Atomic-scale Insights into Ion Dynamics and Structure of Superionic Li_3InCl_6

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Solid-state lithium-ion batteries (SSLIBs) are considered promising next-generation energy storage systems, offering improved safety and higher energy density compared to conventional LIBs.[1] Among solid-state electrolytes (SSEs), halide-based materials such as lithium indium chloride (Li_3InCl_6) stand out due to their higher ionic conductivity, air stability, and higher electrochemical stability window.[2] Building on the pioneering work[3] of Xiaona Li et al., who established a scalable aqueous synthesis and characterized Li_3InCl_6 using electrochemical impedance spectroscopy (EIS) and Rietveld refinement, we addressed the remaining challenge of understanding lithium-ion dynamics at the atomic-scale in Li_3InCl_6.

In this study, we employed advanced solid-state nuclear magnetic resonance (SSNMR) spectroscopy to probe ion dynamics beyond the scope of EIS and diffraction methods. Spin-lattice relaxation measurements of ^{7}Li nuclei enabled the determination of activation energies over multiple timescales, whereas temperature-dependent line-shape analyses provided qualitative insights into lithium-ion mobility. Furthermore, motional narrowing studies afforded a quantitative assessment of ion transport behaviour. Complementary multinuclear NMR (^{6}Li, ^{7}Li, ^{35}Cl, ^{115}In) spectra provided detailed insights into local bonding environments, while the ^{115}In and ^{35}Cl spectra were further corroborated by density functional theory calculations for structural validation and prediction of NMR parameters. This integrated approach uncovered the atomistic origins of ion transport and local ordering in Li_3InCl_6, demonstrating the necessity of atomic-scale probing to fully understand SSEs.

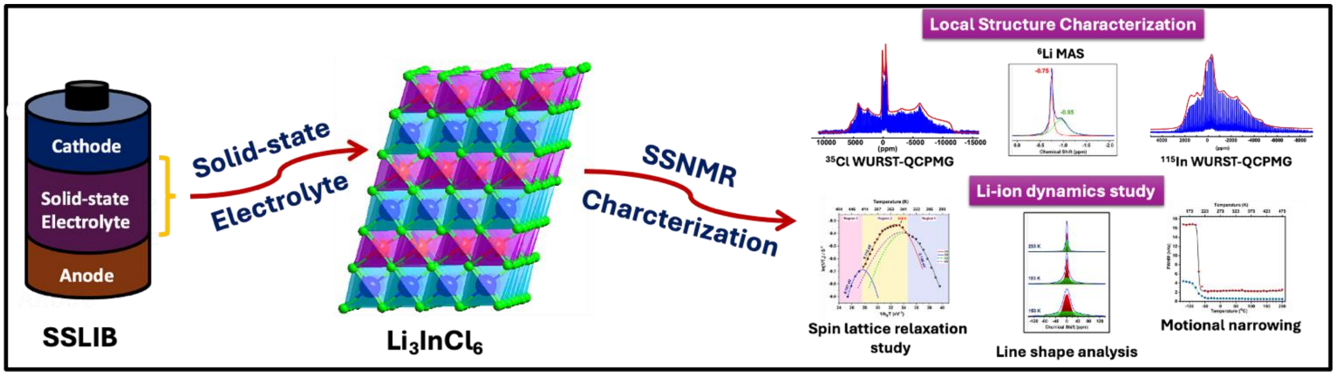

Figure 1: Schematic representation of SSNMR spectroscopic analysis of Li_3InCl_6

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Design and Synthesis of Pillared Metal-Organic Frameworks featuring Olefinic Fragments

