Micro Amounts, Mixed Powders, Great Structural Insights

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Crystal structures are critical to unambiguously determine a compound's identity, absolute configuration, molecular connectivity and crystal form, as well as whether polymorphs coexist or how the solid-state structure may explain a compound's behavior and physical properties. X-ray crystallography is the most commonly used method to obtain crystal structures, but it can be limiting if samples with suitable crystallinity, dimensions and quantity are lacking.

Electron diffraction offers a new solution by providing high-resolution structural insights from submicron-size samples.[1] Scratching the bottom of a beaker to gather nanograms of a crystalline powder may suffice for electron diffraction study. In other words, electron diffraction allows for single-crystal crystallography to be performed on powder samples … grain by grain. This allows for solving crystal structures that were previously unsolvable, but also screening crystallization conditions and automating polymorphs screening over hundreds of nanocrystals spread on a TEM grid.[2]

We will review the fundamentals of electron diffraction, the best practices for sample preparation and demonstrate how it is reshaping research in fields such as pharmaceuticals and natural products.

Figure 1. The XtaLAB Synergy-ED.

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Selective Formation of a 1,2-Diborane(4) and Alcohol-Driven B-B Bond Cleavage to Generate H_2

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Diborane(4), compounds having the chemical formula B_2R_4, are generally used in the form of $B_2(OH)_4$, $B_2(NMe_2)_4$, and B_2pin_2.[1,2] Given their unique reactivity, diboranes(4) (especially $B_2(OR)_4$) have been successfully employed in a variety of transformations, such as: 1,2- and 1,4-diborations, hydroborations, boryl substitutions, catalytic borylation, and Suzuki-Miyaura couplings.[1] However, recent research has exploited their reductive chemistry as an alternative and more sustainable pathway towards hydrogenation or deoxygenation transformations.[2] Literature shows examples of diboranes(4) working with and without a transition metal (TM) to perform hydrogenations using H_2O as the hydrogen source.[2] However, those without TMs often require long reaction times and high temperatures. Herein, we disclose the synthesis of a 1,2-diborane(4) (**Figure 1.**) and probe its reductive chemistry using a series of alcohols (MeOH, MeOD, PhOH). This molecule reduces alcohols in <15 min and releases H_2 as well as borate esters as byproducts. Experimental and computational methods were undertaken to probe the mechanism.

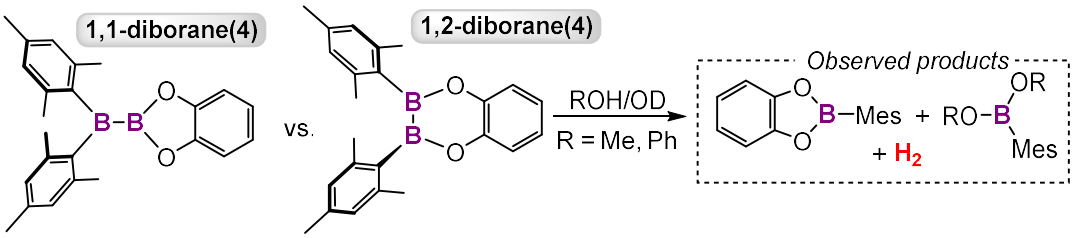

Figure 1. Isomers of Diborane(4)

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Rigid Diboron Compounds for Property and Reactivity Study

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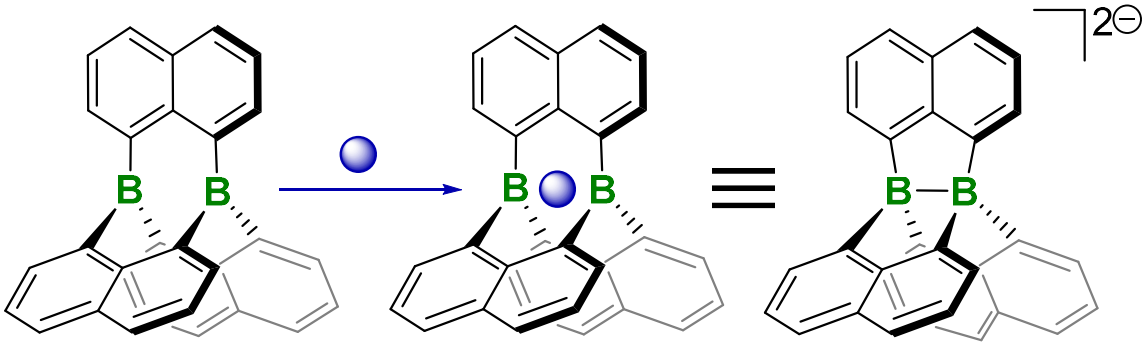
For main group chemists, rigid structures are indispensable tools for constructing constructing scaffolds with precise geometries, enabling applications from catalysis to bioimaging. The study of electron-precise B–B covalent bonds has provided immense insight into the fundamentals of bonding theory. Recently, our group has reported a doubly-bridged diborocine heterocycle, which features the longest B–B ever observed, owing to strain induced by its rigid naphthalene backbone.[1] Based on this, in this presentation we report the synthesis, characterization, and reactivity a series of diboron compounds. Inspired by the stability and novel reactivity imparted by the rigid naphthalene framework,[2] with similar method we synthesized and fully characterized a trinaphthodiborane. Reduction of the trinaphthodiborane afforded a diborapropellane, effectively an encapsulated single electron. Additionally, hydride adduct of the trinaphthodiborane provides a promising platform for studying quantum tunneling through an isomerization process according to density functional theory (DFT) calculations. Collectively, this research exploits rigid naphthalene scaffolds to construct unique diboron architectures, pushing the boundaries of bond theory, developing new paradigms in main-group chemistry.



A diborapropellane via electron encapusulation

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Novel Pincer Ligands for the Synthesis of Stable Polystannanes with Improved Solubility

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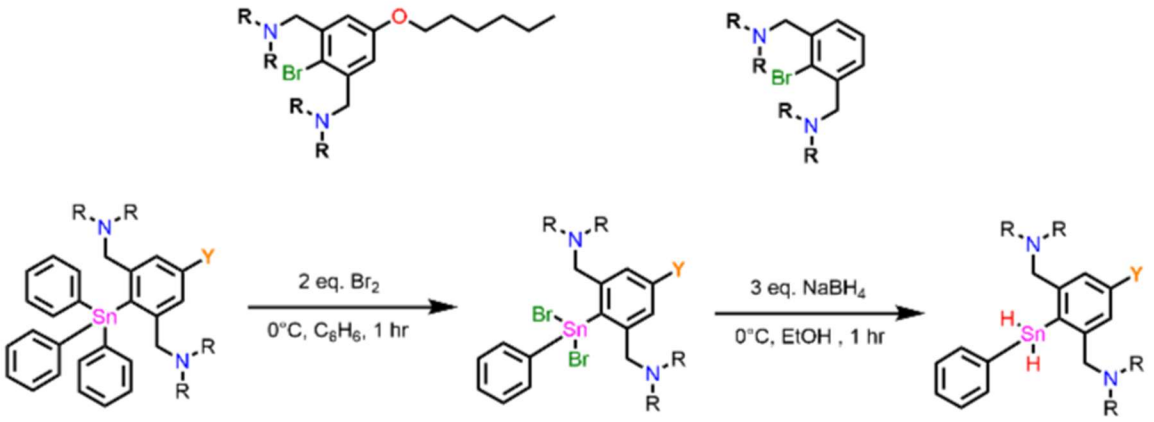
Polystannanes are a class of metallic polymers constructed of catenated tin atoms connected via covalent single bonds. The large and diffuse nature of the Sn-Sn single bonds provide a delocalization effect across the polymer backbone leading to narrow bandgaps which open the possibilities for semiconductor applications. While various methods for the synthesis of higher molecular weight fractions exist, the vulnerability of polystannanes to ambient light and moisture remains a principle challenge in their development.[1] Recent work from the Foucher group has demonstrated that 5-coordinate organotin dihydrides with CO- and CN- chelating ligands can produce stable polystannanes through metal catalyzed dehydropolymerization, although achieving molecular weights higher than 40 kDa still remains a challenge due to their low solubility in organic solvents.[2] Derivatives of van Koten style pincer ligands thereby provides a potential route to increasing the solubility and processibility of the polystannanes in organic solvents while also maintaining the stabilizing effect from the chelating atoms. This work reports the synthesis of pincer ligands and the related tin monomers expected to yield stable polystannanes with improved molecular weights, and processibility in organic solvents.



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Group 4 Borataallenyl Complexes: Synthesis and Small Molecule Reactivity

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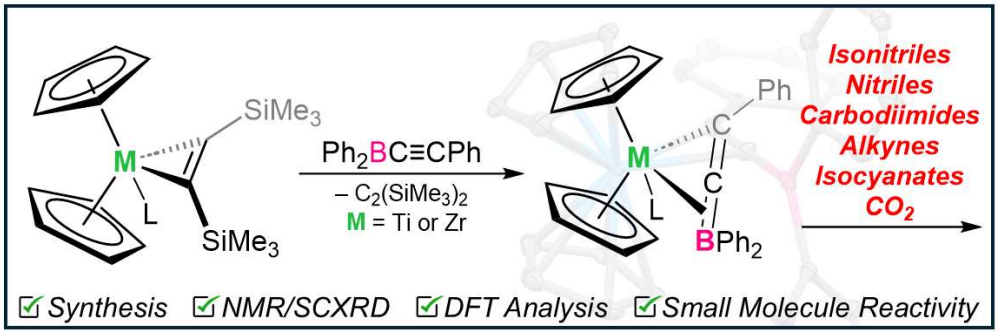
The substitution of a CR group in a hydrocarbon π-ligand for an isoelectronic BR^- unit has provided new opportunities for modification of the electronic environment at a coordinated metal center. However, while cyclic boron-containing π-ligands such as boratabenzenes ($[C_6H_5BR]^-$) and borollides ($[C_5H_4BR]^{2-}$) are well established in the literature, the chemistry of acyclic species (e.g., borataalkene and borataallyl ligands) is significantly less developed; likely in part due to the higher reactivity of acyclic π-ligands relative to cyclic analogues.[1,2] To the best of our knowledge, there are only two literature reports describing complexes with structural features consistent with borataallenyl character.[3,4]

Herein, we discuss the synthesis, structural characterization, computational analysis, and reactivity of early transition metal-borataallenyl complexes, $[Cp_2M(\eta^3\text{-}PhC_2BPh_2)(L)]$ (M = Ti, L = none; M = Zr, L = py). The reactivity of these complexes was explored with a range of unsaturated small molecules, including carbodiimides, alkynes, and isonitriles, and was found to differ significantly from that of boron-free metallacyclopropene complexes (one resonance structure of the borataallenyl complexes is a metallacyclopropene complex with a BPh_2 substituent). This work expands the chemistry of acyclic boron-containing π-ligands and highlights the extent to which boron incorporation in a π-ligand framework can impact bonding and reactivity.



