

Review Article

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Advances in spin crossover metal complexes: a comprehensive review on its gas sensing applications

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Abstract: Spin crossover metal complexes (SCO) are unique class of coordination compounds that can switch between LS and HS (low and high spin) states in response to external

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stimuli like pressure, temperature, gas molecules and light irradiation. This bistable behaviour makes them excellent candidate for many technological applications like data storage, molecular switches, actuators and sensing applications. The sensing mechanism of these complexes is based on the reversible change in their spin state which results in difference in magnetic, electrical and optical responses which can be evaluated with high sensitivity. This review provides a comprehensive analysis of the synthesis methods and characterization techniques of SCO metal complexes with a special focus on their gas sensing applications that remains unexplored in the literature. To address this gap this review comprehensively examines approximately eight published researches in this field, with a particular focus on gases such as ammonia (NH₃), carbon dioxide (CO₂) and volatile organic compounds (VOCs) like ethanol, methanol and alcohol we highlight the sensitivity and selectivity of SCO based metal complexes with their future prospects to enhance their performances for the future gas detection technologies. The review aims to explore the potential of SCO complexes in gas sensing technology and highlight the ongoing progress in this field. To the best of our knowledge this is the first ever review article which is dedicated exclusively to the gas sensing application of SCO based metal complexes to provide a new way for the advancement in this emerging field.

Keywords: spin crossover complexes; gas sensors; coordination compounds; spin transition; selectivity and sensitivity

1 Introduction

Spin-crossover complexes is a class of coordination compounds in which central metal ion (Fe, Co, Mn, Cr and Ni) change their spin states when an external stimulus like pressure, temperature guest molecules (CO₂, N₂, CH₄, O₂) and light

irradiation is applied.¹ The central metal ion is surrounded by the ligands (H_2O , NH_3 , Cl^-) which donate electron pairs to the metal and cause the switch of different spin states which makes SCO materials valuable in the fields like data storage, molecular switches, information technology and in sensing application. SCO is most typically found in iron (II), cobalt (II) and iron (III) molecular complexes. However, it can also occur in organometallic compounds,² metal-metal linked species, and inorganic salts. Spin crossover research often focusses on Fe(II) complexes with nitrogen (N_2) donor ligands due to their significant structural modifications between LS and HS states.³

In octahedral compounds with the d^4 - d^7 electronic configuration, ligand field determines the occupation of antibonding e_g and bonding t_{2g} orbitals. Weak field ligands (Chloride ion Cl^- , Iodide ion I^-) have a low energy gap in between t_{2g} and e_g orbitals (Δ_o), whereas strong field ligands (CO , NH_3) have higher energy difference. There are two feasible electron distributions (Figure 1) based on Δ_o size and spin pairing energy (E_p). When E_p exceeds Δ_o , the electrons in the d-subshell are distributed between the t_{2g} and e_g orbitals, resulting in a HS configuration. When E_p becomes lower than the Δ_o , electrons paired up in t_{2g} in (LS) before entering in the (HS) state.⁴ Transition in these states can be induced by different external factors like temperature, pressure, light, gas molecules depicted in Figure 1. Thermally induced spin crossover promotes LS states at low temperatures while HS states at high temperatures. SCO process is typically shown at a wide temperature range, rather than at a specific point. $\text{Fe}^{II} d^6$, is commonly studied ion in SCO research due to the largest possible shift in magnetic behavior from a diamagnetic LS a HS state with four unpaired electrons in the d subshell. A magnetometer is used to study observed the spin state. There are various significant changes also occur in case of Fe(II) SCO complex.⁵

- Due to the absence of electrons in e_g which is an antibonding orbital the bond length in Fe–N is ($\sim 1.8 - 2.0 \text{ \AA}$) for LS state which is approximately 10 % smaller than the HS state ($\sim 2.0 - 2.2 \text{ \AA}$). This difference is observed by the X-ray crystallography.⁶
- The HS state is mostly pale (yellow or purple), and the LS state is brightly colored (dark red or purple). This is something that UV–VIS spectroscopy can detect.⁷