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While metal–organic frameworks (MOFs) are known primarily for their well-defined crystalline porous structures that make them desirable for a myriad of applications, they also distinguish themselves with their chemical tunability. One strategy for chemical tailoring of MOF structures is post-synthetic modification (PSM) targeting moieties present in their organic building blocks (linkers). In this context, alkene (olefinic) fragments are underrepresented in the realm of MOFs despite their extremely well-established and versatile chemistry. With the majority of reported olefinic MOFs falling into the microporous regime, the PSM opportunities involving bulkier reagents are severely limited. In this presentation, I will talk about a family of UofT (University of Toronto) pillared MOFs constructed around olefinic 1,4-bis(2-(pyridin-4-yl)vinyl)benzene (BPVB) and tetrakis(4-carboxyphenyl)porphyrin (TCPP) linkers. By utilizing a variety of M(II) [M = Zn, Ni, Co] precursors, three structurally distinct frameworks were synthesized and characterized. Most notably, the nickel-based framework represents the first reported example of a stable mesoporous olefinic pillared MOF. In addition to the *de novo* formation of a stable pillared MOF, Ni(II) is also used in a cation exchange process to structurally reinforce zinc-based frameworks.[1]

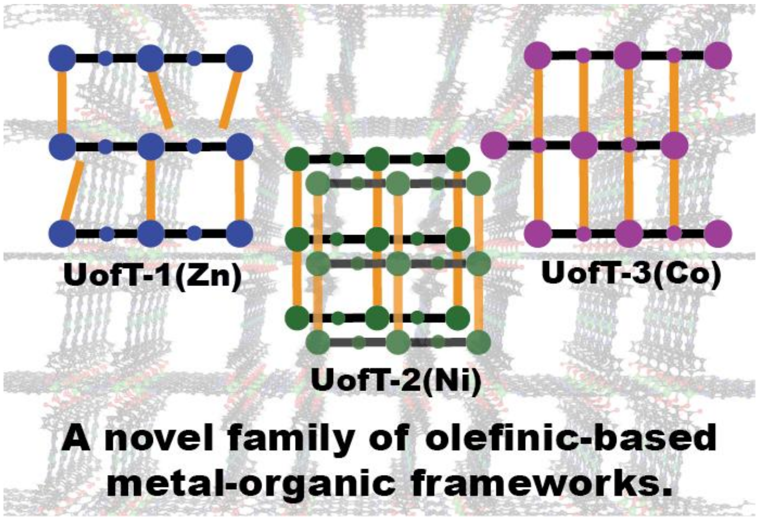

Figure 1. Cartoon representations of the UofT pillared MOFs.

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Polymetallic Clusters of Fe^{III} with mpmH: A Study of a Racemic and Chiral Chelate.

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Historically, polynuclear Fe^{III}-O clusters have been at the heart of the study of molecular magnetism, as well showing utility in other areas including catalysis and metalloenzyme modelling.

Within the field of molecular magnetism Fe^{III} clusters have been shown to possess sought after properties such as SMM behaviour,[1] spin frustration,[2] spin crossover[3] and the magnetocaloric effect.[4] Such clusters are often prepared with a serendipitous self-assembly approach using relatively simple organic ligands. Previous investigations into the chemistry of the methylpyridine-2-methanol (mpmH) ligand has afforded a variety of clusters.[5] A particularly interesting aspect of the mpmH ligand is the ability to prepare both racemic and enantiomerically pure species allowing us to investigate the effect of ligand chirality upon the coordination chemistry.

Here we present a series of Fe^{III} – mpmH cluster compounds ranging in nuclearity from an Fe_2 dimer through to an Fe_{10} decamer. Included is the Fe_6 cluster a chiral cluster prepared from enantiomerically pure mpmH. Single crystal X-ray diffraction data will be presented and the magnetic characterisation of these clusters discussed.

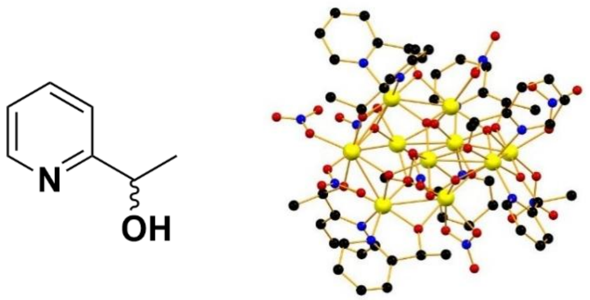

Figure 1: The mpmH ligand (left) and Single crystal structure of the Fe_{10} – mpmH cluster (right).

