MOF-Based Spin Qubit Toward Quantum Computer

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Nobel Prizes in Physics 2022 were given to Professors A. Aspect, J. F. Clauser, and A. Zeilinger due to the experimental evidence of “Quantum Entanglement” in 2022. “Quantum Entanglement” is strongly related to qubits and quantum computers. Computer performance has developed remarkably over the last few decades. A bit of a conventional computer is composed of a combination of 0 and 1, whereas that of a quantum computer is composed of a superposition of 0 and 1, that is, $\psi = a|0> + b|1>$. Hence, it is called a quantum bit (qubits). Therefore, the quantum computer is drastically superior from the viewpoints of performance, speed, capacity, etc. Qubit candidates for quantum computers are created by using superconducting loops, nitrogen vacancies in diamond, trapped atoms, photons, and quantum dots. These candidates have merits and demerits, such as their coherence time, operating temperature, etc. Therefore, I will focus on molecular spin qubits based on molecular magnets with S=1/2.

As for molecular spin qubits for quantum computer, we must increase T_1 (spin-lattice relaxation time) and T_2 (spin-spin relaxation time). Therefore, we will focus on the following three strategies:**(1) Crystal Engineering Method (MOF Method);** To compare 0D [VO(TPP)] and 3D [VO(TCPP-Zn_2-bpy)] (3D-MOF) to investigate the influence of the spin-lattice relaxation (T_1) in 0D and 3D lattices. Due to the rigid lattice of 3D-MOF, the Rabi nutation was observed even at room temperature (Fig. 1). **(2) g-Tensor Engineering Method;** To compare [VO(TPP) and [CrN(TPP)] to investigate the contribution of the anisotropy of their g-values for the spin relaxation. Due to the large anisotropy of g-values, [CrN(TPP)] shows the short life time. **(3) Orbital Engineering Method;** To compare [Ni(cyclam)X_2]ClO_4 and TBA[Ni(mnt)$_2$] to investigate the relationship between the different occupied orbitals and spin relaxation. [Ni(cyclam)(NO_3)$_2$]ClO_4 has the longer life time due to the rigid molecular structure.

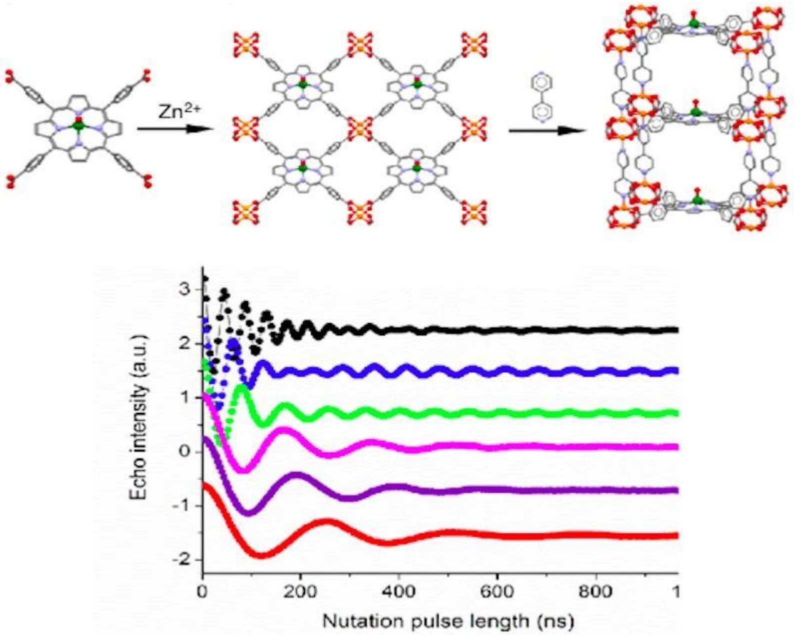

Fig.1. 3D MOF from 0D VO(TCPP) and Rabi Nutation at room temperature.

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Radical bridged Ln (III) based di-nuclear SMMs

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With the escalating demand for high-density information storage, single-molecule magnets (SMMs) have become an important class of bistable magnetic molecules. SMMs can retain the magnetization even after removal of the magnetic field, up to a temperature called blocking temperature (T_B). In this regard, Ln (III) coordination complexes stand out as excellent SMMs due to their inherent magnetic anisotropy. However, detrimental relaxation processes such as Raman and quantum tunneling of magnetization (QTM) aid the demagnetization of these molecules by shortcutting the overall energy barrier (U_{eff}). In this regard, the incorporation of redox-active ligands represents a clever approach in reducing QTM. Radicals can better interact with the deeply-buried 4f orbitals, allowing for direct exchange coupling between the paramagnetic centers, which in turn leads to significant separation between the ground and first excited states, as well as restricts the QTM process. The synthetic difficulties and stability of the complexes are the major challenges for the development of radical coupled SMMs. A well-judged combination of a high axial ligand field and a bridging radical ligand in a dinuclear lanthanide complex provides an SMM with higher U_{eff} and T_B compared to its non-radical analog due to strong magnetic exchange coupling between radical and Ln(III) ions. The bridging ligand must have a highly dense electron density localized towards the metal center. The tetraoxolene-based ligands are promising in this regard. Combining tetraoxolene bridging ligand with a highly symmetric capping ligand we prepared a dinuclear redox active Dy(III) dimer, where the pure m_J states and strong exchange coupling lead to the highest U_{eff} amongst the radical bridged SMMs reported so far.