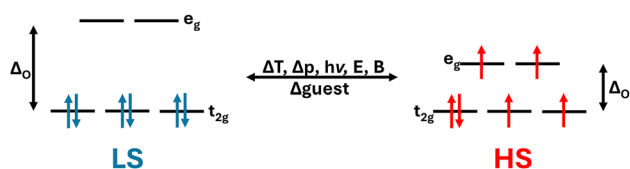


Figure 1: The above figure illustrate the splitting of d orbital in case of Fe(II) ion.¹⁰

- The emission and absorption of heat is observed in SCO from the transition from LS to HS state and vice versa. The (DSC) which is Differential Scanning Calorimetry a useful technique to observe the emission and absorption of heat and also to estimate ΔH (enthalpy) and ΔS (entropy) for the SCO occurrence.^{8,9}
- There are many other techniques to observe the changes in spin state of different complexes like UV/VIS, Raman spectroscopy, Mössbauer, and crystallography.

Studies that examine light and thermal-induced spin transitions for SCO complexes are significant. The high entropy gain at the HS state from electronic and vibrational contributions is cause of the temperature-driven spin state change.^{11,12} The LIESST (Light-Induced Excited Spin State Trapping) phenomenon is how light cause the different spin transitions in SCO. Hauser et al.^{13–15} discovered that in Fe(II) complexes transition from the LS to HS state when the green light is irradiated. Then it was observed that a red light can reverse the transition from HS to LS¹⁶ indicating that the photo-induced transition is reversible process (Figure 2) presents a schematic depiction of potential energy for Fe(II) SCO complex. A commonly used spin-transition method requires an intermediate triple state.^{17–19} The intermediate $^3T_1$ state transforms the $^1T_1$ state generated by photoexcitation

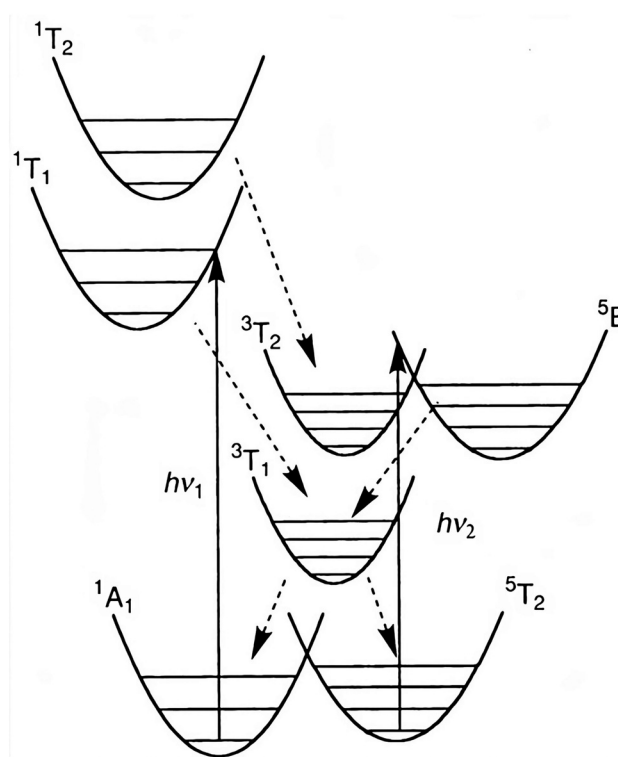


Figure 2: Fe(II) SCO complex showing the LIESST along with reverse LIESST.²⁰

($h\nu_1$) into the metastable $^5T_2$ state which is a requirement for LIESST while the $^3T_1$ state transforms the ^5E state induced by photo-excitation ($h\nu_2$) into the $^1A_1$ state in case of reverse LIESST. The spin-orbit coupling (SOC) between the singlet and triplet states as well as the one between the triplet and quintet states are important components of this mechanism, as it is the crossing of two potential energy surfaces. There are currently very few SOC analyses available that address the spin-crossover phenomenon.²⁰