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Ruthenium-based Defective MOFs as Heterogeneous Catalysts for Hydrogenation of Carbon Dioxide to Formate

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The hydrogenation of carbon dioxide to formic acid has attracted a lot attention as a promising strategy for CO_2 utilization and hydrogen storage[1]. Metal–organic frameworks (MOFs) with open coordination sites and tunable pore structures can provide well-defined environments for specific interactions between active metal sites and reactant molecules. These characteristics of MOFs offer advantages as catalysts in heterogeneous catalysis[2].

In this study, a series of Ru-based MOFs with controllable defect concentrations were synthesized by incorporating varying amounts of 3,5-pyridinedicarboxylic acid (PYDC) as a partial linker replacement during MOF formation. The synthesis procedure following a previously reported method developed by Fischer's group[3].

The catalytic performance using different catalysts is showed in Table 1. Among them, the defective D3-Ru-MOF, prepared with 30% PYDC during synthesis exhibited a higher CO_2 to formate conversion efficiency compared to its non-defective and other counterpart.

The hydrogen pre-treatment step involves exposing the catalyst to hydrogen gas prior to the reaction. This process promotes the formation of Ru–H intermediates at the metal centers within the structure framework, thereby activating the catalyst and ensuring its reactivity for efficient CO_2 hydrogenation. The hydrogen-treated catalyst (H2D3-Ru-MOF) exhibited enhanced stability, achieving a turnover number (TON) of 1258. Its recyclability over four consecutive reaction cycles is illustrated in Figure 1.

This study highlights the potential of Ru-centered MOFs with tailored defect-engineering for efficient catalytic hydrogenation of CO_2 to formate.

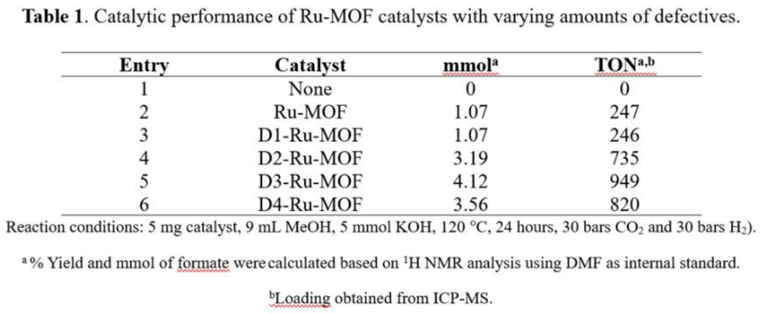

Table 1. Catalytic performance of Ru-MOF catalysts with varying amounts of defectives.

Entry	Catalyst	mmol[a]	TON[a,b]
1	None	0	0
2	Ru-MOF	1.07	247
3	D1-Ru-MOF	1.07	246
4	D2-Ru-MOF	3.19	735
5	D3-Ru-MOF	4.12	949
6	D4-Ru-MOF	3.56	820

Reaction conditions: 5 mg catalyst, 9 mL MeOH, 5 mmol KOH, 120 °C, 24 hours, 30 bars CO_2 and 30 bars H_2).

[a] % Yield and mmol of formate were calculated based on ^1H NMR analysis using DMF as internal standard.

[b] Loading obtained from ICP-MS.

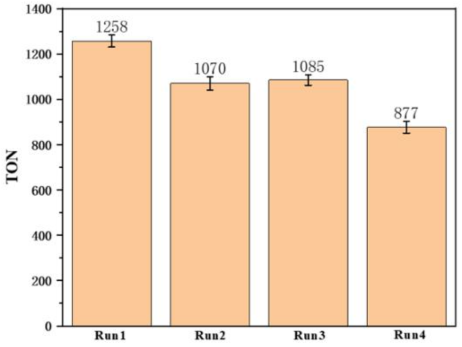

Figure 1. Recyclability tests of H2D3-Ru-MOF.