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Investigations of Ligand Design and Base Effects in the Pd – Catalyzed Buchwald - Hartwig Amination

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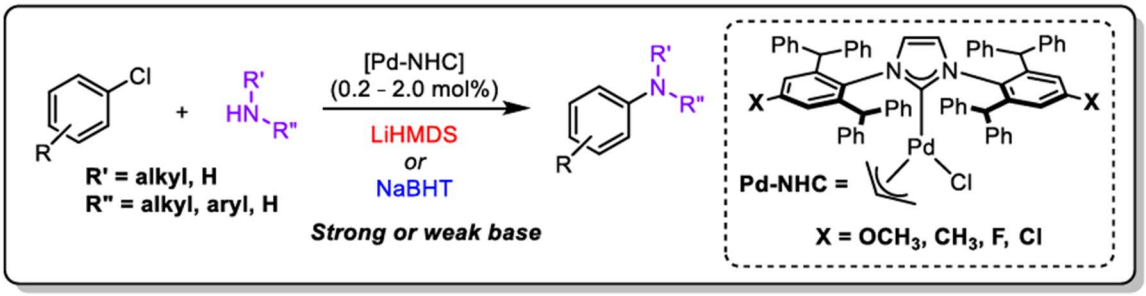
The palladium-catalyzed Buchwald–Hartwig amination (BHA) is an important method for C–N bond formation.[1] Palladium N-heterocyclic carbene (NHC) complexes are known to be highly active in this reaction,[2] yet the interplay between ligand electronic properties and reaction conditions remains incompletely understood. Our group has shown that increasing the electron-donating character of NHC ligands enhances catalytic activity under both strongly and weakly basic conditions.[3]



Building on these findings, we investigated the mechanism of the LiHMDS-mediated BHA of aryl chlorides through kinetic analysis and in situ reaction monitoring by ^{19}F NMR spectroscopy. Initial-rate studies revealed an inverse dependence on LiHMDS concentration, a positive dependence on amine concentration, and zero-order dependence on aryl chloride concentration. These unexpected kinetic trends prompted further investigation of the role of base and amine in solution. Our results support a mechanistic model in which amine–base aggregation limits amine availability for palladium coordination, thereby influencing catalytic efficiency. This work reveals an important role for solution-phase aggregation in Pd–NHC catalyzed amination reactions and establishes a framework for understanding how ligand electronics and base-dependent speciation collectively govern catalytic reactivity.

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Cooperative Reactivity of a Neutral Aluminylene–Gold Complex

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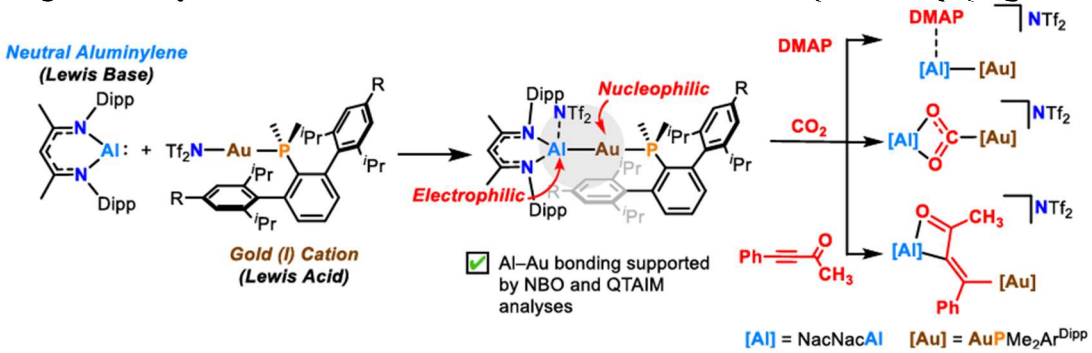
The collaborative use of organometallic and p-block elements has shown great promise for imparting the reactivity necessary to activate inert molecules. A notable strategy is the use of Frustrated Lewis Pairs (FLPs),[1] by which an electron accepting Lewis acid is paired with an electron donating Lewis base and used in tandem to activate small molecules through a push/pull mechanism. While main-group elements like boron, phosphorus, and nitrogen are most prevalent in FLP literature, there has been new-found interest in the development of metal-only FLPs (MOFLPs), which open new avenues of exploration, particularly in catalysis.[2,3] Aluminum thus serves as a compelling candidate for use in such MOFLPs. As a group 13 element, aluminum possesses very similar chemical properties to boron, however, unlike boron, aluminum is a metal, allowing it to display different and intriguing physical and chemical properties. This presentation will describe the isolation and characterization of novel bimetallic FLPs generated through the pairing of a neutral Al(I) source with sterically encumbered Au(I) cations. The resulting species feature highly polarized Au–Al bonds, with substantial nucleophilic character localized at Au arising from the electronegativity difference between the two metals. This unusual electronic structure is reflected in the subsequent insertion of heterocumulenes, including CO_2, into the Au–Al bond. This work complements previous studies by Aldridge and co-workers,[4] while demonstrating previously unobserved reactivity for neutral aluminylenes. Additionally, the cooperative nature of the Au–Al pair is demonstrated through the activation of a ynone substrate, highlighting the potential of heterobimetallic MOFLPs for accessing reactivity distinct from that of either metal center independently (**Figure 1**).[5]



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Mechanistic Studies on Palladium Photochemistry and A Dual-Photoexcitation Approach to Aldehyde Synthesis

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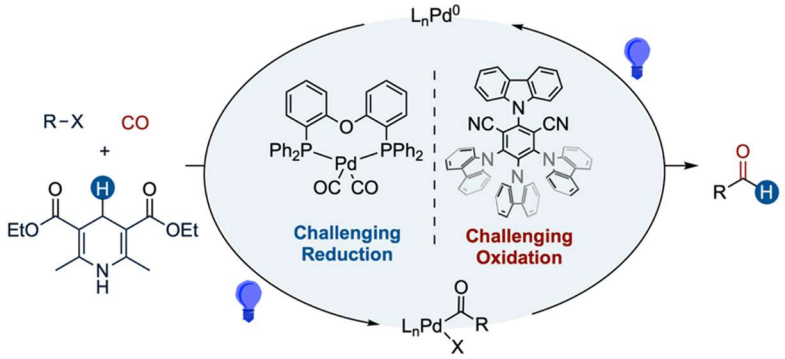
Visible-light photoredox catalysis has enabled access to reactive radicals under mild conditions. These systems are energetically limited by the power of visible-light excitation of a single catalyst, hence their ability to engage more than one strong bond is compromised. Ongoing studies have revealed photoexcited palladium complexes to be selective in powerful single electron reduction events, beyond the description of simple reduction potentials. This has led to the development a catalyst system that merges photoredox catalysis with photoexcited palladium catalysis to power the carbonylative synthesis of aldehydes from alkyl halides. Mechanistic studies show the system incorporates stronger single electron reduction and oxidation events than either alone is capable of, by incorporating the energy of visible-light excitation events at 2 catalysts with distinct and complementary properties. Combined spectroscopic analyses alongside new approaches to photochemical kinetics provides insight to how carbonylative palladium photochemistry functions.



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Dinuclear Platinum Photocatalysts Promoting Low-Energy-Light-Driven Hydrogen Production from Water via S-T Transitions

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Solar-driven hydrogen evolution reaction (HER) from water is regarded as one of the most ideal methods to achieve a sustainable society. In this regard, we have demonstrated that Pt(bpy)- and Pt(tpy)-type complexes can act as single-molecular photocatalysts capable of driving photocatalytic HER only in the presence of sacrificial electron donor EDTA in aqueous media. However, their photocatalytic performances are relatively limited due to the intrinsically narrow absorption band up to *ca.* 450 nm.

In this study, a new dinuclear Pt(II) complex (**Pt_2(bpia)Cl_3**, bpia = bis(2-pyridylimidoyl)amido, Fig. 1a) has been synthesized and characterized in terms of its photochemical and photocatalytic properties. **Pt_2(bpia)Cl_3** shows long-wavelength absorptions derived from the direct triplet population via the singlet-to-triplet transitions (i.e., S-T transitions), revealing its strong acceleration induced by the bimetallic $Pt(II)_2$ core (Fig. 1a). The present study further demonstrates that **Pt_2(bpia)Cl_3** can serve as a single-molecular photocatalyst for HER in aqueous media and exhibit the highest durability among the Pt(II)-based photocatalysts developed in our group. More importantly, **Pt_2(bpia)Cl_3** is the first example of a single-molecular photocatalyst enabling hydrogen production from water via direct S-T transitions under low-energy light irradiation (λ > 580 nm) (Fig. 1b).[1] Moreover, upon replacing the chloride with iodide (Fig. 1a), **Pt_2(bpia)I_3** shows higher HER performance under red-light irradiation conditions (Fig. 1b). Several investigations revealed that the significantly higher catalytic performance for **Pt_2(bpia)I_3** is dominantly attributed to the superior acceptor characteristics of iodide facilitating the reductive quenching by EDTA (Fig. 1b).[2]

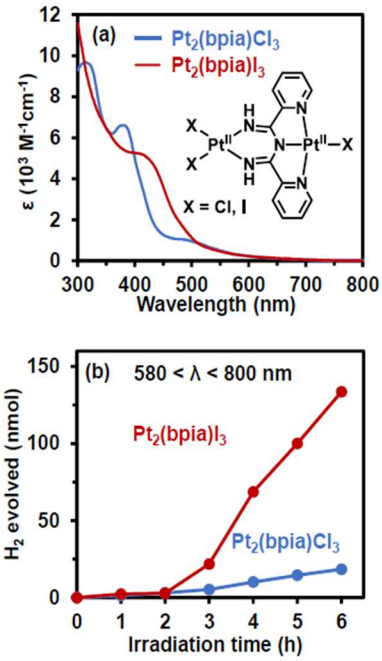

Figure 1. (a) Absorption spectra of **Pt_2(bpia)X_3** in aqueous media. (b) Red-light-driven H_2 evolution photocatalyzed by **Pt_2(bpia)X_3** in the presence of EDTA in pH 5 acetate buffer.