Coordination chemistry and the material sciences have long been interested in the phenomenon of SCO in coordination networks of transition metal ions and molecular complexes due to their vast range of applications.²¹ Spin crossover materials are valuable in areas such as display technologies,^{22,23} data storage²⁴ sensors,^{25–32} actuators^{33–38} and MRI(magnetic resonance imaging) contrast agents^{39,40} due to their potential to show reversible transition states in response to some external stimulus. SCO metal complexes are highly valued due to their ability to switch between two different spin states LS and HS when exposed to external factors. This unique property has made them useful in many areas of science and technology. Apart from their growing emergence in gas sensing, where they offer high selectivity and sensitivity, SCO metal complexes are also being studied for use in memory devices and display technologies as their spin states can store information. Additionally, their ability to respond to external changes has opened up possibilities for biomedical applications such as MRI contrast agents. These wide range uses highlight the potential of SCO metal complexes as multi-functional and adaptable for advanced technologies. Since the 1970s, the research of gas sensor materials has gained significant attention because of the prospective applications in fields such as industrial production, indoor air quality monitoring, household security, automotive industry, and environment monitoring. The initial sensing devices mostly used solid electrolyte cells,⁴¹ ionic conductors,⁴² and semiconducting materials.⁴³ Up to now the most researched and widely used sensors have relied on electrical signal transduction methods using materials such as carbon nanotubes, metal-oxide semiconductors, organic polymer, and moisture-absorbing substances. These sensors are known for their advantages like fast response time and cost effectiveness. However, they have some draw backs, such as high energy consumption poor selectivity. For example, some semiconducting materials require high operating temperature which becomes difficult to attain and it hinder the sensor efficiency.^{44,45}

MOFs (Metal Organic Framework) materials were also being used as gas sensor in ammonia sensing. A research was reported on MOFs that could detect NH_3 at 100 °C based on changes in the corresponding luminescence, but no noticeable $NH_{3(g)}$ sensing results were obtained at room

temperature.^{46,47} The sensing properties can be modified by metal ions and ligands because of its characteristics like surface area, control over pore size and framework structure.⁴⁸ Research efforts have been directed on enhancement of the qualities that a sensor device should possess, such as high sensitivity, selectivity, low energy consumption, quick response time reversibility, and low manufacturing cost. SCO complexes offer high sensitivity and selectivity due to their ability to reversibly switch spin states in response to gas molecules. SCO complexes can provide multiple readouts such as optical color and magnetic shifts enabling multi-model sensing techniques. Their temperature responsive behavior can enhance performance in controlled environments or allowed for combined temperature and gas sensing. As advantages SCO complex have limitations also for example the spin state transition and gas molecules interaction can sometimes be slow, leading to detailed sensor response and many SCO complexes require precise synthesis method which can be costly and time consuming. Despite these disadvantages SCO remain highly valuable and unique in gas sensing applications due to their properties. The reversible spin state transition provides a distinctive mechanism for detecting gas molecules with exceptional sensitivity and selectivity which is often difficult to achieve with conventional methods hence, SCO complexes continue to play a vital role in advancing next generation gas sensing technologies. In order to improve industrial safety and environmental monitoring, in an efficient way SCO complexes are utilizing more in gas sensing technologies from the past few years.⁴⁹ The implementation of gas sensor devices in this framework is particularly significant due to its direct practical implications, as the temperature can be adjusted by incorporating solvent or gas molecules in its crystalline structure.⁵⁰ The design and development of spin crossover metal complexes plays a crucial role to increase the sensitivity and selectivity for gas sensing applications. So, the key design considerations include selecting the suitable metal ions and ligands to induce spin transition properties under the influence of external stimulus such as gas molecules. For example, ligands with high field strength can induce LS state while weak field ligands induce HS state transitions. The spin transition behavior observed by the change in color or optical properties when gas molecules are exposed to SCO complexes make them suitable candidate in gas sensing field. Recent research has demonstrated the successful integration of SCO complexes with metal organic frameworks (MOFs) and supramolecular architectures resulting in highly sensitive and selective gas sensors. Supramolecular $Fe^{II}_4L_4$ cages have shown fast ammonia detection with an excellent colorimetric change from light brown to purple within few seconds due to SCO behavior.⁵¹