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Mn^{2+}-doped (Mg,Zn)$_x$GeO$_y$ Submicron Particles with Tunable, Exciation-Energy-Dependent Dual-Colour Persistent Luminescence

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Multi-color persistent luminescence (PersL) inorganic phosphors hold great potential in applications such as optical sensing, information storage, display, and anti-counterfeiting. In this work, we synthesized dual-color-emitting PersL submicron particles via a sonochemical approach. A quaternary oxide, (Mg,Zn)$_x$GeO$_y$ was chosen as the host lattice, where dual-color emission was achieved by doping with Mn^{2+}, which occupies either tetrahedral or octahedral sites within the structure. By adjusting the ratio of Mg^{2+} and Zn^{2+} precursors, the emission color of the resulted particles (denoted MZGO) can be turned green, yellow, or red/near-infrared (NIR). Unlike most previously reported NIR-emitting PersL phosphors that require deep UV excitation (e.g. 254 nm), our MZGO particles can be effectively activated by UVA light at 395 nm. Detailed characterization revealed correlations between the MZGO electronic structure, Mn^{2+} site occupancy, and the corresponding PersL properties. Furthermore, we demonstrated the potential of MZGO particles for dynamic, multimodal anti-counterfeiting applications by utilizing their excitation-dependent emission colors and PersL durations.

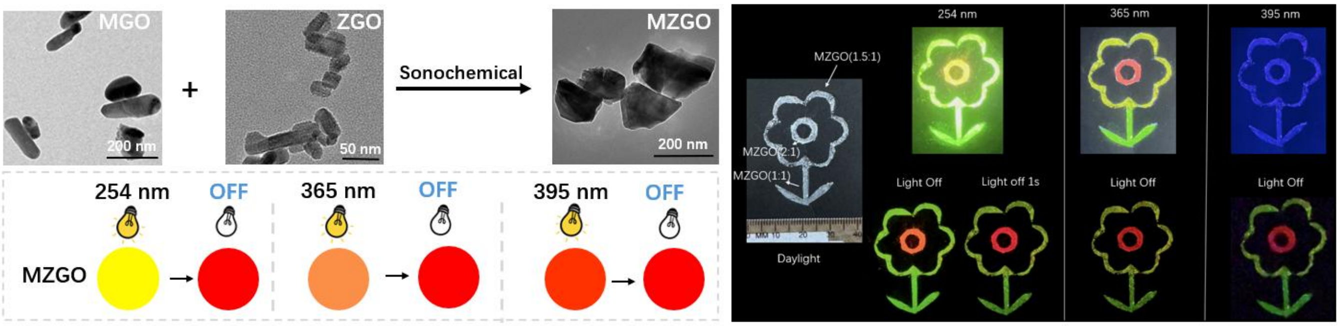

Figure 1. Schematic illustration of the sonochemical synthesis and excitation-energy-dependent dual-colour persistent luminescence of Mn^{2+}-doped (Mg,Zn)$_x$GeO$_y$ (MZGO) particles. TEM images of the colour precursors, MGO and ZGO, as well as the final product MZGO, are shown on the left. The tunable persistent luminescence colour of MZGO under different excitation wavelength are displayed in the middle. The design strategy of the anti-counterfeiting pattern using MZGO with different composition ratios is shown on the right.