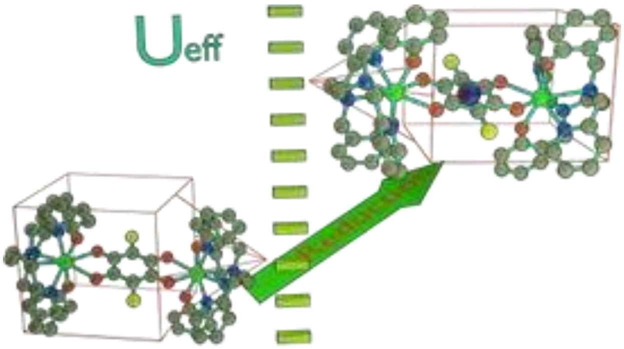

Figure 1. The chloranilate radical bridged Dy_2-SMM molecule shows highest thermal energy barrier amongst the radical bridged lanthanide complexes.

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Density functional dependency of DFT-calculated magnetic anisotropic parameter (D) values on dysprosium(III) metallocene complex

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Since the discovery of the single-molecule magnets (SMMs) with lanthanides by Ishikawa et al.,[1] the SMMs with single lanthanide ion i.e. the single-ion magnets (SIMs) have been actively investigated for applications such as spintronics, quantum computing and so on. In recent years, dysprosium(III) metallocene complexes have been attracted by their higher blocking temperature.[2-4] It is also reported that the introduction of substituents changes in the blocking barrier as well as the molecular structure in the dysprosium(III) metallocene complexes.[5] For a of decade, on the other hand, some magnetic properties of the SMMs have been examined by theoretical calculations. For example, a magnetic anisotropy parameter (D) value is often calculated by the density functional theory (DFT) method. It is, however, well known that computational results such as electronic states, energies, as well as simulated properties are strongly affected by the functional of the density functional theory (DFT) method. In this study, therefore, we examine the DFT functional dependency on the *D* values using the dysprosium(III) metallocene complex: $[(\mathrm{Cp}^{i\mathrm{Pr}5})\mathrm{Dy}(\mathrm{Cp}^*)]^+$ (**Figure 1**).

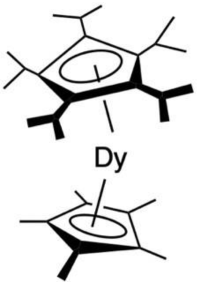

Figure 1. Illustration of the examined Dy(III) complex.

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OL 04

Hysteresis and Trapping Effects in Iron(II) and Iron(III) Spin Crossover Complexes

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The synthesis of multifunctional materials is generally considered as an important step from basic research to more application-oriented research.[1] One way to realize it is spin crossover (SCO) complexes, whose spin state can be switched by a wide range of physical or chemical stimuli.[2] Structural and electronic changes associated with this transition can be exploited for applications e.g. in the field of sensors. One strong advantage of SCO complexes is the possibility to observe bistability (hysteresis), however, it strongly depends on packing effects. We will discuss the impact of crystal packing on SCO properties with a focus on trapping effects.[3] In order to realize applications of such switchable molecules, it is important to synthesize nanostructures that can be integrated into composite materials, for example, by the utilization of diblock copolymer (dBCP) micelles. Here, matrix-induced trapping effects are observed.[4,5]

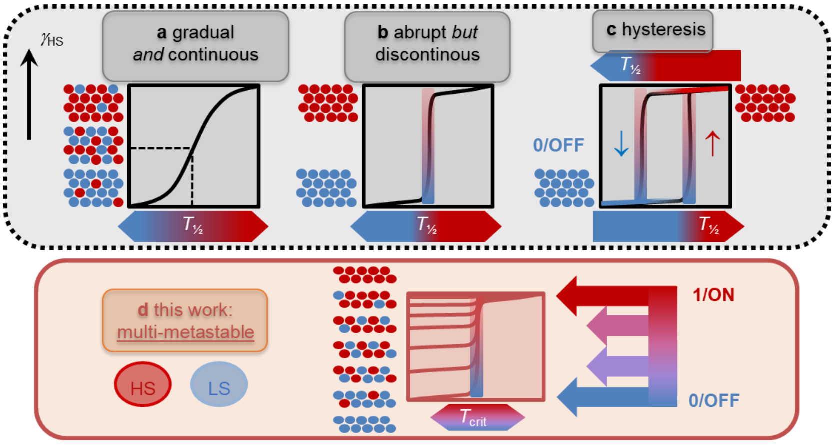

Figure 1. Hysteresis vs. Trapping effects for iron SCO complexes

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OL 05

Stable organic radicals for magnetic applications

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Stable organic radicals have garnered significant interest for their potential in advanced magnetic applications. Over the past decade, the development of numerous organic/main group radicals, aided by N-heterocyclic carbenes (NHCs) and cyclic (alkyl)(amino) carbenes (CAACs), has expanded the scope of radical chemistry.[1,2] These innovations have led to breakthroughs in new catalysis and the creation of novel electronic and magnetic materials. Despite these advancements, current synthetic efforts to obtain highly stable organic radicals remain centered on aminoxyl (TEMPO) or trityl derivatives. Developing new structures for highly stable organic radicals is thus a critical priority. Our group has been at the forefront of this effort, exploring diverse NHC/CAAC-based organic radicals, including unique structural platforms involving nitric oxide. In our pursuit of stable organic radicals, we have designed, synthesized, and characterized 1,2-dicarbonyl radical cations derived from NHCs and CAACs.[3,4] These radicals exhibit remarkable stability in air, water, and under chemical and thermal conditions, often surpassing the stability of established organic radicals like TEMPO and trityl. We believe that our 1,2-dicarbonyl radical cations hold great promise for enhancing the performance and durability of magnetic materials. Their exceptional stability and unique properties make them ideal candidates for innovative magnetic applications. Additionally, we will present our ongoing efforts to develop other structurally interesting and persistent organic radicals, further contributing to the advancement of magnetic materials.