As the SCO compounds have vast range of properties, they have been also utilized in multi-model sensing (detection through different measurable parameters) which is remarkable research in this field. A research was made on methanol and ethanol sensing by SCO.⁵² The research becomes easy with computer simulations, which offer important insights into the mechanics behind the spin-state transitions and gas interactions. Researchers can forecast and adjust the performance of SCO-MOFs by constructing various gas environments, which speeds up the creation of more specific and efficient sensing device.⁵³ In this review we aim to explore the key areas of the topic and to highlight its future prospects. To the best of our knowledge no comprehensive review article currently exists that focuses exclusively on the gas sensing application. It not only covers the general synthesis methods and advanced characterization techniques but also highlights their specific application in gas sensing. We will examine the different types of gases that have been detected by SCO complexes such as ammonia (NH_3), carbon dioxide (CO_2) and volatile organic compounds (VOCs). This review will serve as a valuable resource for researchers to make future advancement in gas sensing technologies.

2 Synthesis of SCO complexes and SCO based thin films

In the synthesis of SCO complexes various methods with different materials have been employed. Every method has gained much importance because of the successful synthesis in the research that has been done for spin crossover complexes. Methods such as solvothermal,⁵⁴ solid-state method, hydrothermal, mechanochemistry, solution-based methods, direct synthesis, wet chemical technique⁵⁵ and many more have been utilized. Each method has its advantages as well as limitations. For example, solvothermal method is known for producing high quality crystals however it requires elevated temperature and pressure which may limit its scalability. Solid state method though solvent free and environment friendly it is slower and less versatile. Solution based methods provide better control over reaction conditions but may involve the use of hazardous solvents. Despite of some disadvantages these methods were utilized to synthesize SCO metal complexes and have been discussed in the various review article regarding to the synthesis of SCO complexes.¹⁰ So herein we'll discuss the methods that have been proved more efficient in the synthesis of SCO complexes due to the easy step mechanism, cost effectiveness and offer better

scalability making them novel for the synthesis of spin crossover complexes from past few years. By focusing on these methods this work aims to provide the advancements in the modern synthesis approaches that have not been discussed in the previous reviews.

2.1 Wet-chemical method

Wet-chemical synthesis was performed to synthesize SCO complex. Ferrous ammonium sulphate hexahydrate ($(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$), sodium thiocyanate (NaSCN) and 1,10-phenanthroline monohydrate were used as major reagent. Zinc chloride and manganese chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) were utilized as doping reagent for SCO complexes because these reagents have the ability to modify electronic and magnetic properties of SCO complex and make them suitable for various practical applications. All the reagents mention above were utilized in the pure form in which they were purchased. In this experiment three different type of SCO complexes were synthesized the first one was un doped $\text{Fe}(\text{phen})_2(\text{NCS})_2$ complex **1** (sample-1), while the other samples 2 and 3 were doped with the reagents mentioned above $\text{Fe}_{1-x}\text{Mn}_x(\text{phen})_2(\text{NCS})_2$ (sample-2), $\text{Fe}_{1-x}\text{Zn}_x(\text{phen})_2(\text{NCS})_2$ (sample-3) here x represents the concentration of doped reagents which was about 30 %. As required for the experimental condition's methanol was used as solvent medium to observed the sensing mechanism of SCO complex. First of all, the solution of Ferrous ammonium sulphate hexahydrate and 1,10 – phenanthroline monohydrate was prepared in ionized water separately. After that the both solutions were mixed so that a dark red solution was prepared while 1:3 ratio was maintained during the complete process. Then the solution of NaSCN was added in the above solution to form a complex **1**.⁵⁶ A dip-coater was utilized to deposit thin layers of complex **1** on glass substrates that had been properly cleaned using 2-propanol and acetone. After that they were dried in vacuum. A slow dipping rate of approximately 0.1 mm/s is used to deposit the films. Different numbers of dipping times result in the deposition of films with differing thicknesses. The films are then subjected to an additional vacuum annealing process at 190 °C to produce the required complex **1** film. The thin films obtained by synthesis which ranged in thickness from 20 to 300 nm, was employed for characterizations. The samples that were prepared for the analysis were kept in a chamber made up of glass that was connected with electrical leads. Inside the chamber the arrangements were made to pass methanol gas and the electrical resistance was measured for all the complexes. Figure 3 shows the optical view of doped and un doped complexes with and without exposure of methanol gas. A clear difference can be seen with color variation.