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Hard Single-molecule Magnet Behavior and Strong Magnetic Coupling in Pyrazinyl Radical-bridged Lanthanide Metallocenes

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Polynuclear lanthanide single-molecule magnets (SMMs) lack strong magnetic communication which renders the design of high-performing SMMs as an ongoing challenge. To overcome the lack of strong magnetic communication between Ln(III) ions, which stems from the core-like electron density of the 4f orbitals, employment of paramagnetic bridging ligands as a direct exchange pathway is a promising avenue.[1,2] With the aim to synthesize such strongly coupled complexes, we sought to utilize for the first time in lanthanide metallocene complexes, pyrazine (pyz) as a bridging ligand. Due to its redox active six-member ring, incorporation of the radical $\mathrm{pyz}^{\bullet -}$ in lanthanide metallocenes afforded a dinuclear family of lanthanide complexes $[(\mathrm{Cp}^*{}_2\mathrm{Ln}^{\mathrm{III}})_2(\mathrm{pyz}^{\bullet -})(\mathrm{THF})_2][\mathrm{BPh}_4]$ (Cp* = pentamethylcyclopentadienyl; THF= tetrahydrofuran; Ln = Gd; (**1**), Dy; (**2**)) which upon removal of the coordinated THF served as a building block for isolating the tetranuclear family $[(\mathrm{Cp}^*{}_2\mathrm{Ln}^{\mathrm{III}})_4(\mathrm{pyz}^{\bullet -})_4]\cdot 10\mathrm{THF}$ (Cp* = pentamethylcyclopentadienyl; Ln = Gd; (**3**), Dy; (**4**)). Magnetic and computational studies reveal one of the highest exchange couplings ($J_{\mathrm{Gd\text{-}pyz}}$ = -22.2 cm^{-1}) for a radical-bridged system, achieved by two significant 4*f*–SOMO interactions. This in combination with the significant anisotropy of the $\mathrm{Dy}^{\mathrm{III}}$, grant **2** and **4** with slow magnetic relaxation at zero field and open hysteresis loops. A giant coercive field of 65 kOe for **4**, renders this complex as the hardest radical-bridged Dy-based SMM.

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Thiatriazinyl Radical Ligands for New Molecule-based Magnets

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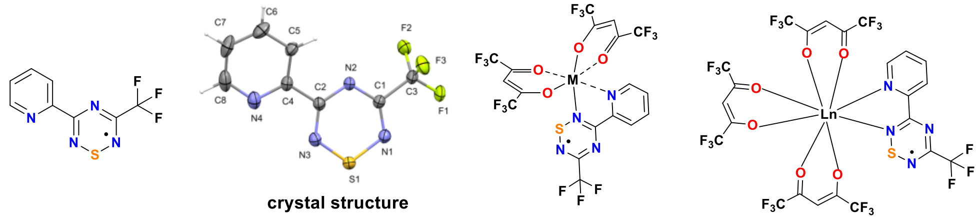
Metal and lanthanide coordination complexes of paramagnetic ligands are of interest in a wide range of fields, including catalyst and sensor design [1-2] as well as molecule-based memory materials.[3-4] Our research group is a leader in the design of neutral radical ligands derived from sulfur-nitrogen five-membered heterocycles, such as 4-R-1,2,3,5-dithiadiazyls (DTDA, where R is a substituent group) and 4-R^1-5-R^2-1,2,3-dithiazoles (DTA, where R^1 and R^2 are substituents or a fused ring extension, and R^1=R^2 or $R^1 \neq R^2$). Metal complexes of these ligands with coordinating R-groups have been shown to exhibit fascinating magnetic, thermochromic, and phase transition properties.[5] Developing comparable ligands and complexes using a six-membered-ring 3-R^1-5-R^2-1,2,4,6-thiatriazinyl (TTA, where R^1 and R^2 are substituents, and R^1=R^2 or $R^1 \neq R^2$) neutral radical with formula $R^1R^2C_2N_3S$ has been an elusive goal owing to synthetic challenges arising from the stability of the related closed-shell anion. However, the possibility of accessing a non-innocent ligand, with both neutral radical and closed-shell anionic oxidation states available, makes the TTA ligand design tantalizing. The metal coordination complexes are anticipated to offer numerous material design possibilities, such as redox control of magnetic properties.

