand promotes the C–O reductive elimination, but further studies are needed.⁷⁷ Stahl and co-workers have also demonstrated the use of 4,5-diazafluorene derivatives as ancillary ligands in the aerobic Pd-catalyzed cross-coupling of indoles with benzene.⁷⁵ The regioselectivity for arylation at the C2- vs. the C3-position of the indole compound was dramatically affected by the identity of 4,5-diazafluorene derivative and the anionic ligand used (Scheme 16).⁷⁵ Stahl,⁷⁸ along with Zhao and Huang,⁸⁰ independently and simultaneously reported the use of the dafo ligand in Pd-catalyzed aerobic dehydrogenation to form double bonds.⁷⁸,⁸⁰

Table 1 Nitrogen-based ligand screen in the Pd-catalyzed aerobic allylic acetoxylation of allylbenzene

9,9-dimethyl-4,5-diazafluorene (Me₂daf) was used as the ligand, a 50% yield of cinnamyl acetate was obtained, the yield was further improved to 81% when dafo was used as the ligand.⁷⁴ The structures of 4,5-diazafluorene derivatives seem to have a large impact on the catalytic results obtained relative to the other nitrogen-donor ligands tested. Both the ability of dafo to withdraw electron density through π back-bonding and the unique ligand bite angle may play a role in catalysis. Recently Stahl reported the mechanistic investigations where they suggest that the dafo ligand promotes the C–O reductive elimination, but further studies are needed.⁷⁷ Stahl and co-workers have also demonstrated the use of 4,5-diazafluorene derivatives as ancillary ligands in the aerobic Pd-catalyzed cross-coupling of indoles with benzene.⁷⁵ The regioselectivity for arylation at the C2- vs. the C3-position of the indole compound was dramatically affected by the identity of 4,5-diazafluorene derivative and the anionic ligand used (Scheme 16).⁷⁵ Stahl,⁷⁸ along with Zhao and Huang,⁸⁰ independently and simultaneously reported the use of the dafo ligand in Pd-catalyzed aerobic dehydrogenation to form α,β-unsaturated aldehydes, ketones, esters, and azobenzenes (Scheme 17). Typically enones and other α,β-unsaturated carbonyl compounds are prepared in stepwise protocols. The aerobic Pd-dafo catalyzed reaction is a much more efficient alternative.

Recently it has been shown that dafo is an effective ligand for the Pd-catalyzed aerobic dehydrogenative Heck reaction to couple furans and thiophenes with cinnamic acid and stilbene derivatives.⁸⁵ In addition a variety of alkenes could be coupled with ferrocene using a Pd dafo catalyst in an aerobic dehydrogenative Heck reaction (Scheme 18).⁸³ A combination of kinetics, competition and ESI-MS (to characterize catalytic intermediates) experiments suggest that dafo plays a role at each stage of the catalytic cycle, i.e., the dafo influences C–H bond activation, insertion of alkenes, the stereo-selective step, and the regeneration of the catalyst with O₂.⁸⁵
Elsevier and co-workers have looked at the influence of various nitrogen chelates on Pd catalyzed C-C bond formation reactions.79 Zerovaent mono and binuclear palladium and platinum bis(quinone) complexes of dafH and dafo have been prepared, where the 4,5-diazafuorene derivative either acts as a chelate, monodentate, or bridging ligand.17,81,82 In the reaction of cinnamyl chloride with benzyl Grignard, the regioselectivity when palladium complexes of 4,5-diazafuorene derivatives are used is extremely high for substitution at the less substituted allylic carbon with less than 5% of the homocoupling product, a sharp contrast to when phoshine complexes are used.79

[Rh(daf)(COD)] can catalyze the hydrogenation of olefins, however it is not as fast a catalyst as [Rh(PPh₃)₃Cl] or [Ru(PPh₃)₃Cl₂], and does not hydrogenate internal olefins.19 Wilkinson’s catalyst [Rh(PPh₃)₃Cl] dissociates in solution and produces hydride species under H₂. In contrast, no hydride was observed when a solution of [Rh(daf)(COD)] was exposed to H₂.