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OL 06

Spin switching in Fe(II) compounds by solvent absorption-desorption processes

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Molecular-based materials able to absorb and desorb small volatile molecules are an exquisite tool for energy and environmental sciences. The potential of these systems relies on measurable physical changes experienced by the material upon interaction with the gas molecule.[1] One type of those materials are Spin-Crossover (SC) compounds, which can switch from high- (HS) to low-spin (LS) sate upon external stimuli such as temperature, light or inclusion of guest molecules. In the last years, we have developed a unique family of SC compounds featuring ligands with pyridyl and pyrazolyl units, able to absorb reversibly some volatile molecules at room temperature while maintaining, in some cases, its crystallinity (Figure).[2] These processes involve relevant optical, crystallographic and magnetic changes, converting those materials into promising room-temperature switches, sensitive to gases, and thus potential chemical sensors.

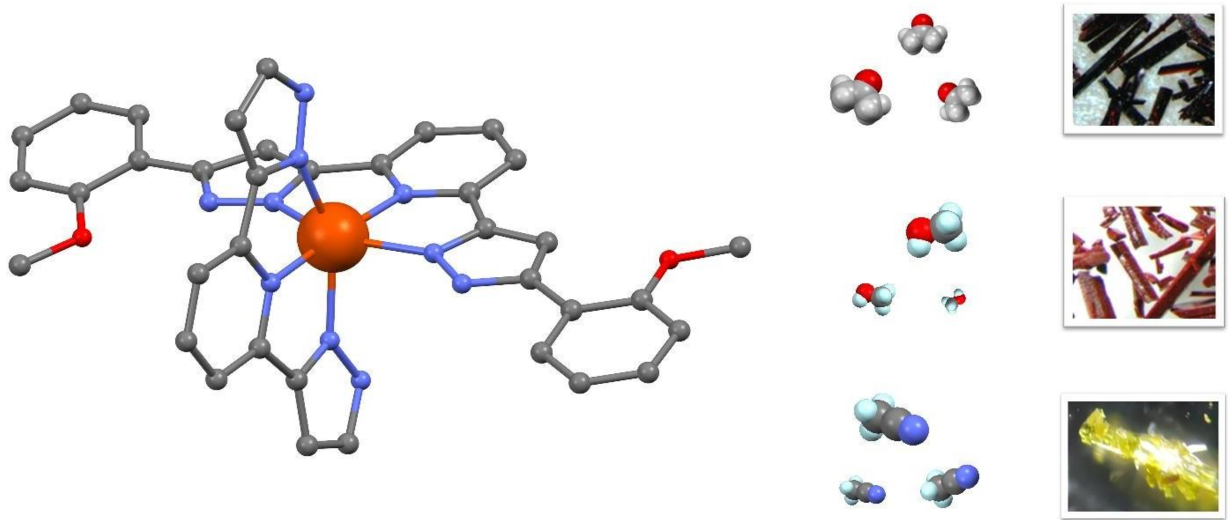

Figure 1. Influence of the solvent molecules in the crystal lattice in a designed Fe(II) SC compound.

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OL 07

The template effect of a SiF$_6^{2-}$:Toward the formation of heteroleptic Fe(II) coordination multifunctional helicates

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The anion SiF$_6^{2-}$ exerts a strong template effect, driving the exclusive assembly of two different bispyridylpyrazolyl ligands into a triple stranded Fe(II) dinuclear heteroleptic helicate, engendering a new class within the large family of coordination helicates.
The obtention of homoleptic and heteroleptic compounds, as well as the SCO behavior of them are strongly affected by the nature of the guests. This conclusion is derived from whe we compared the magnetic behavior shown by different compounds encapsulating SiF$_6^{2-}$ or ClO$_4^-$.
We demonstrate that within the cavity of coordination metallohelicates, the presence of H-bonding groups can be exploited to drive the exclusive formation of heteroleptic assemblies via a template effect. This can be exploited to introduce combinations of functions or properties within the assembly thanks to the ability of incorporating different ligands into the architecture. To generalize this methodology, the preparation of analogues of different divalent metals is now under investigation.

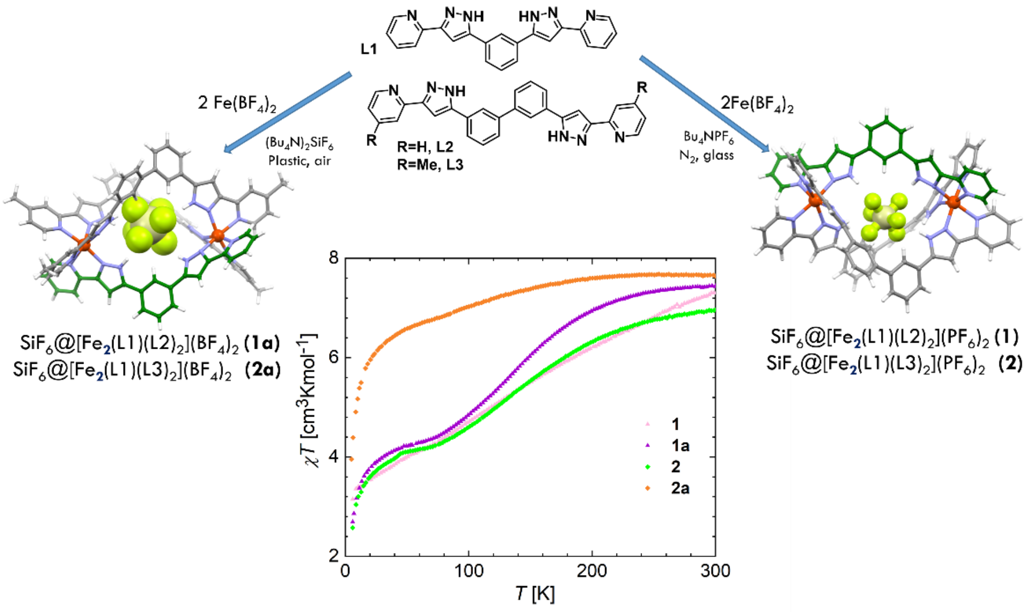

Figure 1. Representation of SiF$_6^{2-}$@[Fe$_2$ L1(L$_x$)$_2$]Y$_2$supramolecular assemblies (where Y= PF$_6^-$or ClO$_4^-$and L$_x$ = L2 or L3) and their magnetic studies. Compounds 1, 1a, 2 and 2a exhibit a sharp increase of χT with T at very low temperature, caused by HS Fe(II) centers not following the Curie law in this range.