Using our experience designing asymmetric TTA frameworks, incorporating halogenated and aryl substituents such as 3-trifluoromethyl-5-aryl-1,2,4,6-thiatriazinyl,[6] we report a new TTA chelating ligand (3-trifluoromethyl-5-(2-pyridyl)-1,2,4,6-thiatriazinyl, pyCF$_3$TTA) and the first metal and lanthanide complexes (Figure 1) of a *paramagnetic* TTA of the type M(hfac)$_2$pyCF$_3$TTA and Ln(hfac)$_3$pyCF$_3$TTA (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonato-; M = Mn, Fe, Co, Ni; Ln = Nd, Gd, Dy, Tb). Synthetic, structural, and preliminary magnetic data are presented.



pyCF$_3$TTA radical M(hfac)$_2$pyCF$_3$TTA Ln(hfac)$_3$pyCF$_3$TTA

Figure 1. The crystal structure of pyCF$_3$TTA, its transition, and lanthanide complexes.

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Crystal Engineering of Radical-Radical Cocrystals

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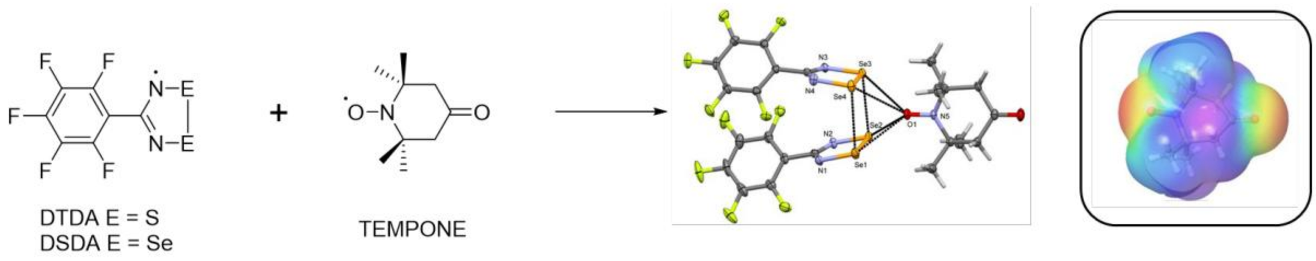
In 1928 Heisenberg proposed that bulk (ferro)magnetic order would only ever be achieved in systems containing heavy atoms (i.e. metals, their oxides, nitrides etc) [1]. Indeed, the first observation of bulk ferromagnetism in an organic radical was not observed until 1991, albeit at 0.6 K [2]. Since then approaches to develop new organic magnets with higher ordering temperatures have been explored. In 1993 Peter Day suggested that magnetic ordering in organic materials would not occur above room temperature [3] and, while ordering temperatures up to 70 K have been achieved [4], radical magnetism at room temperature continues to be elusive. Our research has recently focused on the cocrystallization of radicals to afford radical-radical cocrystals as potential routes to organic ferrimagnets [5,6]. The current study explores the cocrystallization of dithiadiazolyl (DTDA, E = S, Fig. 1) and diselenadiazolyl (DSDA, E = Se, Fig 1) radicals with TEMPONE [6]. This presentation reports recent experimental and computational studies on the relative energetics of DTDA…O-N< vs DTDA…O=C< interactions, reflected in competing regions of $O^{\delta-}$ for TEMPONE (Fig. 1(inset)) [7].



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When Stoichiometry Speaks: How Intrinsic Defects Drive Self-Activated Luminescence in Zn_2GeO_4 nanoparticles