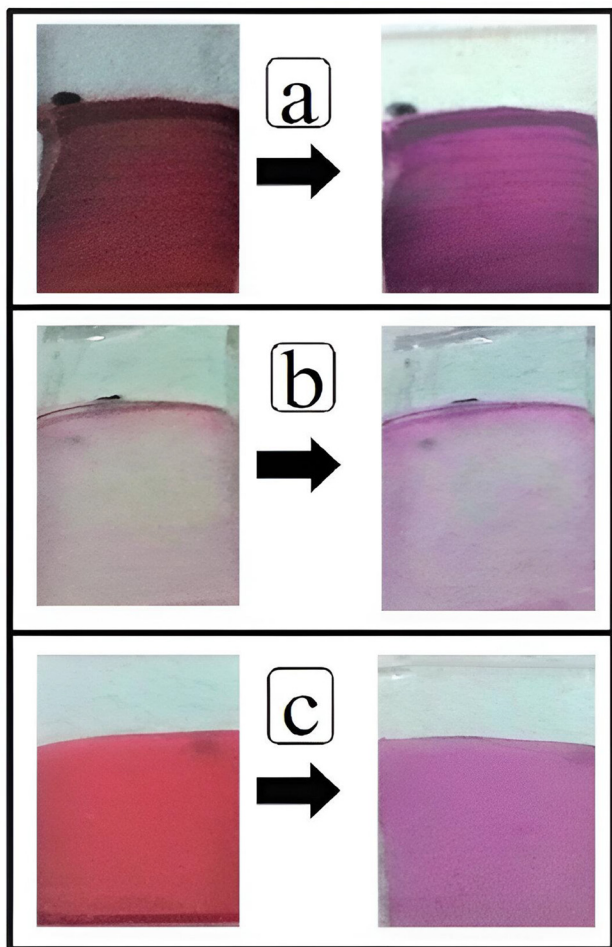
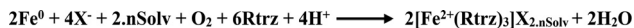


Figure 3: Optical view of doped and un doped complexes with and without exposure of methanol gas. (a) Sample 1(un doped) (b) sample 2 (doped with Mn) (c) sample 3 (doped with Zn) left side indicates absence of methanol while right side with methanol exposure.⁵⁷

2.2 Direct synthesis method

One-step metal complex synthesis known as “direct synthesis” begins with zero-valent metals or their oxides.⁵⁸ This method is remarkable because of its novel experimental strategy, cost effectiveness short synthesis time and easy control over the entire process. This was the first approach to synthesize the SCO complex of the triazole family by direct synthesis method. In this research Fe^{II} complex with 4-R-1,2,4-triazoles was utilized.⁵⁹ These complexes gained popularity owing to simple way they are synthesized, with different variety of functional structures. Triazolic compounds have found several uses because of these factors, including the creation of chemical sensors,⁶⁰ thermochromic pigments, memory devices,⁶¹ and many more. In this experiment four different types of SCO complex were selected. 1- $[\text{Fe}(\text{NH}_2\text{trz})_3]\text{SO}_4^{2-}$, $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{BF}_4)_2$ and other two was $[\text{Fe}(\text{Htrz})_2(\text{trz})]\text{BF}_4$ (where NH_2trz = 4-amino-1,2,4- triazole, Htrz = 4-H-1,2,4-