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Gated CO_2 Adsorption in 1D Porous Coordination Polymers of Phenazine-Linked Paddlewheel Diruthenium Complex

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Low-dimensional coordination polymers such as one-dimensional (1-D) chains often exhibit gated guest sorption accompanying structural transition at a temperature (T_G),[1,2] which is associated with an external pressure of the guest (P_G) characteristic to the material and guest used. This phenomenon can be evaluated in the Clausius–Clapeyron (CC) equation of $d(\ln P_G)/d(1/T_G) = \Delta H_G/R$, where ΔH_G and R are the transition enthalpy and gas constant, respectively. In this study, gated CO_2 adsorption was investigated in a 1-D chain based on a benzoate-bridged paddlewheel diruthenium(II,II) complex with a phenazine (phz) linker, $[Ru_2(p\text{-}MeOPhCO_2)_4(phz)]$ (**1**; $p\text{-}MeOPhCO_2^- = p$-anisate).[3]

Surprisingly, **1** underwent gate-opening (GO)/-closing (GC) at a much higher $T_{GC} = 385$ K under $P_{CO2} = 100$ kPa (Figure 1a) than those previously reported for such chain compounds, which usually appeared in the temperature range of 200–270 K.[1,2] CC analyses gave a similar ΔH_G value for these compounds (inset of Figure 1a), indicating that the transition entropy ΔS_G in each system plays a key role in shifting T_G; **1** results in a much smaller $|\Delta S_G|$ in the series. The crystal structure of the CO_2-accommodated phase ($\mathbf{1\supset CO_2}$, Figure 1b) revealed that Only **1** produced a CO_2-accessible 2-D topological pore in its CO_2-adsorbed phase $\mathbf{1\supset CO_2}$ (Figure 1c). whereas the others reported previously produced 1-D or discrete (0-D) topological pores for CO_2 accommodation. These findings strongly reflect the degree of freedom of CO_2 molecules in pores, which is related to ΔS_G.

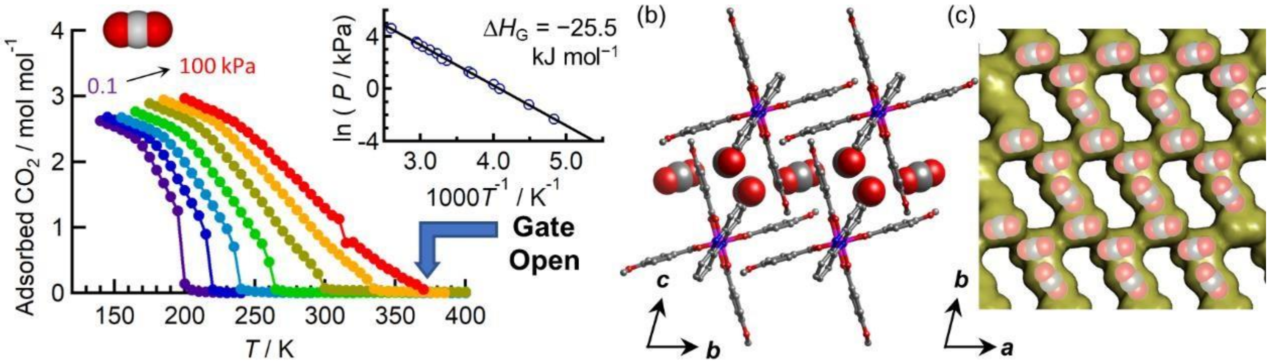

Figure 1. (a) CO_2 adsorption isobar. (b) Structure of $\mathbf{1\supset CO_2}$. (c) Connolly surface of micropore for $\mathbf{1\supset CO_2}$.

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Cooperative Adsorption and Gas Separations in Metal–Organic Frameworks

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The tunability of metal–organic frameworks offers the possibility of designing powerful new adsorbents that selectively adsorb and release gas molecules in a cooperative manner. An initial example of such a material was realized in mmen-Mg_2(dobpdc), which exhibits step-shaped CO_2 adsorption isotherms arising from a cooperative insertion mechanism that leads to ammonium carbamate chains running along the pore surface.[1] This mechanism has now been widely elaborated, leading to diamine-appended adsorbents that cycle at high capacity in the presence of water, and are capable of efficiently separating CO_2 from flue gas emissions, air, natural gas, and biogas.[2] Stabilization of the materials through functionalization with appropriately structured tetraamines further enables cooperative CO_2 capture at high temperatures, as well as regeneration via steam stripping.[3] This type of cooperative mechanism has been extended to the selective adsorption of CS_2, and a related mechanism has been shown to be operational in alcoholamine-appended frameworks. In addition, efforts to expand the scope of cooperative adsorption have led to new metal-organic frameworks containing: (i) chains of high-spin iron(II) sites that can cooperatively adsorb CO via a spin transition mechanism,[4] (ii) chains of redox-active cobalt(II) sites that exhibit negative cooperativity upon uptake of O_2, and (iii) binuclear metal complexes that enable the cooperative adsorption of NH_3 through a ligand insertion mechanism.[5] Finally, the first porous materials that can effectively capture gases such as CO_2 at elevated temperatures in the range 200-300 °C will be introduced.

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Semiconductive nature of metal-benzenethiolate coordination polymers

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Sulfur-coordinated coordination polymers (S-CPs) have attracted considerable attention in recent years owing to their diverse potential applications. The inorganic (–M–S–)$_n$ structures formed in the S-CPs give rise to unique optoelectronic properties such as visible light absorption and high charge mobility. Although the (–M–S–)$_n$ network structures in S-CPs may have a strong influence on the semiconductor nature of S-CPs, there have been no systematic studies on the correlation between network structures and electronic properties.