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Zn_2GeO_4, is a wide-bandgap oxide with applications spanning photocatalysis, energy storage, electroluminescent devices, and optical security. As an optical material, Zn_2GeO_4 has been extensively studied for its defect-mediated luminescence, where intrinsic defects such as oxygen vacancies, zinc interstitials, Zn and Ge vacancies, and antisite defects play pivotal roles in governing its emission characteristics. Recently, its self-activated persistent luminescence (PersL), which is a unique manifestation of its defect-related optical behavior, has sparked significant interest among researchers. The role of intrinsic defects and their correlation with the self-activated PersL mechanism is still an active field of investigation. In this work, three different stoichiometric compositions of Zn_2GeO_4, designated Zn-deficient (ZGeO-D), stoichiometric (ZGeO-S), and Zn-rich (ZGeO-R), were synthesized using a hydrothermal method, which allows precise control of the Zn/Ge ratio in the resulting product. XRD confirmed orthorhombic Zn_2GeO_4 across all samples, while excess Zn leads to the formation of ZnO in ZGeO-R. ZGeO-R exhibited dual UV/blue-green bands, ZGeO-S displayed sharp near-UV emission, and ZGeO-D showed a broadened blue-green afterglow. Both Zn-rich and Zn-deficient samples portrayed superior PersL characteristics to their stoichiometric counterpart, with ZGeO-R leading with the longest PersL. By performing excited energy-dependent X-ray excited optical luminescence (XEOL) measurements, element-specific channels that were responsible for the observed emission bands were identified. We found that the afterglow was associated with Zn-related defects, while ZGeO with Ge-related defects, favors fast recombination. These results collectively emphasize the profound influence of intrinsic defect chemistry on self-activated PersL in Zn_2GeO4.

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Synthesis of Stable Polystannanes using Pincer Ligands with Enhanced Solubility

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Homopolymers of heavier group 14 elements have been of growing interest as new methods for their synthesis become available. In particular polystannanes show promising electronic properties as a result of the large diffuse *5sp*^{3} orbitals involved in the bonding of the polymer backbone. The optical bandgap of the Sn-Sn bonds has been reported to be lower than the single bonds of lighter group 14 analogues, with aryl substituents enhancing this effect further.[1][2] One of the main issues affecting the synthesis of these materials is their vulnerability to light and moisture. Previous research has indicated hypervalent compounds can stabilize the Sn-Sn bond by contributing electron density into a non-bonding orbital of the tin atom through a 3 center 4 electron bonding system.[3] Previous research from the Foucher group has successfully created polystannanes which were stable under ambient conditions, although the molecular weight of the polymers was too low to create suitable films.[4] The research presented here details the synthesis of a pincer ligand utilizing long chain aliphatic groups to improve solubility. The increase in solubility is expected to keep the growing polystannane in solution longer and improve yields.

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Towards Tuneable 2D Heterostructures for Clean Energy Catalysis: Defect and Interface Engineering in WS_2-Based Materials

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The growing demand for clean energy technologies, coupled with the environmental burden of electronic waste, has intensified interest in sustainable catalytic materials derived from earth-abundant elements. Although benchmark catalysts, such as noble metals (Pt, Ir, Ru) and metal oxides, offer high activity, they suffer from high costs and rigid electronic structures. With the advent of two-dimensional (2D) materials, such as WS_2, researchers have leveraged their atomic thickness and higher surface area to design more effective catalysts. Beyond individual monolayers, stacking chemically distinct materials into heterostructures enables the creation of electronically and chemically distinct interfaces. These cannot be achieved by single components alone.[1,2] Engineered heterointerfaces enable precise tuning of charge transfer and catalytically active sites, offering an expedient strategy to enhance catalytic efficiency.[3] WS_2, a transition metal dichalcogenide, exhibits superior magnetic susceptibility and unique optoelectronic properties compared to the well-studied MoS_2 analog, making it a compelling candidate for the hydrogen evolution reaction and electrochemical CO_2 reduction.[4–6] Nevertheless, challenges remain in scalable synthesis and a fundamental understanding of the impact of heterostructure interfaces on catalytic performance. Herein, we aim to develop of synthetic method of controlling sulfur vacancies during the synthesis of WS_2, further incorporating dopants to systematically tailor the local electronic environment and promote interfacial charge transfer. By systematically pairing doped WS_2 with other select 2D partners, we can develop a library of heterostructures to further probe how dopants and interfacial chemistry synergistically influence catalytic behaviour. This work positions 2D heterostructures as a tunable platform bridging sustainable resource recovery with next-generation catalytic design for energy conversion applications.

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