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From Isocyanide Complexes to Carbenes and Back

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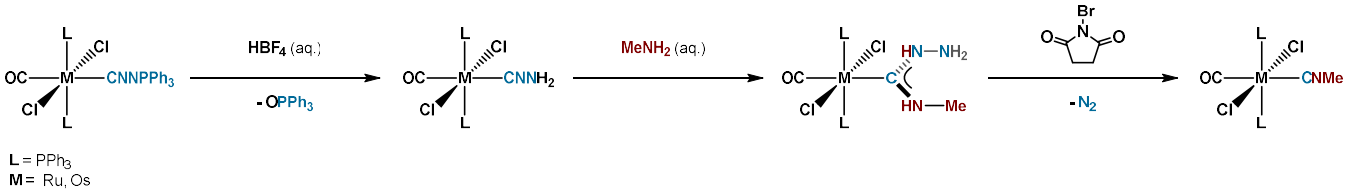
Recent interest in *N*-isocyanides as single carbon atom transfer agents, heterocycle precursors and tunable donor ligands has highlighted the importance of this traditionally underexplored class of compounds.[1-5] The bench stable, solid *N*-isocyanide $CNNPPh_3$ offers a convenient entry into the coordination chemistry of *N*-isocyanides, undergoing acid catalyzed hydrolysis to the parent *N*-isocyanide, $CNNH_2$, upon metal coordination.[6] Herein, we describe the coordination chemistry of $CNNPPh_3$ with Ruthenium and Osmium leading to a family of complexes of the general formula $MCl_2(CO)(CNNR_x)(PPh_3)_2$. Reaction with primary amines provide access to a series of carbene complexes, that subsequently undergo extrusion of N_2 to regenerate coordinated isocyanides. This unusual transformation offers a promising strategy for accessing isocyanide complexes that may otherwise be difficult or inaccessible through conventional synthetic routes.



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Silyl-substituted Phosphinidenes

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The chemistry of low-valent main-group elements has expanded rapidly due to their unique bonding environments and potential applications in small molecule activation and catalysis.[1-3] In particular, phosphinidenes R–P, P(I) compounds, have recently attracted considerable attention.[4-6] Our group has previously reported several families of transient and isolable phosphine-stabilised phosphinidenes.[7-10] In all known R–P systems, the R group is an N–, P– or C(sp^2)–based ligand. Here we report the first case of a silyl-supported phosphinidene.

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Alkyne Insertion at a Nickel-Aluminum Heterometallic Complex

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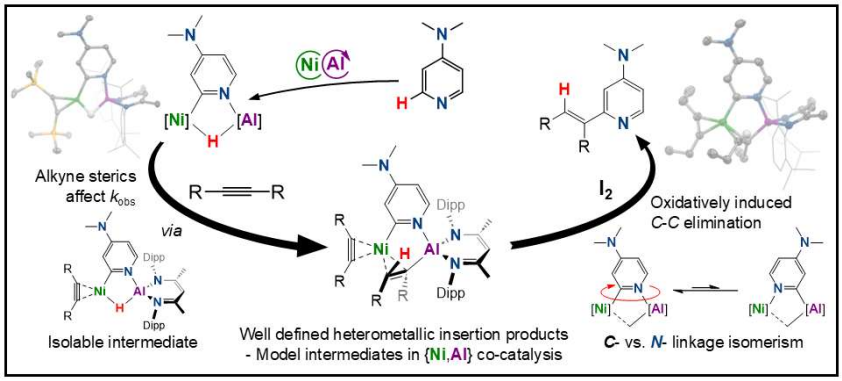

Cooperative Ni–Lewis acid catalysis has emerged as an effective strategy for the selective C–H functionalization of heteroarenes,[1] yet the elementary steps following C–H activation remain poorly understood. In particular, direct experimental insight into the migratory insertion step, which governs C–C bond formation and potentially product regioselectivity, has been lacking. Herein, we demonstrate that a heterobimetallic {Ni–Al} complex derived from the C–H activation of a pyridine undergoes efficient and selective hydrometallation of alkynes under mild conditions. This reaction provides direct access to structurally well-defined intermediates relevant to cooperative pyridine functionalization catalysis. A broad range of internal alkynes undergo rapid insertion to furnish five-membered {Ni–Al} metallacycles featuring alkenyl fragments that are σ-bound to aluminum and π-bound to nickel. Kinetic and mechanistic studies establish that alkyne insertion is non-reversible and that both steric and electronic effects govern the rate of insertion and the coordination mode of the bridging pyridyl ligand. Oxidatively induced reductive elimination affords a corresponding vinylpyridine product, establishing the competence of these species in C–C bond formation. These findings provide the first direct experimental characterization of migratory insertion intermediates relevant to cooperative {Ni–Al}-catalyzed pyridine functionalization and define mechanistic principles governing substrate coordination, insertion, and product formation.[2]

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Rational Design of a Main Group Catalyst for Suzuki Cross-Coupling Reactions with Esters

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Catalysis is a pillar of green chemistry because it allows to reduce the amount of waste generated and the energy input required for chemical transformations. The 20th century advent of transition metal coordination chemistry has enabled an explosion of catalytic processes.[1] In recent years, there has been growing interest in exploring the potential of more earth-abundant, non-metallic elements in catalysis.[2] This prospect would allow chemists to benefit from new, unique or previously underdeveloped reaction mechanisms and methods and cheaper catalysts. In this context, we have designed a catalyst independent from precious metals and applied it for the coupling of small organic molecules into larger chemicals in a similar process to palladium-catalyzed technologies known as cross-coupling, which were honored with the 2010 Nobel Prize for Chemistry.[3] Specifically, we have experimentally tackled the cross-coupling of esters, a common organic functional group, which are traditionally inert towards metal catalysts. This metal-free approach provides alternatives to metal-based paradigms and expands the current scope of cross-coupling reactions, thus allowing the development of complementary synthetic methods and routes. Finally, we have recently conducted an extensive mechanistic study and the results support a proposed catalytic cycle in which many aspects of metal-catalyzed cross-couplings are retained.

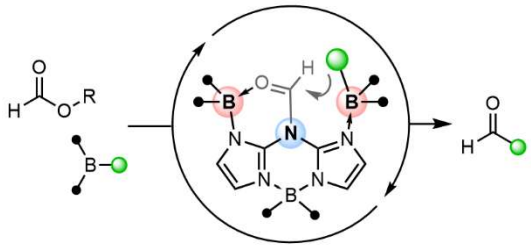

Figure 1. A metal-free catalyst for the cross-coupling of esters and organoboranes.

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Redox Cooperativity in Cu/TEMPO-Catalyzed Alcohol Oxidation

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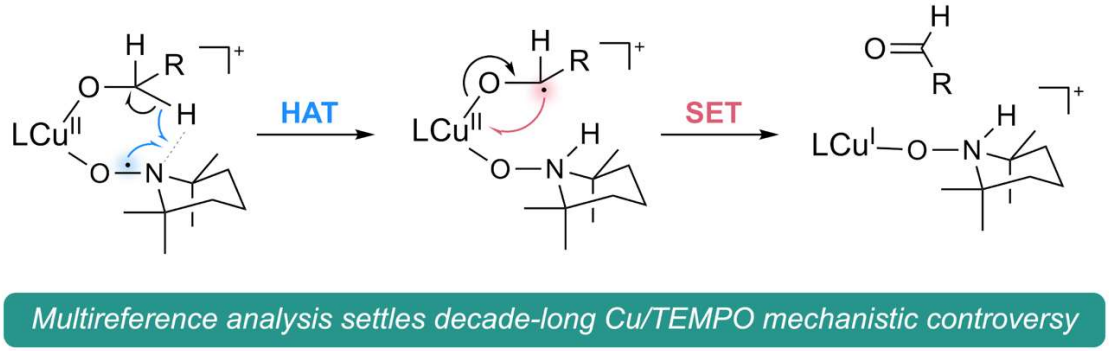
The mechanism of Cu/aminoxyl-catalyzed aerobic alcohol oxidation has been widely debated. Two pathways with fundamentally different modes of C-H activation have been proposed: hydride transfer to an oxoammonium-like intermediate or hydrogen atom transfer (HAT) to the aminoxyl radical followed by single-electron transfer (SET) to copper. At the heart of the debate is the electronic structure of the key Cu-aminoxyl intermediate, for which conflicting descriptions have emerged from previous computational and spectroscopic studies. Using multireference *ab initio* (CASSCF/MR-DDCI3) methods, we show that the reactive intermediate is dominated by an open-shell singlet Cu(II)–aminoxyl configuration ($|J| \approx 3400\ cm^{-1}$), with only minor Cu(I)–oxoammonium character. Intrinsic bond orbital analysis reveals a stepwise HAT/SET mechanism, in which the two electrons of the C–H bond transfer to different acceptors in succession. These findings reconcile all experimental observations, establish a direct analogy with the Cu(II)–radical active site of galactose oxidase, and provide a unified mechanistic basis for understanding redox cooperativity and selectivity across Cu/aminoxyl catalyst systems.



Multireference analysis settles decade-long Cu/TEMPO mechanistic controversy

TiBis(2-Adamantyl)Magnesium: Synthesis, Structure, and Applications of a Versatile and Shelf-Stable 2-Adamantyl Anion Equivalent

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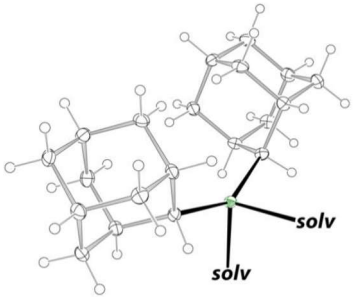

Figure 1. Crystal structure (30% probability ellipsoids) of solvated bis(2-adamantyl)magnesium.

The adamantyl substituent is used extensively in pharmaceuticals[1] and materials[2], as well as in phosphine ligands[3] and metal complexes for catalysis[4]. The 1-adamantyl group (1-Ad), where adamantyl is bound at the bridgehead position, is most widely used, in part due to the ease by which the 1-adamantyl cation is formed. The 2-adamantyl group (2-Ad), where the bridge position is substituted, is underutilized and so are anionic adamantyl precursors. To provide better building blocks for adamantyl chemistry, we are developing potent and stable 2-adamantyl anions. While arguably the most powerful 2-adamantyl anion is 2-adamantyl lithium, its synthesis is poorly reproducible, and the compound is so unstable that it is poorly characterized and can be used *in situ* only. The last several years have seen, in increasing order of carbanionic character, reproducible syntheses of (2-Ad)ZnBr, $(2\text{-Ad})_2$Zn, and (2-Ad)MgBr, which are all shelf-stable. We now report the synthesis and application of $(2\text{-Ad})_2$Mg as a nucleophile for organic and organometallic chemistries. It is, in practical use (as tested in transmetallation onto molybdenum) a more powerful transmetallation agent than (2-Ad)MgBr and is shelf-stable for months in solution or in crystalline form as the THF/dioxane adduct.