In this study, we investigated the effect of (–M–S–)$_n$ dimensionality on the semiconductive properties by systematically synthesizing S-CPs based on benzenethiol-derived ligands. Specifically, we synthesized three Pb(II) S-CPs with a formula of [Pb(x-SPhOMe)$_2$]$_n$ (x = *ortho* (**KGF-32**), *meta* (**KGF-33**), and *para* (**KGF-34**); HSPhOMe = methoxybenzenthiol). Single-crystal X-ray diffraction showed that **KGF-32** and **KGF-34** featured holodirected coordination spheres, but 1D (–Pb–S–)$_n$ chains with [PbO_2S_4] octahedra and 2D (–Pb–S–)$_n$ layers with [PbS_6] octahedra, respectively. Conversely, **KGF-33** features a 1D (–Pb–S–)$_n$ chain comprising a hemidirected [PbS_5] coordination sphere (Figure 1). Notably, time-resolved microwave conductivity and first-principles calculations revealed that the 2D-extended (–Pb–S–)$_n$ layer with the holodirected [PbS_6] octahedron observed in **KGF-34** served as a pathway for electron mobility.[1] In the presentation, we will also discuss the influence of weak intermolecular interactions between (–M–S–)$_n$ structures on the photoconductivity.[2]

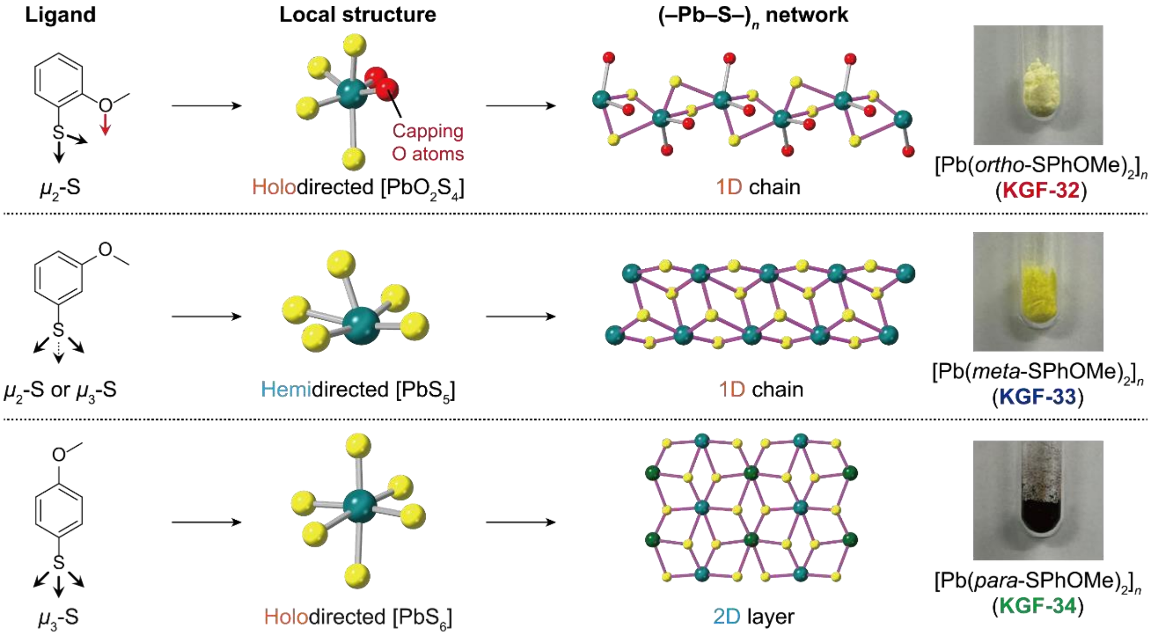

Figure 1. Schematic illustration of structures for [Pb(x-SPhOMe)$_2$]$_n$ (x = *ortho*, *meta*, and *para*)

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The CISS Effect in MOF Materials

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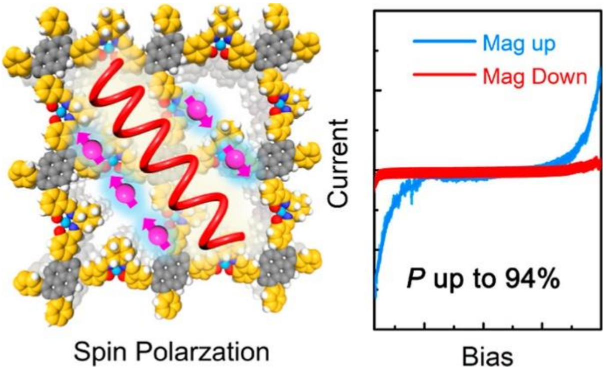
The chirality-induced spin selectivity (CISS) effect describes a phenomenon wherein charge transport through certain chiral molecules or structures shows a distinct chirality-dependent electronic spin polarization. This effect fundamentally shapes the design and efficiency of various technological and biological systems, including spintronics. With extensive research over decades, a variety of chiral materials, such as hybrid lead-iodide perovskites, and helical DNA, have been identified as efficient electron spin filters that preferentially transmit one certain spin orientation of electron. In principle, a chiral system with a high spin polarization ratio indicates a significant potential for enhancing the efficacy of spintronic filters and devices, showcasing its capacity to selectively propagate electrons based on spin. However, most chiral materials achieved spin polarization ratio below 80%, with the corresponding spin tunneling devices registering as low as 1% (0.2%). So, it remains a synthetic challenge to design chiral materials with high and stable spin polarization ratios. In this work, we demonstrated that for the first time covalent organic frameworks (COFs) can be an attractive platform to develop efficient spin filter materials with high CISS through tuning chirality.