[Rh(dafH)[PPh₃]₂(H)Cl] was also found to be a selective olefin hydrogenation catalyst, and can even hydrogenate internal olefins and substrates with pyridyl or carbonyl groups.20 The chloride counterion appears to play a role in catalysis, i.e., if the counterion is replaced with triflate the catalyst [Rh(PPh₃)₃Cl] dissociates in solution and produces hydride species under H₂. In contrast, no hydride was observed when a solution of [Rh(daf)(COD)] was exposed to H₂.

Recently it was shown that 1,5-dihydro-2H-cyclopenta[2,1-b:3,4-b'j]dipyrindin-2-one [a 4,5-diazafuorene derivative with keto-enol tautomerism], L⁷, can be coordinated to Ru(II) to give [Ru(L⁷)[bpy]₂][PF₆]₂.117 [Ru(L⁷)[bpy]₂][PF₆]₂ was used as a photosensitizer in dye-sensitized solar cells (DSSCs) and as a catalyst for the transfer hydrogenation of ketones.117

The complex [MoO₂Cl₂(dafo)] was quite an active and selective olefin epoxidation catalyst when compared with other phosphine ligands and substrates with pyridyl or carbonyl groups. The chloride counterion appears to play a role in catalysis, i.e., if the counterion is replaced with triflate the complex is inactive towards olefin hydrogenation. Exogenous chloride anions however appear to slow down the catalysis.

One interesting catalytic application of 4,5-diazafuorene derivatives is the introduction of a catalytically active metal to the surface of nanoparticles to create nanocatalysts. Silica-coated magnetite nanoparticles (SMNPs) were silanated with 3-aminopropyltriethoxysilane, the exposed –NH₂ group was reacted with dafo to give the imine that was subsequently reduced to the amine (Scheme 21A).120 The 4,5-diazafuorene-functionalized SMNPs were coordinated with Pd(II) to give a Pd-4,5-diazafuorenyl SMNP catalyst for C(sp²)–H amination (Scheme 21B).120 An elegant feature of this heterogeneous SNMP nanocatalyst is that it can be separated from the reaction mixture by using an external magnet, and reused successfully in subsequent cross-coupling reactions. Using a similar protocol silica nanospheres were functionalized with a 4,5-diazafuorene-imine group, and subsequently reacted with ferric chloride.121 The silica nanosphere-based iron nanocatalyst was used to perform the one-pot coupling reaction of a terminal alkyne, dichloromethane, and amines to give propargylamines.121 In addition, the silica nanosphere-

![Scheme 18](image1.png)

**Scheme 18** Pd-dafo-catalyzed aerobic Heck coupling reaction of an alkene with ferrocene.83

![Scheme 19](image2.png)

**Scheme 19** (A) α-Vinylidenation of aldehydes to give trisubstituted allenes, or an α-vinylidenation/γ-vinylidenation cascade to give tetra-substituted allenes.118 (B) Aerobic C–C bond cleavage reaction with aldehydes which yields an ynone product. Both reactions are catalyzed by an Au–dafo/amine catalyst system.119

![Scheme 20](image3.png)

**Scheme 20** Pd catalyzed aerobic aryl C–H amination.86
based iron catalyst could be recycled at least seven times without any appreciable loss of catalytic activity.\textsuperscript{121}