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The Coordination Chemistry and Reactivity of Difluorothiopyrophosphates

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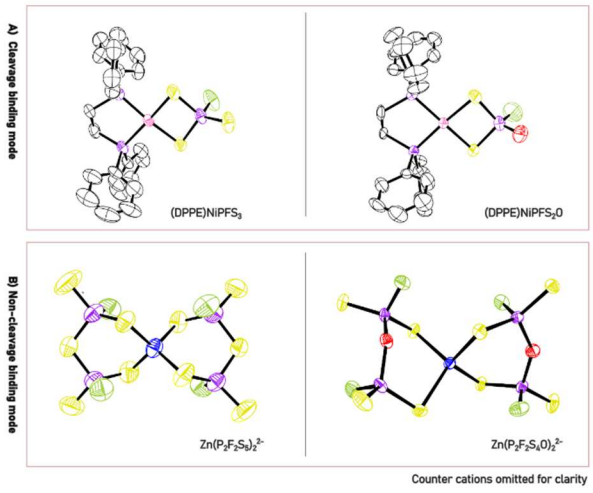
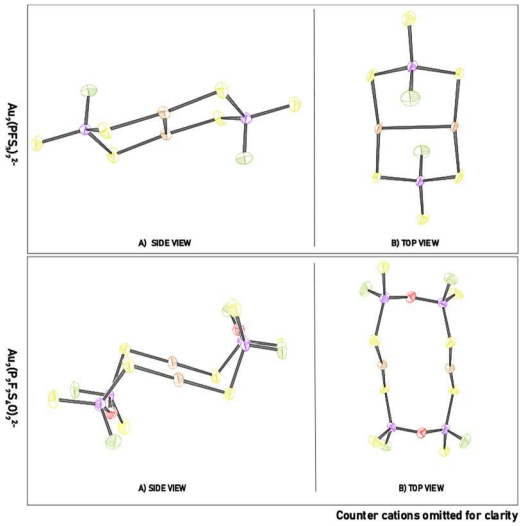
Difluorothiopyrophosphate dianions $P_2F_2S_5^{2-}$ and $P_2F_2S_4O^{2-}$, while known in the literature, are among the most understudied pyrophosphates. This is particularly highlighted by the paucity of information regarding their coordination chemistry[1,2]. To address this, we improved the synthesis of these anions and explored their reactivity with late transition metals. Our experiments show that their coordination can be simplified into either a cleavage or a non-cleavage binding[3,4]. This depends strongly on the metal centre, yielding particularly interesting results, especially for gold(I).





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A Family of Dy-Based Low-Symmetry Complexes Applied to Magneto-Luminescence Thermometry

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Lanthanide (Ln^{III}) complexes are a promising platform for the development of remote optical sensors due to their remarkable spectroscopic properties arising from 4f-4f transitions, such as narrow absorption and emission bands, as well as long excited-state lifetimes.[1] These features are often sensitive to external stimuli, including changes in temperature and magnetic fields, and have recently been explored for magneto-optical thermometry sensing.[2] In this regard, the magnetic circularly polarized luminescence (MCPL) technique relies on the differential emission of the left- and right-handed circularly polarized light induced by an external magnetic field. The use of this technique to study Ln^{III} compounds as magneto-optical thermometers is a relatively unexplored field, with only one seminal work reported in the literature for Dy^{III}.[3]

In this work, we report two distinct Dy^{III} complexes, $[Dy(acac)_3(tppo)]$ (**1**) and $[Dy(acac)_3(mdppo)]$ (**2**), ($acac^-$ = acetylacetonate, tppo = triphenylphosphine oxide, mdppo = methyldiphenylphosphine oxide). Subtle modifications of the phosphine oxide ligand induce controlled structural distortions around the metal centre, which directly influence the overall properties of the complexes. Temperature-dependent emission spectra, focusing on the transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$ of Dy^{III} (**Figure 1**), show that these structural distortions have a significant impact on the emission profile, which highlights the potential of these complexes for magneto-optical thermometric applications. Ongoing work is focused on MCPL measurements to further elucidate the relationship between molecular structure, emission behaviour, applied magnetic fields, and thermometric performance.

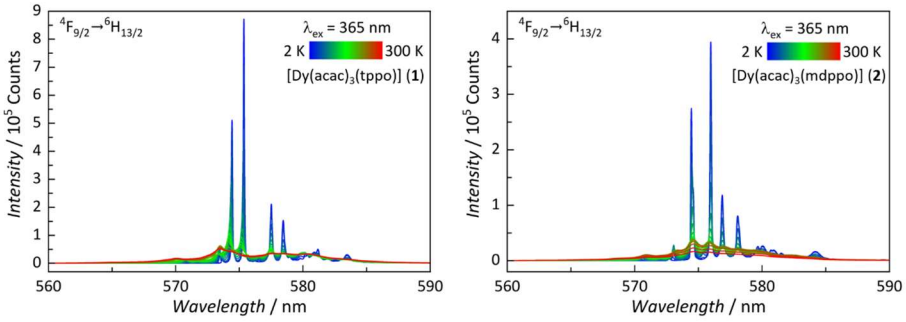

Figure 1. Temperature-dependent emission spectra of complexes **1** (left) and **2** (right).

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Regenerable, Luminescent Triarylborane-Functionalized Lanthanide Metal-Organic Frameworks as Solid-State Sensors

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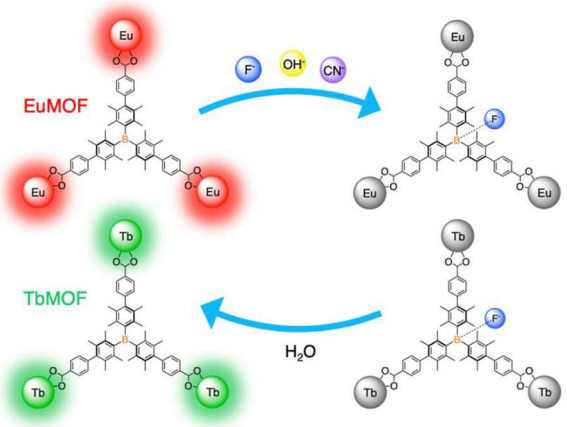
Fluoride anions (F-) are commonly found in everyday items and are known to have positive medicinal uses. Despite their importance, overconsumption can lead to health issues.[1] To address this, we synthesized two triarylborane-functionalized lanthanide metal-organic frameworks (LnBMOFs) able to detect trace amounts fluoride, acting as solid-state luminescent sensors.[2] The LnBMOFs, **EuBMOF** and **TbBMOF**, were synthesized using europium and terbium, respectively. These metal ions show strong luminescent properties when coordinated to a triarylborane ligand via the antenna effect.[3]



The electrophilic nature of this ligand allows for a high affinity to F-, making it an ideal candidate for sensing, whilst also providing steric bulk to enhance the selectivity and stability of the LnBMOFs.[4] Upon investigation, these systems proved capable of sensing other molecules including CN^- and OH^- but also a wider scope of anions including PO_4^{3-}, SO_4^{2-}, NO_3^-, and Cl^-, while maintaining a high degree of sensitivity. The structural design of these LnBMOFs provide a turn-on/off effect with some anions, where the luminescence is regenerated and maintains stability through several cycles upon washing with water.

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High-Throughput in-situ Pressure Measurements of Li-ion Batteries

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Batteries are proving to be a key player in reaching decarbonization goals, from powering electric vehicles to electrifying and stabilizing the grid. With the ever-growing range of applications for batteries, a diverse portfolio of battery materials will be needed to best meet the needs of each use-case. The most commercialized materials today are not well-suited for high cycling rates (fast charging) and are made of source materials mired in ethical concerns. On the anode side, Nb-based materials such as $TiNb_2O_7$ (TNO) have shown promise as high-powered anodes. However, they also show a critical flaw: they gas during cycling, in fact, they even gas at OCV[1]. On the cathode side, the most commonly-used materials in electric vehicle batteries in both Europe and North America are nickel-manganese-cobalt oxides (NMC). Similarly to TNO and LTO, high-nickel alternatives to NMC also experience gassing[2].

With the increasing ubiquity of Li-ion pouch cell batteries in portable electronic devices, minimizing gas evolution is a crucial optimization criterion when designing an energy storage system. Not only is gassing in batteries linked with a drop in performance, but a swelling pouch cell can damage the surrounding electronics as well as pose a safety risk of its own. Recognizing this problem, we have designed a first high-throughput cell capable of simultaneously measuring the gas production from 16 different battery materials during cycling. Importantly, the cell design successfully seals all 16 batteries individually to enable pressure measurements from each material. Measuring gas evolution quickly and efficiently in a high-throughput manner will enable us to discover battery compositions that minimize gassing without sacrificing other performance metrics. The design involves 16 batteries assembled in a single cell, a clear shift compared to previous efforts that simply made a multi-channel traditional tester[3]. This new tool has been validated on both anode (TNO) and cathode (NMC) materials.

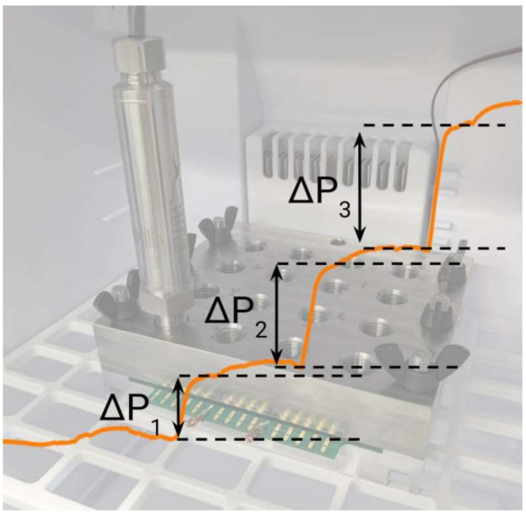

Figure 1. An example of the pressure output (orange) from an anode material superimposed on a picture of the high-throughput pressure cell.

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Quantifying Oxygen in Transition Metal Dichalcogenides using X-ray Absorption Spectroscopy

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Canada has committed $334.3 million over five years to strengthen its quantum technology ecosystem and support emerging technologies in advanced electronics.[1] This investment is driving demand for advanced materials with controlled properties that can be reliably integrated into functional devices. Two-dimensional (2D) materials are promising for advanced electronics because their atomically thin structures give rise to unique electronic and optical properties, enabling technologies such as field-effect transistors and photodetectors. Among 2D materials, transition metal dichalcogenides (TMDs) such as WS2 have emerged as a promising platform because atomic-scale changes can tune their material properties.[2] One way to tune WS_2's properties is through elemental substitution, where one element replaces another, typically sulfur. However, during synthesis, oxygen can similarly substitute for sulfur creating $WS_{2-x}O_x$; however, the extent of oxygen substitution remains unclear. If left uncontrolled, oxygen substitution leads to etching, degrading material quality, limiting TMD integration into electronic devices. Current methods such as X-ray photoelectron spectroscopy and electron microscopy can identify substitutional oxygen but cannot directly quantify substitutional oxygen or fully distinguish its local environments.[3] To address this gap, we synthesized a series of $WS_{2-x}O_x$ samples with systematically varied oxygen incorporation. We characterized the structural and local chemical environments using Raman spectroscopy, X-ray diffraction, and X-ray absorption spectroscopy (XAS). XAS is particularly well suited to this challenge because it is element-specific and sensitive to changes in local bonding environments.[4] The extended absorption fine structure (EXAFS) was used to quantify oxygen substitution by tracking changes in tungsten's local coordination environment. Furthermore, 2D correlation spectroscopy was applied to resolve systematic spectral changes across the sample series and found an evolving EXAFS feature near k = 5 $Å^{-1}$ correlated with oxygen incorporation. These results demonstrate XAS's potential to quantitatively track oxygen incorporation in $WS_{2-x}O_x$ and provide a pathway for characterizing oxygen-related defects across TMDs.