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MicroED study of metal-organic frameworks

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In this communication we will report our latest results on using MICRO-ED to obtain single crystal structures of a series of 3D and 2D meta-organic frameworks (MOF) with spin crossover properties or obtained by mechanochemistry.

MICRO-ED is a unique technique that allows to ascertain crystal structure of nanocrystals. Its applications to MOFs are being unveiled as we speak, since one of the main problems in MOFs is the crystallization into suitable single crystals. The technique is extremely powerful in this respect, and it requires an understanding of both TEM and single crystal X-ray crystallography. Mechanochemistry is a clean synthesis technique that fits into UNs Sustainable development Goals, since it generates no waste, it requires no solvents and the yield of products is 100%, which is very relevant for high cost reagents like lanthanoid ion salts. We present two case studies: a) Spin crossover MOFs; b) mechanochemical obtention of Eu(III) luminescent MOFs.

In case study a), we successfully characterize a MOF with spin-crossover properties using simple sonication to obtain nanocrystals. MOFs with switchable spin crossover (SCO) behaviour offer a unique platform due to their dynamically tunable magnetic properties. Characterization of the structure of hydrated **$[\mathrm{Fe_2(H_{0.67}bdt)_3}]$**[1] helps us understanding the importance and the nanostructural role of the H_2O molecules, which we know are crucial for the switchable properties of the material.

In case study b) we use mechanochemistry to prepare the luminescent 2D MOF **$[\mathrm{Eu(MeCOO)(PhCOO)_2}]$**.[2] Using mechanochemistry has many advantages, but the products obtained are usually highly amorphous or nanocrystalline. In this case study, we successfully use MICRO-ED single crystal structure solution to unambiguously obtain the crystal structure of the Eu 2D MOF.

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Post-synthetic assembly based on Schiff-base condensation using formylbenzoate-bridged paddlewheel $[Ru_2^{II,II}]$ complexes

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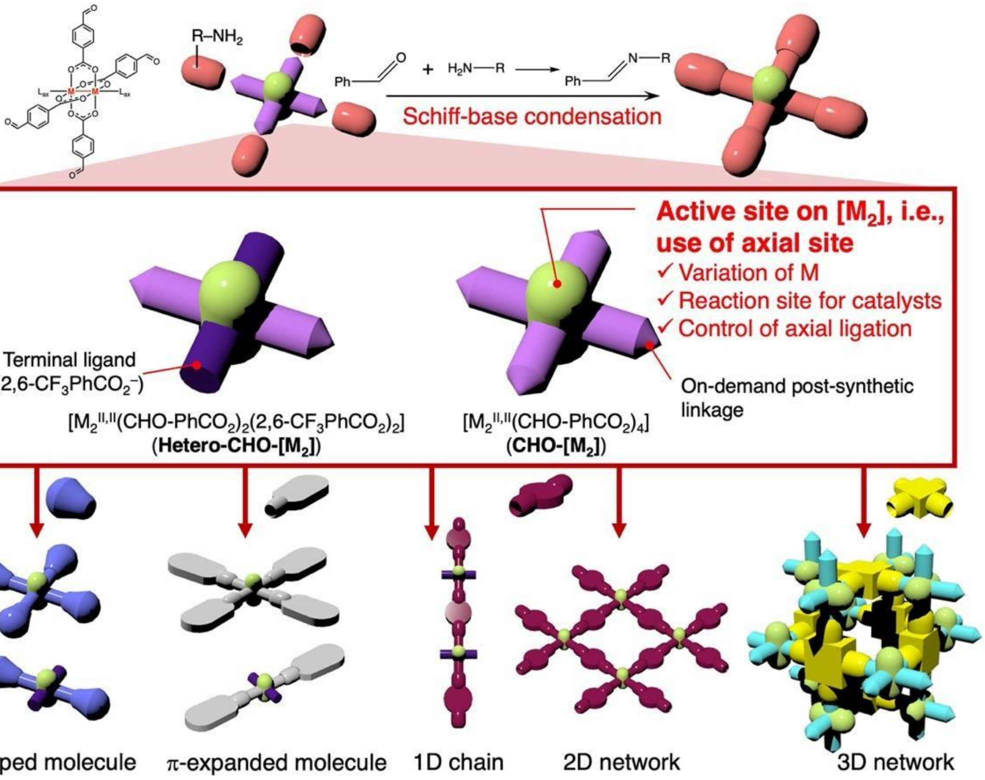
Paddlewheel-type diruthenium(II, II) complexes ($[Ru_2^{II,II}]$) have attracted considerable attention owing to their outstanding redox, magnetic, and catalytic properties. However, the conventional synthetic method for $[Ru_2^{II,II}]$ using equatorial carboxylate ligand exchange requires multiple steps, including the reduction of $[Ru_2^{II,III}]^+$ to the $[Ru_2^{II,II}]$ species, which sometimes leads to issues in terms of purity and yield. Furthermore, the synthesis of metal-organic frameworks linking the equatorial carboxylate ligands of $[Ru_2^{II,II}]$ is very difficult. Namely, incorporating substitution-reaction-inert metal ions from second and third transition metals into $[M_2]$-based MOFs is challenging. We demonstrate a novel one-step synthetic approach to $[Ru_2^{II,II}]$ assemblies using a combination of new formyl-substituted benzoate-bridged $[Ru_2^{II,II}]$ complexes and various aryl amine ligands [1,2].