Scheme 1: The reaction is elaborating the Fe-triazole complexes where Rtrz is 4-R-1,2,4-triazole and X is anion.⁶²

triazole, trz^- = 1,2,4-triazolato anion). Scheme 1 describes how the transition metals dissolved oxidatively in the liquid phase. Organic solvents and water both can be utilized in direct synthesis. Iron powder with 4-R-1,2,4-triazole (R = NH_2 (1, 2), H (3, 4)) and ammonia/alkali salts with corresponding anion ($(\text{NH}_4)_2\text{SO}_4$ for 1, NaBF_4 for 2 – 4) was used for the successful implementation of direct synthesis method as a first approach to SCO complexes. The reaction was performed in slightly acidic conditions to promote the dissolution of Fe. The mixture was stirred roughly for one week and the SCO complexes formation was observed as the reaction progressed. After that, a NdFeB magnet could be used to readily separate the reaction mixture from the remaining iron. Centrifugation was used to separate the precipitate from the solvent. The SCO behavior shown by all four of the compounds produced by direct synthesis method indicates the effectiveness of this method for the synthesis of spin-transition metals complexes.

2.3 Mechanochemical synthesis method

The term “mechanochemistry” represents a material’s reaction when mechanical energy is applied, mainly by grinding when the material is solid. Although it was utilized in the synthesis of composites and inorganic materials, and it has also been utilized in the synthesis of co-crystals, molecular system, supramolecular networks and coordination complex.^{63,64} Because of their large temperature range of functioning and relative simplicity of chemical modification, the triazole-based 1D SCO coordination polymers have drawn a great deal of attention from the application perspective. One member of this family, $[\text{Fe}(\text{atrz})_3]\text{SO}_4$ (where atrz = 4-amino-1,2- 4-triazole), has previously been synthesized via solution-based methods.⁶⁵ For the very first time $[\text{NH}_4]_2[\text{Fe}(\text{SO}_4)_2] \cdot 6\text{H}_2\text{O}$ sample was prepared using mechanochemical procedures, and atrz were crushed for 5 min in a mortar and pestle in the absence of solvent. The traces of purple color were visible after 30 s which was an indication of LS state product. The complete sample was turned into purple after 4 min and at room temperature no more color change can be seen. The precipitation of water molecules due to hydrated metal salt caused the dampness of product. It was ground for a minute and heated at high temperature until it was completely dried. This general process was used to synthesize the SCO active materials for the first time using this effective method. The experimental details are elaborated in (Figure 4).