### III.3. Photophysical and photochemical applications

#### III.3.1. As photosensitizers.

Ru complexes of dafo of the form [Ru(dafo)\_n(bipyridine ligand)]\_2^{2+} were studied as analogues to the well-known [Ru(bpy)]\_3^{2+} complex because of their potential applications as photosensitizers in photochemical water-splitting processes and DSSCs. Replacing one bpy ligand in the parent complex [Ru(bpy)]\_3^{2+} with a dafo ligand results in very little change in the room temperature absorption spectra, and very little change in the low temperature emission spectra ($\lambda_{\text{max}} (77 \text{ K}) = 578 \text{ nm}$ for [Ru(bpy)]\_3^{2+}, $\lambda_{\text{max}} (77 \text{ K}) = 574 \text{ nm}$ for [Ru(dafo)(bpy)]\_2^{2+} in EtOH/MeOH (4:1)).\textsuperscript{9,10} The most substantial difference is that the emission quantum yield of [Ru(bpy)]\_3^{2+} in water ($\phi (298 \text{ K}) = 0.042$, $\tau (298 \text{ K}) = 630 \text{ ns}$) is 50 fold larger than that of [Ru(dafo)(bpy)]\_2^{2+} ($\phi (298 \text{ K}) = 8 \times 10^{-4}$) and the lifetime of [Ru(dafo)(bpy)]\_2^{2+} was so short that it could not be determined.\textsuperscript{9,10} The dafo ligand with a longer N–N distance was found to be lower than bpy in the spectrochemical series which translated into an energetic lowering of ligand field excited states and a dramatic decrease in emission intensity on approaching room temperature.\textsuperscript{9,10}

A series of multinuclear Ru(\textit{n}) complexes supported by multinucleating ligands possessing two or more chelating 4,5-diazafluorenmoieties have been explored.\textsuperscript{122–138} The spacers between the coordinating 4,5-diazafluorenyl moieties have been varied substantially to allow for the metal–metal separation, and the degree of intramolecular charge transfer to be finely tuned. In some cases disappointingly the Ru(\textit{n}) complexes had extremely short excited state lifetimes at room temperature on the order of ~0.03 ns (e.g., Ru complex of the ditopic ligand with an adamantyl spacer).\textsuperscript{122}

One of the major challenges in the field of DSSCs is to identify molecules that can efficiently harvest sunlight when incorporated into mesoscopic semiconductor thin films such as mesoporous TiO\_2. Ru(\textit{n}) complexes of 4,5-diazafluoren derivatives have been investigated as sensitizers for TiO\_2, especially for their ability to inject electrons into TiO\_2 from their excited states. Following adsorption of [Ru(dafo)(bpy)]\_2^{2+} onto TiO\_2 it was noted by Heuer, Meyer and coworkers that the dafo ligand engaged in a ring-opening reaction resulting in a coordinated 3-(CO\_2H)-2,2'-bipyridine ligand with the carboxylate group anchoring the complex to TiO\_2.\textsuperscript{6,5} The control experiment of independently anchoring the analogous Ru(\textit{n}) complex of 3-(CO\_2H)-2,2'-bipyridine gave comparable results; however, the excited-state injection yield for the [Ru(dafo)-(bpy)]\_2^{2+}/TiO\_2 system was consistently lower.\textsuperscript{6,5} Ru(\textit{n})-dafo complexes with either one or two 4,4'-dicarboxy-2,2'-bipyridine (dcbpy) ligands to anchor the complex onto TiO\_2 have also been explored.\textsuperscript{69,139} The thermal stability of [Ru(dafo)(dcbpy)(SCN)]\_2 at high temperatures has also been investigated where the final products are Ru and Ru\_2; again the ring-opening of dafo seems to play a role in complex decomposition.\textsuperscript{64} Another ligand design tested to anchor Ru(\textit{n}) polypyridine complexes to TiO\_2 was an ambidentate ligand (4,5-diazafluoren-9-ylidene)-malonic acid (dfm), which has a 4,5-diazafluorenyl chelate functionalized at the 9-position with carbazole groups,\textsuperscript{140} ary1 groups,\textsuperscript{144} or bis(thiophene)pyrrolyl groups,\textsuperscript{139} have all been used to create DSSCs based on TiO\_2.