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Unravelling of a [HS−LS] ↔ [LS−HS] Equilibrium in SCO Fe(II) Dinuclear Helicates Using Paramagnetic NMR Spectroscopy

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Multistable spin crossover (SCO) species are of great interest for spintronics as they offer a versatile way of exploiting the switching ability of their individual active spin centers.[1] A chemical design method to prepare functional SCO molecules is the self-assembly of ditopic ligands with Fe(II) in form of triple stranded helicates, $[Fe_2L_3]^{4+}$, where the metals are ensured to display the right crystal field conditions.[2] Of the numerous examples, some of them have shown the ability to present three different spin states; [LS-LS], [LS-HS] and [HS-HS].[3] We present here a ligand forming helical dinuclear Fe(II) SCO complexes able to encapsulate Cl^- or Br^-, $X@[Fe_2L_3]^{3+}$, exhibiting the three possible spin states, modulated by the guest.[3] These can be switched through various external stimuli and can be studied in solution using paramagnetic NMR spectroscopy.[4] These investigations have allowed to unravel for the first time a [HS−LS] ↔ [LS−HS] equilibrium. Solid state and solution properties of this family of supramolecular functional materials will be described.

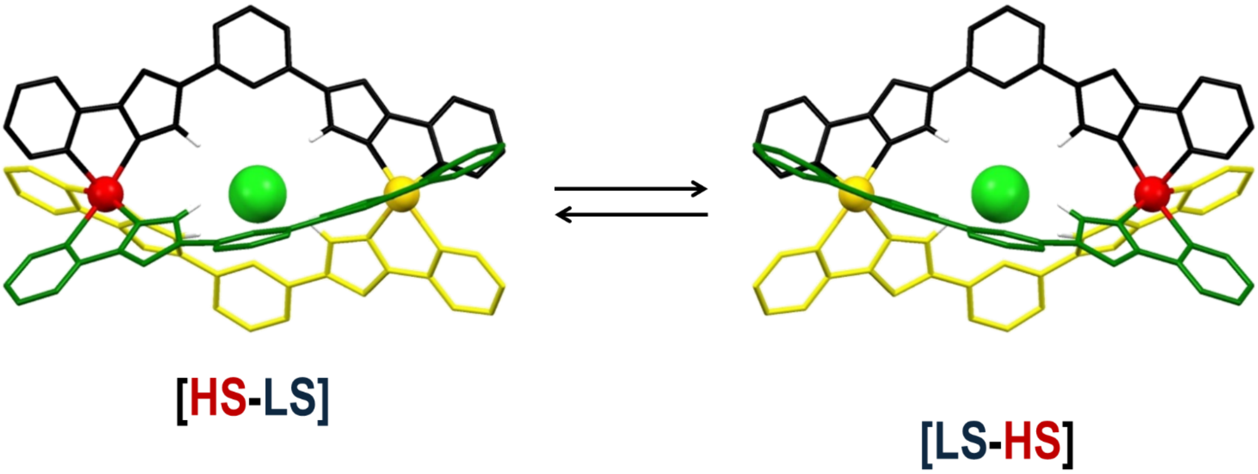

Figure 1. Representation of a $X@[Fe_2L_3]^{3+}$ (X=Cl or Br) supramolecular assembly, ant the [HS−LS] ↔ [LS−HS] equilibrium that they exhibit in solution.

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In situ NMR search for switchable magnetic compounds

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Spin-crossover (SCO) complexes are exploited in data storage, switching and (bio)sensing applications, e.g., as thermometers and pH-dependent probes for magnetic resonance imaging (MRI). The current method of choice to identify them is the Evans technique of NMR spectroscopy, which requires isolation and purification of each prospective candidate, making the search for new SCO compounds a tedious process. An alternative is following NMR chemical shifts with temperature (or other stimuli), which only needs a correct assignment of a few signals of the studied compound in the NMR spectra.[1] Although admixtures or side products (even paramagnetic) thereby become a non-issue, they are still actively avoided, as is the common wisdom in synthetic chemistry.

We, however, argue that this approach can significantly speed up the search for new SCO compounds if applied to several metal complexes at once produced by simple mixing of different ligands with a metal salt or by ‘one-pot’ synthetic pathways[2] that include pre- and post-modifications by reversible (de)protonation in an NMR tube. When tested on a series of homo- and heteroleptic complexes of terpyridines and 2,6-bis(pyrazol-3-yl)pyridines[3] (Fig. 1) functionalized by pH-sensitive groups, it helped us to discover new SCO compounds and ways to control their spin state even for those of them for which it was previously deemed impossible.

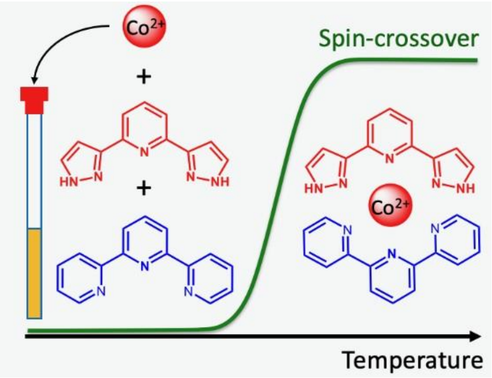

Figure 1. *In situ* NMR search for an SCO in a mixture of homo- and heteroleptic complexes.

A simple (‘visual’) analysis of NMR spectra collected from mixtures of different compounds and products of their *in situ* modifications without their isolation thus emerges as a powerful tool for a rapid search for new switches, thermometers and pH-dependent probes for MRI boosted by wide possibilities for chemical modifications in heteroleptic complexes.