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Modeling Covalency with Molecular Analogues of Conductive Metal-Organic Frameworks

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2-D metal-organic frameworks (MOFs) with metallic or semiconductor charge mobilities continue to expand with ever increasing diversity in their molecular composition and hence orbital interactions. Predicting the charge transport behavior emerging from these structures presents many challenges, such as the need for plane-wave calculations rather than molecular intuition. To evaluate the utility of a local, molecular orbital perspective in rationalizing 2-D MOF conductivity, here we report that molecular analogues of common building blocks of metal-organic frameworks were modeled using density functional theory (DFT) and Atoms-In-Molecules analysis. Delocalization index, Löwdin spin population, Mayer bond order and nucleus-independent chemical shift (NICS) values were compared across all models, revealing increased electronic delocalization of sulfur-based molecular systems versus their oxygen analogues. The models corresponding to extended frameworks with high reported experimental conductivities, Cu_3(BHT) and Ni_3(BHT)$_2$, demonstrated a closer match in delocalization index, well-distributed spin population and increased bond orders relative to their oxygen analogues. NICS analysis showed a partial decrease in the aromaticity of sulfur-based systems, rather than either the preservation or total disruption of aromaticity observed in oxygen-based models. These computational metrics were applied to N-heterocyclic benzimidazolium dithiocarboxylate ligands as a predictor of conductivity in a novel framework material. These findings predict strong covalency and hence conductivity in a potential copper-based NHC-$BICS_2$ extended framework.

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Accelerated Discovery of Disordered Rocksalt Cathode Materials

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Disordered rocksalts (DRX) are promising cathode materials for lithium-ion batteries due to their high theoretical specific capacities and the potential to replace critical elements with earth-abundant alternatives such as manganese.[1] However, their practical application remains challenging due to high electrochemical overpotentials and limited cycling stability, particularly at high voltages. Tailoring DRX composition through metal doping offers a versatile approach to modifying their structural and electrochemical properties, yet systematically exploring the extensive compositional space remains experimentally challenging. In particular, we aim to identify dopants that modify the local structure of the rocksalt framework to facilitate Li-ion diffusion and reduce electrochemical overpotentials. Lower overpotentials are essential for practical applications, as they reduce energy losses during charge and discharge, improve energy efficiency, and can help mitigate unwanted side reactions associated with high operating voltages.

Here, we present a semi-automated high-throughput workflow for the synthesis and electrochemical investigation of doped DRX materials $Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$. A mechanochemical, microwave-assisted synthesis enables the parallel preparation of 64 compositions in less than one working day. Using a commercially available kitchen microwave reduces synthesis time and energy requirements while minimizing reliance on specialized equipment.[2] The synthesis is integrated into a high-throughput characterization workflow comprising powder X-ray diffraction (PXRD), cyclic voltammetry (CV), and galvanostatic intermittent titration technique (GITT).[3,4] In particular, GITT provides insights into Li-ion diffusion kinetics, electrochemical overpotentials, and internal resistance, enabling the investigation of structure–property relationships. Parallel measurements combined with automated data analysis enable systematic investigation of dopant effects on phase formation, structural characteristics, and electrochemical properties.

By integrating rapid synthesis with complementary structural and electrochemical characterization, this workflow enables the efficient screening of doped DRX materials and the identification of promising compositions. It provides a versatile experimental platform for investigating structure–property relationships and guiding the development of DRX cathode materials with improved electrochemical performance.

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Replacing Toxic and Precious Metals with Earth-Abundant Alternatives from Metals to Inorganic Salts and Metal Complexes

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Many sensing and energy technologies still depend on toxic or precious metals, including lead in galvanic oxygen sensors, platinum for hydrogen evolution, and iridium and ruthenium for water oxidation and photosensitization. Inorganic chemistry, extended metals, inorganic salts and molecular complexes, offers earth-abundant alternatives at every level of structure. In this presentation, I will discuss three such substitutions, namely tungsten for lead, nickel and boride materials for precious-metal electrocatalysts, and copper for ruthenium and iridium photosensitizers.

At the metallic end, tungsten metal replaces the consumable lead anode of galvanic dissolved-oxygen sensors. The resulting Pb-free sensor monitors trace dissolved oxygen without a toxic heavy metal. For water electrolysis, nickel oxyhydroxide electrocatalysts prepared from simple nickel salts serve as alternatives to IrO_2 and RuO_2 for the oxygen evolution reaction, and Raman and X-ray absorption spectroscopy link local nickel coordination to catalytic activity. As replacements for Pt/C in hydrogen evolution, I will discuss a series of transition metal diborides (CrB_2, MoB_2, VB_2 and mixed Cr/Mo and V/Mo phases). Controlled oxidative electrochemical activation improves their hydrogen evolution activity up to a threshold potential, beyond which over-oxidation drives phase change and degradation. This behaviour defines a practical activation window for boride electrocatalysts.

At the molecular end, copper(I) bis(diimine) complexes offer earth-abundant alternatives to Ru- and Ir-based photosensitizers. Ligand design tunes their excited-state behaviour and enables both heterogeneous photoelectrodes for light-driven oxidation and homogeneous energy-transfer photocatalysis. Together, these results show that earth-abundant elements (W, Ni, Cr, Mo, V and Cu) can take the place of Pb, Pt, Ir and Ru across sensing, catalysis and energy conversion. Understanding the structure and stability of each material under operating conditions makes these replacements practical.

Solid-State Structures and Self-Assembly Properties of Oxocarbons

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The simplest, best-known representatives of oxocarbons are the linear carbon oxides carbon monoxide (CO) and carbon dioxide (CO_2), well-known gases under ambient laboratory conditions, readily obtained through combustion of organic compounds. The only complex, cyclic oxocarbon structurally characterised in the solid state to date[1] is mellitic trianhydride. Aside from several literature reports, limited largely to descriptions of synthetic procedures,[2–4] studies of other oxocarbons have been confined mainly to theoretical work.[5]

Here, we present the first insight into the solid-state structures and molecular recognition properties of two polycyclic oxocarbons, $C_{10}O_{10}$ and $C_{12}O_{12}$, that can be regarded as oligomers of carbon monoxide. These oxalate-based neutral oxocarbons have been isolated as solid-state complexes (cocrystals) with ether- or ketone-type organic solvents tetrahydrofuran, dioxane, acetone, that are found to consist of discrete or extended motifs based on surprisingly short (2.5-2.8 Å) and stabilizing (ca. 40 kJ mol^{-1}) C···O contacts, that can be almost 20% shorter than the expected sum of van der Waals radii of carbon and oxygen atoms. Notably, this structural investigation demonstrates that these tetrel-type interactions can sustain the formation of one-dimensional (1-D) zig-zag chain or ladder motifs, as well as three-dimensional (3-D) open framework architectures in the solid state. The ability to generate extended structures based on short C···O tetrel bond interactions, confirmed through experimental studies, as well as *ab initio* Crystal Structure Prediction (CSP) approaches, now creates entirely new opportunities for the design of solid-state structures and materials. Notably, the presented results will introduce a different, non-conventional perspective of carbon oxides: not as ambient gases or fleeting, metastable species, but as versatile building blocks for crystal engineering based on an almost completely unexploited type of non-covalent interactions.

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From Molecular Design to Guest Sequestration: Crystal Engineering of Boron-Based Assemblies

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Boronic acids are versatile and valuable reagents in organic synthetic chemistry, with applications in supramolecular chemistry, porous materials, pharmaceutical, and crystal engineering.[1] This work explores the assembly of organoboronic acids and bipyridines in the organic solid state, focusing on hydrogen-bonded and B-coordination assemblies.[2] Our research also involves the use of boron-based materials to direct the [2+2] photodimerization in the solid state (i.e., crystal-to-crystal transformations). More recently, we demonstrated that boroxine organic assemblies (BOAs) can sequester and separate large polycyclic aromatic hydrocarbons (PAHs), establishing the first-generation BOA-based constitutional dynamic library (CDL).[3] We envisage that these findings will advance the development of boronic acid-based assemblies in organic solids, broadening the scope of crystal engineering toward functional materials with potential applications in areas such as molecular recognition, purification processes, and materials science.

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Controlled Oxygen Doping Regulates Thermal Reactivity in MoS_2

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Molybdenum disulfide (MoS_2) has attracted extensive attention for its exceptional electronic, optical, and catalytic properties, making it a key material for transistors, sensors, and energy devices.[1,2] Defect engineering has emerged as an important strategy for modifying the properties of MoS_2. Its performance is strongly influenced by structural defects, including oxygen substitution at sulfur sites.[3,4] However, systematic control of oxygen substitution in MoS_2 during chemical vapor transport (CVT) remains challenging. The effect of substitutional oxygen on the chemical reactivity of MoS_2 is therefore not well understood. Our previous study showed that thermal annealing of MoS_2 in N_2 leads to phase transformation involving molybdenum dioxide (MoO_2), followed by the formation of molybdenum trioxide (MoO_3) as the final oxidation product. Oxygen substitution modifies the local defect environment of MoS_2, and systematic variation of the substitution level is therefore expected to alter its phase-transition behavior. In this work, we establish controlled oxygen substitution in CVT-grown MoS_2 and investigate how the resulting doping density influences its thermally induced phase transformation. A systematic correlation is observed between the level of oxygen substitution and the characteristic phase-transition temperature during thermal treatment. This correlation provides a potential approach for evaluating and quantifying oxygen doping density in MoS_2 through thermal reactivity measurements.