#### III.3.2. As emitters.

Light-emitting electrochemical cells (LECs) are an attractive alternative to organic light-emitting diodes (OLEDs). LECs can be easily prepared with a solution-based process as they only require a single emissive layer, use air-stable electrodes such as gold, and can operate at very low voltages with high power efficiencies.\textsuperscript{145–148} Cationic Ir(\textit{m}) complexes of 4,5-diazafluorene derivatives, which are conductive and phosphorescent, can be used effectively in LECs.

Cationic Ir(\textit{m}) complexes of the form [Ir(\textit{L})\_3(dfppz)]\_2\_n[PF\_6] (\textit{n} = 5, 8, 9, 10, 11) with cyclometallated 1-(2,4-difluorophenyl)-pyrazole (dfppz) have been prepared, where the parent 4,5-diaza-9,9'-spirobi fluorourene ligand (L\textsuperscript{1}) is substituted at the 3,6-positions with one (L\textsuperscript{9}) or two (L\textsuperscript{10}) pendant phenyl groups (see Fig. 5 for labelling scheme).\textsuperscript{148} Interestingly these pendent phenyl groups can engage in π–π stacking interactions with the dfppz ligand(s) within complexes; these interactions may limit the elongation of the Ir–ligand bonds in the excited state protecting the metal centre.\textsuperscript{148}

A white-light emitting LEC was created using a mixture of red-, green- and blue-emitting cationic Ir(\textit{m}) complexes, where the green and blue emitters have 4,5-diazafluorene derivatives substituted at the C9-position with gem-diaryl (L\textsuperscript{10}) or gem-dialkyl (L\textsuperscript{11}) groups (Fig. 5).\textsuperscript{146} Substitution at the C9-position was found to be crucial for the synthesis of Ir(\textit{m}) complexes with high photoluminescence quantum yields.\textsuperscript{146} Likewise, Ir(\textit{m}) complexes [Ir(L\textsuperscript{1})(ppy)]\_2\_n[PF\_6] (where ppy is a cyclometallated 2-phenylpyridine derivative) A and B (Fig. 5) show high...
electroluminescence efficiencies: 7.1%, 22.6 lm W\(^{-1}\) for orange A, and 7.1%, 26.2 lm W\(^{-1}\) for green B,\(^{145}\) owing to the spirotwisting structural feature of L\(^1\), which limits self-quenching phenomena without greatly perturbing the energy gaps of the compounds.

A conceptually interesting approach toward incorporating three functions into a single molecule, a luminescent chromophore with hole and electron transport capability was explored by the Wong group. In luminescent Ir(III) complex C (Fig. 5), the ligand L\(^{2}\) has an electron-transporting 4,5-diazafluorene site, and hole-transporting \(-\text{NPh}_2\) groups.\(^{147}\) Unfortunately the LEC device performance using this tri-functional Ir(III) complex was rather low. There is no MLCT contribution to the lowest transition for the complex in the triplet state.\(^{147}\)

Luminescent lanthanide complexes exhibit very sharp emission bands. The design and tuning of sensitizing ligands that allow for efficient ligand-to-metal energy transfer is an area of particular interest. Luminescent lanthanide tris(β-diketonate) complexes of various 4,5-diazafluorene derivatives such as dafH,\(^{94–96,149}\) 9,9-diaryl substituted 4,5-diazafluorene,\(^{150}\) 4,5-diazafluoren-9-amine derivatives,\(^{151}\) and 4,5-diaza-9,9′-spirobi- fluorene\(^{152}\) have been synthesized and characterized. Several of these lanthanide complexes exhibit NIR luminescence\(^{94–96}\) and photo- and electroluminescence,\(^{150,152}\) and even triboluminescence.\(^{149}\)