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Steric control of spin states and reactivity in peroxocobalt(III) complexes: From boring to interesting

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The relationship between spin states and reactivity in peroxocobalt(III) complexes was investigated, emphasizing the role of steric modulation on supporting ligands. We synthesized and characterized two peroxocobalt(III) complexes, $[Co^{III}(MDAP)(O_2)]^+$ (**2**^{Me}) and $[Co^{III}(ADDAP)(O_2)]^+$ (**2**^{Ad}), featuring pyridinophane ligands with methyl and adamantyl N-substituents, respectively. The steric bulkiness of the N-substituents was found to influence the spin states and reactivity of these complexes significantly. Notably, **2**^{Ad}, with a bulky adamantyl group, facilitated nitrile oxidation to hydroximatocobalt(III) complexes, demonstrating spin crossover behavior between $S = 0$ and $S = 1$. In contrast, **2**^{Me}, with a less bulky methyl group, remained in an $S = 0$ state and showed no such reactivity. Both **2**^{Ad} and the previously studied $[Co^{III}(TBDAP)(O_2)]^+$ (**2**^{Tb}) exhibited similar spectroscopic and geometric features due to the steric effects inducing a weak ligand field on the cobalt(III) center. The study further revealed that the redox potential of a series of complexes is influenced by the ligand field strength, with values of –0.01 V for **2**^{Me} and 0.29 V for both **2**^{Ad} and **2**^{Tb}. Density Functional Theory (DFT) calculations supported these findings, providing insights into the electronic structures and emphasizing the critical role of spin states in the reactivity of peroxocobalt(III) complexes. This work demonstrates that manipulating steric effects on ligands can control the spin states and reactivity of peroxocobalt(III) complexes, offering potential pathways for designing catalysts with tailored reactivity.

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Make the design molecular again: metal cage complexes for spintronic devices

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Despite the proliferation of spintronic devices that revolutionized data storage, the potential of the molecular approach, which potentially gives unrivaled control over the properties of a device, remains largely untapped. Molecular spintronics aims to create devices with a unique 'spinterface', a crucial yet elusive element encompassing a 'ferromagnet – molecular compound' interface[1]. These devices are often built as vertical heterostructures of two ferromagnetic electrodes separated by a film of a molecular compound and an optional oxide tunnel barrier. The downside to this approach as of now is the use of chemical compounds with the inherent variability in their molecular structures upon chemical modifications exploited to alter their behaviour in a device. Such a variability is the reason why even the closely related molecules can produce films with diverse structures and morphologies and, therefore, diverse electronic and spin transport properties. This mismatch between the extent of chemical modifications and their impact makes it extremely challenging to identify which factor, such as a change in the structure or in magnetic or redox properties, is to be blamed for the observed variations in the device performance. Without this knowledge, however, the vast potential of the molecular design for fine-tuning the properties of a given device goes down the drain.

We aim to recover this potential by introducing cage complexes into the molecular spintronic devices. In these complexes, a macrocyclic ligand securely encapsulates the metal ion, thereby shielding it from the environment and ensuring the structural rigidity of the molecule, which is lacking in compounds found in molecular spintronic devices. Their neutrality, high chemical and thermal stability make them amenable to reproducible manufacturing processes, such as vacuum sublimation, setting them apart from most of other molecular magnetic materials. The use of different metal ions and functionalizing ligands, while leaving the core structure of the cage complexes intact, allows inducing a wide range of magnetic behaviors, including single molecule magnetism[2] or spin-crossover[3], thereby tuning the transport properties or creating stimuli-responsive multifunctional devices. The possibility of a selective step-by-step modification of cage complexes makes them ideal candidates to introduce incremental changes into the molecular layer of these devices.

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Light-Induced Thermal Hysteresis of an Ultrathin Film of Iron(II) Spin-Crossover Molecules Adsorbed on a Metal Surface

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Among the various types of hysteresis observed in spin-crossover (SCO) compounds, light-induced thermal hysteresis (LITH) [1] stands out as particularly spectacular. LITH is characterized by the emergence of a new thermal hysteresis loop within the photo-induced region during thermal cycles under constant irradiation, occurring in the thermally activated regime. This phenomenon arises from the direct competition between low-spin (LS) to high-spin (HS) molecular photoexcitation and HS to LS thermal relaxation of the metastable state. Here, we report on the photoexcitation of $[Fe^{II}((3,5-(CH_3)_2Pz)_3BH)_2]$ (Pz = pyrazolyl) [2] ultrathin films, with thicknesses ranging from 0.9 to 5.3 monolayers, adsorbed on Cu(111) substrate. Using X-ray absorption spectroscopy measurements, we confirm the anomalous light-induced spin-state switching [3] observed for sub-monolayer coverage and demonstrate that it is confined to the first molecular layer in contact with the metallic substrate [4]. For higher coverages, the well-known light-induced excited spin-state trapping effect is recovered. Combining continuous light excitation with thermal cycling, we demonstrate that at low temperature LITH is measured for the thicker films, while for sub-monolayer coverage, the light enables extension of the thermal conversion [4,5] over a large temperature range. Mechanoelastic simulations [4,6] underline that, due to the intermolecular interactions, opposite behaviours are observed in the different layers composing the films. Such light-induced interface effects need to be considered when electronic devices [7] incorporating ultrathin spin-crossover molecular films operate under light, and open new potentialities to design information storage devices [8] at the nanoscale: write information with light and then erase it with temperature.

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OL 19

Quantum Computing with Molecules

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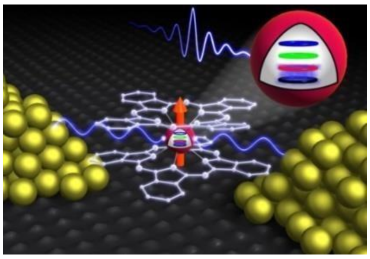
Nuclear spin states in molecules will be proposed to act as quantum registers for Quantum Computing (QC). We report on the implementation of metal complexes into nanometre-sized spintronic devices by a combination of bottom-up self-assembly and top-down lithography techniques. The controlled generation of magnetic molecular nanostructures will be shown and persistence of their magnetic properties under confinement in Molecular Quantum Devices will be proven. The Hilbert space spanned by the nuclear spins will be engineered synthetically and addressed both electrically and optically, partially at the single molecule level.[1-13] Finally, we will report im the implementation of Grover ´s quantum search algorithm within the nuclear spin register of a $TbPc_2$ Qudit.[10]



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