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Supramolecular Chemistry of Organoantimony(III) in the Solid State

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Development of the halogen bond as a robust supramolecular synthon in recent years has prompted interest in late row pnictogens as alternative donor-acceptor sites.[1,2] Relative to halogens however, the supramolecular chemistry of pnictogens engaging in homoleptic interactions is not well understood.[3,4] We present our discoveries and modelling of novel polymorphs and co-crystals based on organoantimony(Sb) compounds, and propose that direct Sb···Sb short contacts have been previously overlooked as a general and fundamental aspect of the solid-state chemistry of antimony.[4]

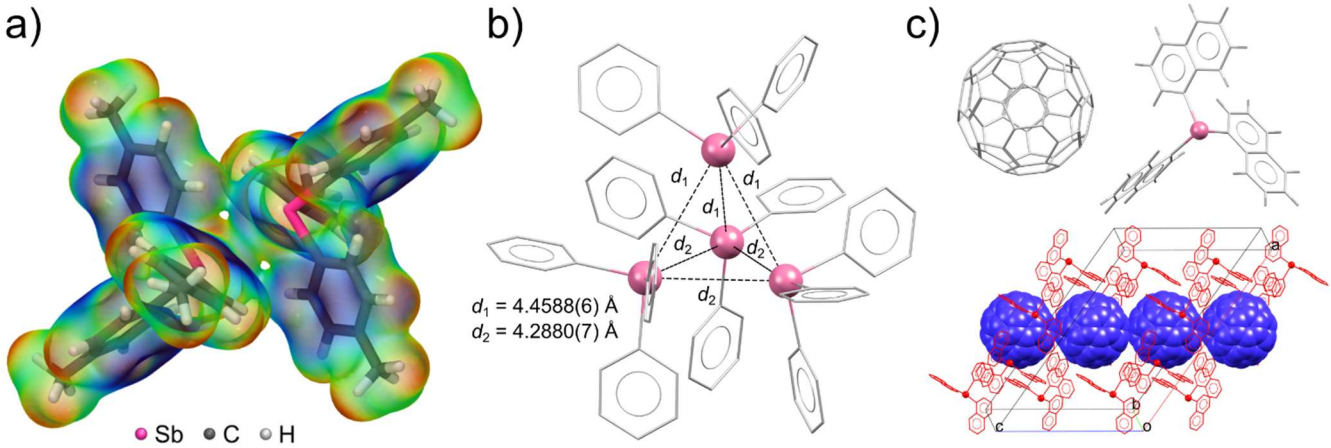

Figure 1. Structural Excerpts a) Electrostatic surface potential map of Sb···Sb bonded dimer in Sb(*p*-Tol)$_3$ Form II[4] **b)** Sb···Sb bonded tetrameric motif in SbPh$_3$ Form III **c)** (Top to bottom) Asymmetric unit of Sb(α-naphth)$_3$●C$_{60}$ with completed molecular fragments, packed unit cell of Sb(α-naphth)$_3$●C$_{60}$. Components are colorized for contrast, and C$_{60}$ subunits are rendered with a space-fill model.

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Combinatorial Study of Deformable Lithium Boracite Solid Electrolytes

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In lithium-ion batteries, solid electrolytes (SEs) are an attractive alternative to their liquid counterpart due to their potential for improved energy density, lifespan and safety. However, solids typically do not have the ability to form efficient contacts by wetting the electrode like liquids do. This issue is worsened by the lack of deformability often found in oxides. $Li_4B_4M_3O_{12}X$ boracites are deformable glass-ceramic SEs that have received attention for their low processing temperatures. These materials hold great promise by utilizing the low glass transition temperature to promote intimate mixing between the SE and the cathode to design an all-solid-state battery. Nevertheless, very few compositions have been studied, and no work includes determination of the deformability of the material, nor does previous work include the other necessary properties for solid electrolytes such as a large stability window.

Since the elemental composition of the electrolytes greatly influences their proprieties, a thorough study to find the ideal composition from innumerable doping possibilities is clearly necessary. Herein, we have adapted a melt-quench glass synthesis approach to the high-throughput synthesis of $Li_4B_4Ga_3O_{12}Cl$-type boracites, matching literature results. Furthermore, we document previously unreported properties such as poor stability against humidity leading to proton conduction as well as its deformability and stability window (Fig. 1).[1]

Beyond the proof of concept, we have used a high throughput screening to test the effect of 61 elements simultaneously. We quantify each dopant's influence on conductivity, deformability and other relevant characteristics pertaining to electrolytes in all solid-state batteries. We pinpoint a few promising dopants with significant impact on these key properties at less than 2% doping level. This thorough screening of these materials will dramatically accelerate our development of these promising materials.

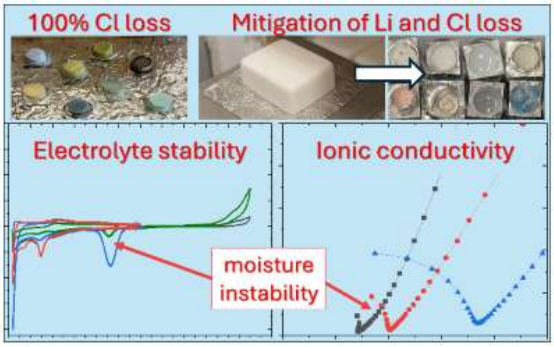

Figure 1. Graphical abstract outlining challenges faced during synthesis development

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Strategies in the Systematic Functionalization of Arenes

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Multi-functionalized arenes have been a long-standing synthetic challenge to achieve in organic chemistry. Current methods to synthesize highly complex benzenoid motifs in a combinatorial approach utilize systematic cross-coupling reactions.[i] However, the limitation of exploiting halogenated arenes as a cross-coupling partner poses issues with regioselectivity when halogens handles are installed (typically by electrophilic aromatic substitution)[ii]. This is because S_EAr is often difficult to install meta-substituents as meta-directors are deactivating (making S_EAr difficult) and overcoming the constraints of *ortho*- and *para*-directors leads to unfavorable regio-isomers. Other methods such as cycloaddition[iii] and utilizing benzyne intermediates[iv] can also lead to the synthesis of poly-functionalized arenes, though again, not without the same issues of regio- and chemo-selectivity. Recently, the Lumb lab has made quinones an attractive building block for the functionalization of arenes. The hydroquinone, resulting from the reduction of para-quinone, can be used as a scaffold for a poly-arene. Suitable reagents react with quinones to undergo a reductive conjugate addition to append an additional functional handle to the hydroquinone product, providing an adduct for a redox neutral transformation.[v] This work describes the appendage of a main group-based functional handle to a quinone, allowing for a combinatorial approach to obtain poly-functionalized arenes.

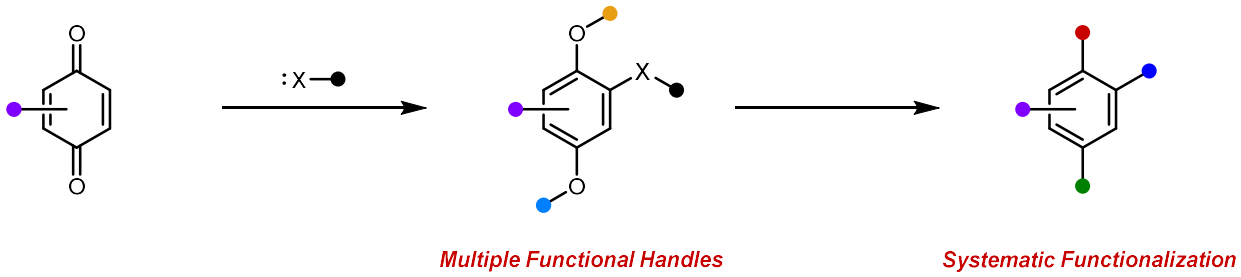

Figure 1. An approach to synthesize poly-substituted arenes from quinones and organophosphorus (III) reagents.

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From Molecule to Monolayer: Designing Aminosilane Inhibitors for Area-Selective ALD

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Area-selective atomic layer deposition (AS-ALD) exploits surface chemistry to confine deposition to specific surface regions, minimising the need for lithographic steps[1]. This work presents a systematic study of the structure-function relationships in amino-substituted silanes designed for use as AS-ALD inhibitors, with an emphasis on thermal volatility and surface selectivity. The goal is to improve the environmental impact of aminosilane production scale-up by exploring alternative synthetic pathways.

A more environmentally benign nucleophilic substitution route to the synthesis of disubstituted amines with chlorosilanes was undertaken using triethylamine as a sacrificial base, enabling access to a diverse inhibitor library while avoiding pyrophoric reagents and metal-containing intermediate chemistry[2]. Thermal behaviour was evaluated by thermogravimetric analysis, as well as by measuring pressures at which 1 Torr of vapour is produced, and by determining decomposition temperatures using differential scanning calorimetry. Surface coverage of viable aminosilanes was assessed in a home-built ALD reactor equipped with an in-situ quartz crystal microbalance to measure adsorption and selectivity on metal and dielectric surfaces. Compounds exhibiting selective adsorption were subsequently assessed for growth inhibition of diethylzinc/water ALD relative to the bare surface on patterned metal/dielectric wafers.

Reaction-enabled random sequential adsorption (RE-RSA) simulations were used to model surface packing while accounting for the change in molecular footprint following inhibitor chemisorption. The simulations provide predicted surface coverages, packing densities, and residual gap sizes between adsorbed species[3]. Predicted surface coverages were compared directly with experimental QCM measurements to evaluate simulation accuracy, while packing densities and residual gap sizes demonstrate how surface packing influenced inhibitor passivation and subsequent ALD precursor adsorption.

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Synthesis and Post-Assembly Modification of Azide Decorated Silver Organic Chalcogenolates

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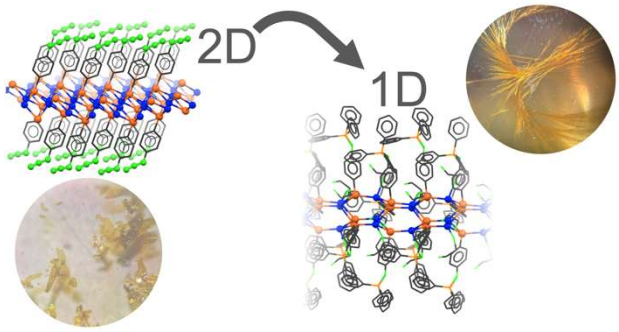

Ultrathin 2D semiconductors represent a major advancement in technology that has captured significant research interest in the areas of physics, chemistry, material science, and nanotechnology. Metal organic chalcogenolates represent an interesting class of 2D semiconductors with properties similar to those of 2D metal halide perovskites.[1] Silver phenylselenolate ($[AgSeC_6H_5]_\infty$),[2] dubbed mithrene in 2018, is one such metal organic chalcogenolate semiconductor with a direct bandgap of 2.65 eV, giving it a distinctive blue luminescence at room temperature.[3] A recent perspective published last year has highlighted the specific promise of being able to functionalize the para-position of the aryl moiety to guide key material aspects such as optoelectronic properties and structure of the product.[1,4] Another recent advancement has shown that polydentate amines can dissolve the 2D coordination polymers,[5] which were previously thought to be insoluble.

In this work, we show that it is possible to incorporate azide moieties on the metal organic frameworks, allowing for rapid testing of the effect a variety of para-substituted aryl rings have on the synthesis and properties of new silver chalcogenolate structures. This presentation will report on the preparation and photophysical properties of such azide-functionalized 2D nanomaterials, and describe post-assembly modifications achieved through a Staudinger reaction with triarylphosphines.

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Chromophore Engineering for Cu(I)-driven Photocatalysis in the Near-Infrared

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Photocatalysis mediated by low-energy light wavelengths has the potential to enable safer, more sustainable synthetic methods while avoiding photodamage and permitting larger-scale applications. In a previous study, we showed that a Cu(I) complex with phenanthroline-type ligands catalyzes singlet oxygen formation under orange (640 nm) and red (740 nm) light irradiation.[1] Recently, we developed a series of Cu(I) catalysts bearing phenanthroline-type ligands with substituents designed to extend the aromatic system, thereby red-shifting their photocatalytical response into the near-infrared (NIR), achieving up to 65% conversion under 850 nm irradiation using benzylamine dimerization as the model reaction. We have examined how the photophysical and electrochemical properties of the ligands and their Cu(I) complexes correlate with photocatalytic activity in the NIR.