Green phosphorescent Re(II) complexes of various 4,5-diazafluorene derivatives have been investigated for their performance in OLEDs.\(^{153–156}\) In comparing [Re(N\(^\Lambda\)N)(CO)\(_3\)]Br type complexes of dafoH and a 9,9-di(ethoxyphenyl) substituted 4,5-diazafluorene derivative, both complexes give approximately the same emission wavelength, however the complex with bulky groups at the C9 position alleviates to a large extent the self-quenching at high doping concentrations.\(^{153}\) A dinuclear Re(II) complex of 9,9′-bi-4,5-diazafluorenyl can serve as a highly efficient green phosphorescent emitter in OLEDs with a maximum luminance of 2026 cd m\(^{-2}\) and a peak current efficiency of 8.2 cd A\(^{-1}\).\(^{154}\) Non-doped devices containing [L\(^1\)]\(\text{Re(CO)}_3\)]Br had outstanding performance with a further improved peak luminance of 8531 cd m\(^{-2}\) and maximum current efficiency of 16.8 cd A\(^{-1}\).\(^{156}\)

The phosphine Cu(I) complexes of 3,3′-methylene-4,4′-diphenyl-2,2′-biquinoline (mdpbq) exhibited red phosphorescence (Fig. 6).\(^{157}\) Complexes of the extremely rigid mdpbq ligand showed decent photoluminescence quantum yields in 20 wt% poly{methylmethacrylate} (PMMA) films, 0.56 and 0.43 for [Cu(mdpbq)(PPh\(_3\))\(_2\)]\(\text{BF}_4\)]\(\) and [Cu(mdpbq)(DPEphos)]\(\text{BF}_4\)], respectively.\(^{157}\) The OLEDs doped with these Cu(I) complexes gave a current efficiency up to 6.4 cd A\(^{-1}\) for a multi-layer device.\(^{157}\)

Ag–dafo complexes with either carborane-based diphosphines, or simple classical diphosphine ligands of the general formula [Ag(dafo)(P–P)]OTf are luminescent. The emissions seem independent of the phosphine ligand or the coordination environment of the Ag\(^+\) ion.\(^{158}\) The free dafo emits at 537 nm (τ = 5 ns), while the luminescent Ag–dafo complexes emit across the blue to orange region of the spectrum with lifetimes also in the ns range, similar to free dafo.\(^{158}\) The dafo ligand centred transitions seem to be responsible for the luminescence behaviour of [Ag(dafo)(P–P)]OTf and [Ag(dafo)(PPh\(_3\))OTf] complexes, where the electron density at the Ag centre tuned by the different phosphine ligands modified the emission energy.\(^{158}\)

### III.3.3. As harmonophores in non-linear optics

There is great interest in utilizing coordination complexes as harmonophores with second-order non-linear optical (NLO) properties since the metal centres offer additional means of tuning the electronic properties which affect the NLO response. The metal centres could not only allow for either metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT) to take place, but also modulate the energy of intraligand charge transfer (ILCT) transitions. Moreover, the metal centre is tunable in terms of the identity of the metal element, oxidation state, and coordination sphere. Complexes of 4,5-diazafluorene derivatives have found use in this field.

Ir complexes of the form [Ir(L\(^\Lambda\)L)\(\text{ppy})\)]\(\)\(^{157}\) where the bidentate L\(^\Lambda\)L is either dafoH, 9-fulleriden-4,5-diazafluorene, or cyclo- metallated 9-fulleriden-4-azafluorene can be used as harmonophores with second-order NLO properties.\(^{159}\) The introduction of the fullerene moiety weakens the interaction between the cationic Ir(III) complex and the anion, which also leads to an overall increase in the NLO response with large and negative \(\mu_\parallel\) values (−600 to −2190 × 10\(^{-4}\) esu).\(^{159}\) For the charge neutral complex with cyclo- metallated 9-fulleriden-4-azafluorene ligand the \(\mu_\perp\) value is lower than the cationic complexes.\(^{159}\) In addition the second-order NLO properties of...
Ru(n) complexes of the forms [Ru(N\(^{+}\)N)(PPh\(_3\)]\(_2\)Cl\(_2\)] and [Ru(N\(^{+}\)N)(CO)\(_3\)]Cl\(_2\)] where the N\(^{+}\)N chelate is either dafH or 9-fulleriden-4,5-diazafluorene, have also been examined.\(^{165}\)