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Crystal Engineering of Halo-Pyrimidine-Based Cyclobutanes through Solid-State Photodimerization

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Crystal engineering is emerging as a technique of choice for the synthesis of functional materials for various applications.[1] Solid-state synthesis has been proven to provide access to molecules that are difficult to obtain using conventional (solution-based) organic synthesis. Reactions in the solid-state help to perform organic syntheses that are efficient, sustainable, and atom economical. This approach generates products that occur quantitatively and without side products. Pyrimidine based molecules have shown interesting biological properties for use in medicine, material science, agrochemical, and molecular recognition.[2] We describe a crystal-engineering strategy to synthesize halo-pyrimidine-based cyclobutanes through the organization of unsymmetrical alkene building blocks. Solid-state organization was then exploited to facilitate intermolecular [2+2] photodimerization as the resulting crystal packing positions the reactive alkenes for selective cyclobutane formation.[3] Single-crystal structure analyses establishes the molecular structures and stereochemistry of the alkenes and resulting photoproducts. We also examine structure-function relationships of the cyclobutanes *in vitro* by profiling androgen-receptor mediated transcriptional activity, receptor translocation, and cell viability.

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Polymorphism Resulting in Spin Crossover-Like Behaviour in the 4-pyDTA Radical System

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Main group thiazyl (S and N containing) radicals have proven to be promising candidates for designing tuneable magnetic materials. Research into methods for tailoring their magnetic properties includes various approaches including the synthesis of radicals with varying structural motifs,[1] the co-crystallisation of multiple radicals into one phase,[2] and incorporation of radicals into porous materials.[3] Such approaches have been fruitful in affording materials with properties varying from ferromagnetism,[4] canted anti-ferromagnetism[5] and spin crossover.[6]

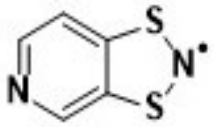

Figure 1. Structure of the 4-pyDTA radical.

The work presented here focuses on the preparation of thiazyl radicals containing pyridine motifs for investigation as magnetic materials. Investigation of the 4- pyDTA radical (Figure 1) reveals substantial polymorphism affording three individual phases. The transition between two phase results in thermal hysteric spin crossover behaviour.

This presentation will discuss the synthesis and characterisation of 4-pyDTA. To further understand this behaviour, we use variable temperature and variable time magnetometry, EPR, SCXRD, PXRD and DSC data. These techniques provide us with a picture of the structural changes between the three phases and point to phase transitions unlike those seen in previous SCO-thiazyl systems.

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A Step Toward More Efficient Hydrogen: Heteroleptic Ruthenium Complexes as Photosensitizer for Hydrogen Production

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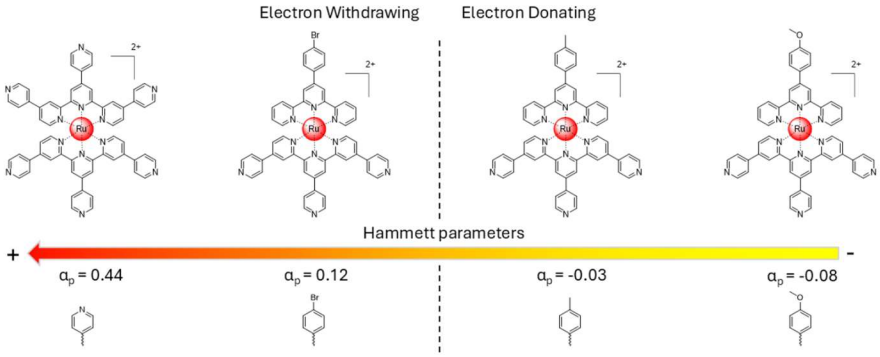
The recent climate crisis has focussed attention on the need for green and affordable energy; however, many avenues are available to produce green energy.[1] One of the most promising ways is the photocatalyzed production of H_2, as sunlight is the most abundant and widely available energy source on Earth.[2] Our first target is a novel molecular platform to harness energy emitted from the sun. Thus, a polytopic tridentate polypyridine-based ligand bearing three exterior pyridyl moieties, 4,4',4''-tris(4'''-pyridyl)-2,2':6',2''-terpyridine (Py_3Tpy), allows for facile electron transfer to appended cobalt catalysts to complete the H_2 Evolution Reaction (HER).[3] Py_3Tpy coupled with an electron-donating terpyridine yields highly stable and Ru heteroleptic complexes with exceptional H_2 production. We present herein three new Ru(II) complexes as well as their incredible results in the HER surpassing any ruthenium-based photosensitizer in the current literature.[4,5] This marks a step toward efficient and green H_2 production from light.



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An Approach to Develop Photoactive Pillared Metal-Organic Materials

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Metal-organic materials (MOMs) are a versatile platform to control solid-state reactivity through the deliberate assembly of metal centers and organic linkers into extended structures. Among MOMs, pillared-primitive cubic (**pcu**) networks provide an attractive system to exploring relationships between network topology, structural robustness, and photoreactivity. While network topology is widely used to describe framework architecture, and **pcu** frameworks typically exhibit porous structures, a role of topology as it relates to chemical reactivity remains comparatively underexplored. In this context, our group has very recently reported the development of a non-porous, pillared-**pcu** MOM that exhibit the property of water capture. The capture is achieved by stacking of pillars that undergo a [2 + 2] photocycloaddition reaction to create cavities that result in uptake of water from the atmosphere.[1] Herein, we investigate the synthesis and solid-state photoreactivity of members of a family of Cd(II)- and Zn(II) -based pillared-**pcu** MOMs. We explore how the spatial arrangement of photoactive linkers influences [2 + 2] photocycloaddition reactions and associated structural changes. We seek to understand how the networks accommodate chemical reactivity while maintaining structural integrity, aiming to establish structure-reactivity relationships that inform on the use of network topology as a design element for the rational design of robust, photoreactive MOMs.

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A Water-Soluble 'Turn-on' Fluorometric Sensor for Zn^{2+} and Cd^{2+} Detection, Quantification and Discrimination in Freshwater Samples

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We designed a simple, fully water-soluble 4′-hydrazineyl-2,2′:6′,2″-terpyridine-based fluorescent chemosensor that achieves "turn-on" detection of Zn^{2+} and Cd^{2+} in water at picomolar concentrations[1]. The sensor exhibits rapid fluorescence turn-on responses, exceptional sensitivity below the regulatory limits for drinking water, and excellent selectivity against 20 competing metal ions. The lowest limits of detection (LOD) and quantification (LOQ) were found to be 0.029 nM and 0.095 nM for Zn2+ and 0.098 nM and 0.328 nM for Cd^{2+}. Our sensor is well below regulated amounts of these ions as Governmental regulations allow an aesthetic objective (AO) of 76.5 µM for Zn^{2+} and a maximum allowed concentration (MAC) of 62.3 nM of Cd^{2+}. This sensor demonstrates effective differentiation between Zn^{2+} and Cd^{2+} ions which has proven to be a major challenge in the literature[2-4]. Due to the solubility of this sensor in water, experiments were done to observe environmental impact, including reusability and testing in real freshwater samples. The sensing strategy was validated by ICP-MS and successfully applied to Lake Ontario water samples, demonstrating accurate quantification and excellent recovery. Furthermore, the sensor is recyclable 20 times through EDTA treatment and can be readily translated into low-cost paper-based test strips for rapid, on-site analysis. Collectively, this work introduces a rare example of a fully water-soluble, reusable fluorescent sensor that combines ultrahigh sensitivity, analyte discrimination, and practical field deployment, offering a powerful platform for environmental monitoring. Combined experimental and computational studies reveal the nature of the coordination nature of the metal complexes and their properties.

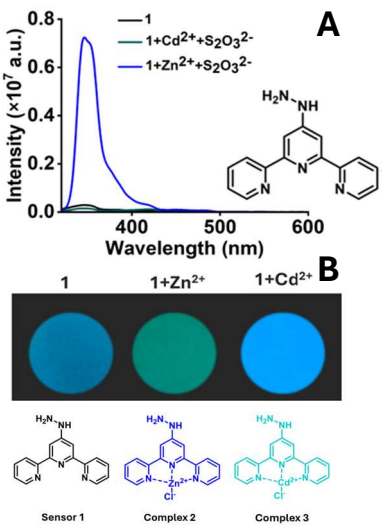

Figure 1. ***A****:* fluorescence emission spectra of **1** with target metals and excess $Na_2S_2O_3$ (aqueous phosphate buffer (pH 6.1), excitation at 278 nm), **B** paper test strips dip-coated with **1** and exposed to aqueous solutions of zinc and cadmium (photographed under 245 nm excitation) and respective structures.

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Development of Silver Precursors for Thermal Atomic Layer Depsosition

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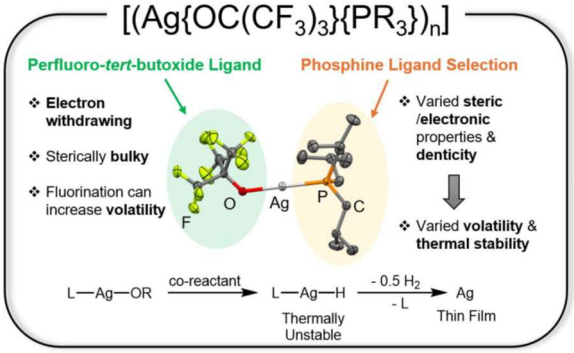
Atomic layer deposition (ALD) is a thin-film deposition technique which relies upon sequential self-terminating reactions between a precursor molecule and a co-reactant, which are delivered to a substrate surface in the vapor-phase, separated by inert gas purge steps. ALD affords thin films which are more uniform and conformal than those deposited using other techniques, and is particularly important in the microelectronics industry, for microprocessor and memory device fabrication. While ALD processes for metal oxides, nitrides, and sulfides are well established,[1] the deposition of elemental metals remains considerably more challenging.[2-3] The difficulty arises from the requirement to reduce the metal in a precursor molecule from a positive oxidation state to the zero-oxidation state, using only volatile reagents, and generating only volatile by-products.

Among elemental metals, silver is an attractive thin-film material for microelectronic and photonic device fabrication, owing to its low electrical resistivity, high thermal conductivity, and excellent reflectivity in the visible region of the electromagnetic spectrum.

In this work, we investigate a series of silver(I) alkoxide complexes, $[(Ag\{OC(CF_3)_3\}\{L\})_n]$ (L = phosphine, amine, and isocyanide), as potential precursors for ALD of elemental silver. Their solid-state structures, thermal stability, and volatility will be discussed, as well as solution reactivity with pinacolborane (HBpin; pin = $OCMe_2CMe_2O$) to afford silver metal via transient silver(I)-hydride intermediates. Thermal ALD of highly reflective silver films using $[(Ag\{OC(CF_3)_3\}\{P^iPr_3\})_n]$ and HBpin will also be described.[4]



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Opening the Cyclic Siloxane Precursor Ring in Thin Film Deposition of Siloxane-Based Polymer Networks

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Siloxane-based polymer networks are known for their excellent chemical and physical properties like thermal stability and chemical inertness, especially when there is cross-linking.[1–4] For state-of-the-art applications, it is preferred that the films are deposited using a vapor phase method. Molecular layer deposition (MLD) allows for precise and controlled growth, as it is a cycle-wise process where a substrate is exposed to alternating chemical vapors.

MLD of siloxane-alumina was demonstrated using 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (D_4^{Vinyl}) and trimethyl aluminum (TMA).[5] Ashurbekova *et al.* proposed a ring opening mechanism, as illustrated in Figure 2. The D_4^{Vinyl}-TMA MLD process was further studied in this work to elucidate the growth mechanism.

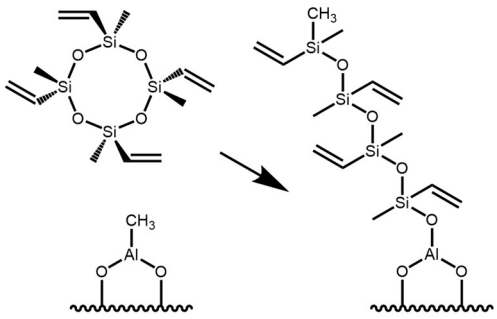

Figure 2. *Illustration of how the ring of the D_4^{Vinyl} precursor opens upon adsorption on a surface containing Al.*

In situ quartz crystal microbalance (QCM) studies during the deposition process revealed that the initial adsorption of both D_4^{Vinyl} and TMA on a Al_2O_3 surface is larger than the adsorption during steady-state growth. The presence of a metal atom with a π-acid nature at the surface is proposed to be responsible for the ring opening. The larger number of Al atoms in the initial substrate close to the incoming D_4^{Vinyl} during MLD versus the lower number in the siloxane-alumina film enhances adsorption during the first MLD cycles.

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Exploration of Gallium Complexes with $N_2O_2^{n-}$ Formazanate Ligands for Applications as Lewis Superacids and Bioimaging Agents

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Formazans (R^1–NH–N=CR^3–N=N–R^5) are a historical class of compounds that contain a nitrogen-rich, π-conjugated backbone which affords their characteristic intense colour and redox chemistry.[1] These properties prove advantageous for their use as dyes for cell-viability assays in chemical biology[1,2] and as redox-active materials for redox-flow batteries.[3] Furthermore, properties of these compounds can be easily tuned through structural modification of the substituents (R^1, R^3, R^5) on the nitrogen-rich backbone. Expanding the family of group 13 complexes containing tetradentate formazanate ligands beyond boron and aluminum,[4,5] herein we report a series of gallium complexes bearing $N_2O_2^{n-}$ (n = 1, 2, 3) formazanate ligands.[6,7] The propensity of these complexes to form six-coordinate metal centres was explored using fluoride ion affinity studies, which revealed moderate to strong Lewis acidity (FIA_{vac} = 448–1189 kJ/mol, FIA_{solv} = 219–389 kJ/mol) of the gallium formazanate core. Taking advantage of the air and moisture stability of one of the derivatives, the radiosynthesis of gallium-68 formazanate complexes was demonstrated with >85% radiochemical yield at room temperature in 15 minutes. These findings provide the foundation for further development of gallium formazanate systems for applications as radioimaging and theranostic agents as well as Lewis superacids.

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Tuning Solid-State Photochemistry Through Chromophore Expansion

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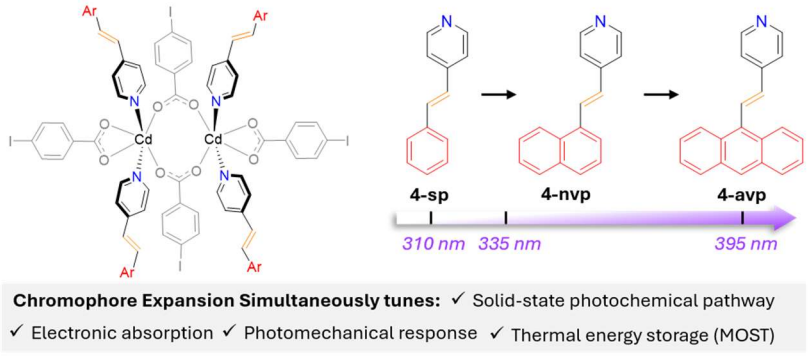

Controlling solid-state photochemical reactivity requires precise organization of photoactive molecules within a crystal lattice. Here, we investigate a family of structurally related binuclear cadmium(II) pseudo-paddlewheel complexes, $Cd_2(4\text{-IBz})_4(4\text{-ArVP})_4$ (4-IBz = 4-iodobenzoate; 4-ArVP = arylvinylpyridine), to examine how systematic chromophore expansion influences photochemical behaviour. Expanding the aromatic system from phenyl to naphthyl to anthryl produces distinct absorption profiles, reaction pathways, and mechanical responses while retaining a common coordination motif. Upon irradiation, the complexes exhibit markedly different solid-state behaviour, ranging from crystal fracturing to single-crystal-to-single-crystal transformations involving olefin [2+2] cycloaddition and anthracene [4+4] photodimerization. Notably, the anthracene-containing complex undergoes reversible photodimerization and exothermic cycloreversion, demonstrating its potential for molecular solar thermal (MOST) energy storage. These findings highlight chromophore expansion as a strategy for tuning photochemical reactivity and introducing energy-storage functionality into coordination crystals.

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Ethenolysis as an On-Purpose Linker Cleavage Strategy for Delamination of Metal-Organic Frameworks

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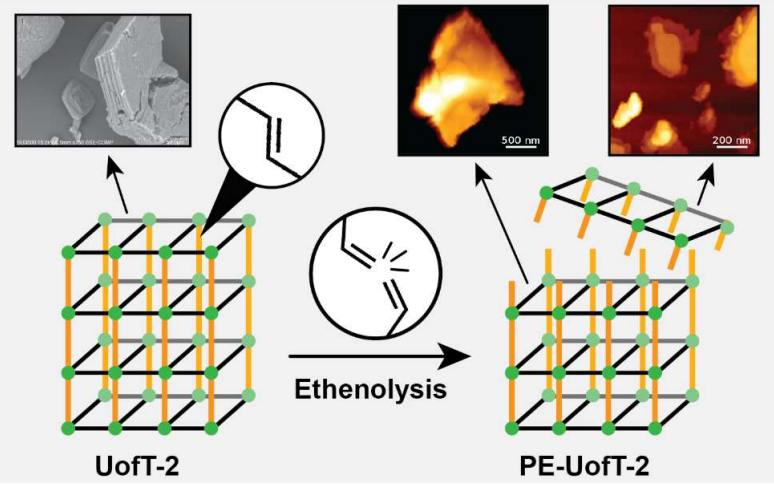
Metal-organic frameworks (MOFs) are a unique class of hybrid organic-inorganic materials that distinguish themselves with their highly porous crystalline structures, making them desirable for a variety of applications. The successful implementation of MOFs in various industries relies on the ability to precisely tailor their structures in a post-synthetic fashion. On-purpose cleavage of organic linkers has recently gained traction as one of the strategies for morphological tuning of MOFs due to its ability to deliver a range of desirable outcomes, such as their dimensional reduction or porosity enhancement. Although several classes of chemical transformations have been leveraged to date for that purpose, they all require harsh and/or aqueous reaction conditions that may be unsuitable for tuning of less stable MOFs. Herein, I establish the ethenolysis reaction, a variant of iconic olefin metathesis, as a new tool for on-purpose cleavage of MOF linkers. In this talk, I will demonstrate that the ethenolysis of the three-dimensional pillared MOF, **UofT-2**, causes delamination of the material with decrease of the bulk crystallite thickness and evidence for formation of MOF nanosheets. Crucially, ethenolysis-driven linker cleavage proceeds under anhydrous/anoxic conditions and without the need of applying harsh reaction conditions.



An Extended π-Conjugated Building Block for Solid-State [2+2] Photocycloadditions

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The solid state has emerged as a powerful medium for directing organic reactivity through precise molecular organization utilizing crystal engineering principles.[1] Template-directed cocrystallization has been widely explored to achieve topochemical [2+2] photocycloaddition by pre-organizing molecules in accordance with established geometric criteria. Despite these advances, most studies have primarily focused on enabling cycloaddition, with comparatively limited attention toward achieving controlled reversibility in the solid state. Here, we present a system based on an extended π-conjugated organic building block that can enable reversibility in the solid state. We use a cocrystal approach to direct the molecule to undergo a photocycloaddition transformation. We also show how the work extends to target reversible cycloaddition–cycloreversion processes and, in doing so, aligns with emerging concepts in the field of molecular solar thermal energy storage (MOST) materials[2], where reversible photoinduced transformations enable release of heat. Overall, the work will highlight the potential of combining ligand design and cocrystal engineering to develop metal-free, solid-state photo-switchable materials.

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RAFT-Enabled Synthesis of Well-Defined Au(I) Metallopolymers for the Preparation of Low-Dispersity N-Heterocyclic Carbene-Functionalized Gold Nanoparticles

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Normal and mesoionic N-heterocyclic carbenes (*m*NHCs) are constituting a well-established ligand class for the stabilization of metal complexes and nanoparticles (NPs) thanks to their extensively investigated strong metal-ligand interactions. The development of functionalized *m*NHCs through the simple and accessible click chemistry and bottom-up approach is leading to the improvement of plasmonic nanomaterials stability and the preservation of their optoelectronic properties by the reduction of organometallic complexes into nanomaterials.[1] Polymerized NHCs on the surface of the plasmonic NPs have previously resulted in the formation of plasmonic nanomaterials with highly stable polymer networks on their surface under various conditions without disrupting their plasmonic behavior nor catalysis activity.[2,3] The main drawback of this approached reported by our group remains the non-controlled polymerization technique (CuAAC polymerization), resulting in broad size dispersity of the resulting NPs. The implementation of controlled radical polymerization techniques has emerged as a robust strategy to achieve low dispersity ($Đ$ < 1.2) while maintaining well-defined macromolecular architectures and high structural fidelity. To this end, we have opted for the RAFT (Reversible addition-fragmentation chain transfer) process, utilizing trithiocarbonate-bearing *m*NHCs as our primary synthetic platform. This strategy facilitates the construction of highly uniform polymers through a controlled 'living' mechanism, integrated with the robust coordination chemistry of *m*NHC ligands. We are aiming to show the effects of macromolecular architectures design effect on the resulting nanoparticle dimensions while securing monodisperse cores with superior colloidal stability.

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