The greater absolute values of \(\mu_{1,907}\) for complexes with the fullerene substituted ligand compared to those with unsubstituted dafH suggest the importance of a highly polarizable C\(_{60}\) group.\(^{165}\)

Ru(n) bipyridine complexes of 4,5-diazafluorene-9-imine derivatives with long alkyl chains off of the imine moiety have been incorporated as surfactants into Langmuir–Blodgett thin films and have activities for second order harmonic generation that are 2.6 to 3.6 times greater than that of the organic standard (E)-N-methyl-4-(2-(4-octadecyloxyphenyl)ethenyl)-pyridinium iodide.\(^{161}\) Similarly [Re(N\(^{+}\)N)(CO)\(_3\)] complexes of similar 4,5-diazafluorene-9-imine derivatives can also be incorporated into stable Langmuir–Blodgett thin films, though a lower than expected measurement for the second-order harmonics NLO signal was observed.\(^{162}\)

Zn(n) complexes of the highly conjugated push–pull 4,5-diazafluorene-9-ylidine ligand family terminated with either an N\(_2\)-N-dibutylamino or an azulenyl moiety exhibit amongst the highest reported \(\mu_{1,907}\) value for a Zn(n) complex.\(^{163}\) With respect to the free ligands, coordination to Lewis acidic Zn(n) enhances the \(\mu_{1,907}\) value presumably by red-shifting the ILCT transition.\(^{163}\)

**III.3.4. As luminescence sensors.** Ru polypyridine complexes of 4,5-diazafluorene derivatives possessing a crown ether moiety attached to the ligand backbone have been synthesized. In most cases the binding with alkali metal cations was studied, where both the spectroscopic and electrochemical properties of the complex were perturbed by cation binding.\(^{131,135,137,164,165}\)

Duan, Bai, and coworkers reported [Ru(L\(_{13}\)](bpy)\(_2\)]\(_2^+\) (where L\(_{13}\) is 4,5-diazafluoren-9-one-2,4-dinitrophenylhydrazide) as a selective chromo- and fluorogenic dual responding fluoride sensor.\(^{166}\) Not only does the presence of F\(^-\) enhance the luminescence intensity but also triggers a dramatic color change from yellow to magenta. The Ru(n) complex could even be adsorbed onto paper to allow for the preparation of colorimetric testing strips for F\(^-\) concentration in water. Interestingly, even when the concentration of F\(^-\) is as low as 1 mg L\(^{-1}\), the color change is visible to the naked eye.

**IV. Conclusions**

Since the first report on the synthesis of dafH, the chemistry of dafH derivatives as ligands has evolved into a vibrant field. From the fundamental chemistry point of view, the parent compounds dafH and dafo can be derivatized in many ways to achieve the desired functions. In particular, the functionalization at the C9 position has been in the spotlight for generating new ligand series. Many of the ambidentate derivatives have been utilized to construct coordination polymers, self-assembled macrocycles, and heteromultimetallic complexes with great specificity. The reactive nature of the 9-position of dafH, dafo amongst other ligands gave raise to the actor-ligand behavior in the corresponding metal complexes, which distinguish dafH derivatives from bpy. From an applications point of view, dafH derivatives have found use in many areas.
Their use as ancillary ligands in catalysis has been fruitful, especially in transformations performed under oxidizing conditions. The photochemistry and physics of metal complexes of 4,5-diazafluorene derivatives have been studied as emitters in solid state lighting, photosensitizers in DSSCs, and harn- 

References