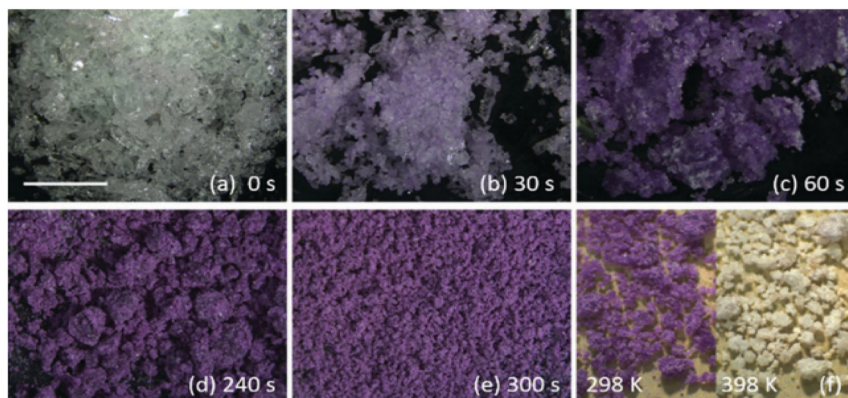


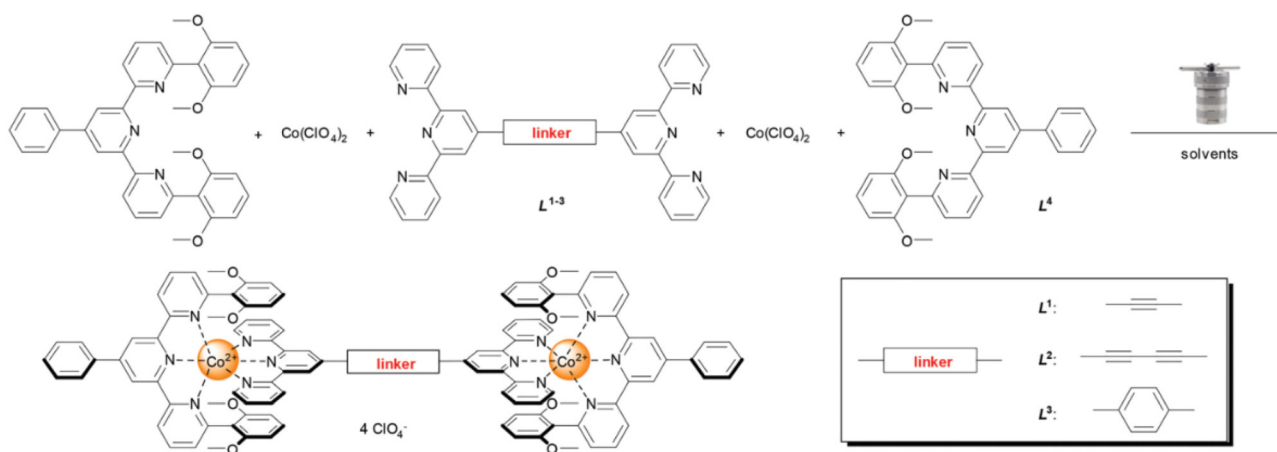
Figure 4: General synthesis process of SCO active materials. (a) Is the depiction of the reagents combined in pestle and mortar before grinding (b–e) display the formation of LS from the variation of color (f) display the change in color (showing transition from LS to HS) at different temperatures (298 to 398 K).⁶⁶

3 Structural characterization of SCO complexes and SCO based thin films

Characterization techniques are an important and very crucial to evaluate materials sensing, structural and magnetic properties. As by using different techniques it becomes easy for the researchers to verify the successful synthesis of the complexes and also their performance under different conditions can be observed. So, in SCO complexes we can analyze how the transition of different spin states occur by applying external stimulus. The characterization techniques like single-crystal X-ray diffraction (SCXRD),^{67,68} Mössbauer Spectroscopy,^{69,70} Infrared spectroscopy (IR),⁷¹ UV–VIS spectroscopy,⁷² Raman spectroscopy,⁷³ Fourier transform infrared spectroscopy (FTIR), Transmission electron microscopy (TEM),⁷⁴ Differential scanning calorimetry (DSC)⁷⁵ and Magnetic susceptibility measurements⁷⁶ are widely used up till now. Electrical resistance measurement is helpful in understanding the sensing mechanism of SCO for its application as

gas sensors. So herein we will discuss all the characterization techniques in a systematic way from structural to electronic, magnetic and thermal properties so that a complete view of SCO complexes can be easily understood.

The structural analysis of three dinuclear cobalt SCO complexes were carried out by (SCXRD). The synthetic mechanism of the dinuclear SCO cobalt^{II} is illustrated in (Scheme 2). Lattice solvent was present in all the structures (Co-1, Co-2, Co-3) and the solvent concentration was measured by the structural modifications with the help of gravimetric and thermal analysis. Herein we discuss about only one dinuclear cobalt complex (Co-1). For Co-1, the molecular structure has a symmetry center. The special asymmetric unit is made up of two chloroform molecules and two perchlorate ions, a cobalt^{II} ion, a L⁴ unit and half of an L¹ unit. An inversion mechanism was used to create the entire molecule. The conjugated planes of two terpy units are almost perpendicular to one another in the structure, and substituted terpy ligand L⁴ and the single terpy unit in L¹ hexa-coordinate the cobalt(II) ion (shown in Figure 5a). The six Co–N have the average bond length of 2.3039(2) Å at the



Scheme 2: Synthetic mechanism of cobalt(II) SCO complexes by utilizing 2,6-dimethoxyphenyl substituted terpy ligand (L⁴) and ditopic terpy ligands (L¹⁻³).⁵⁴

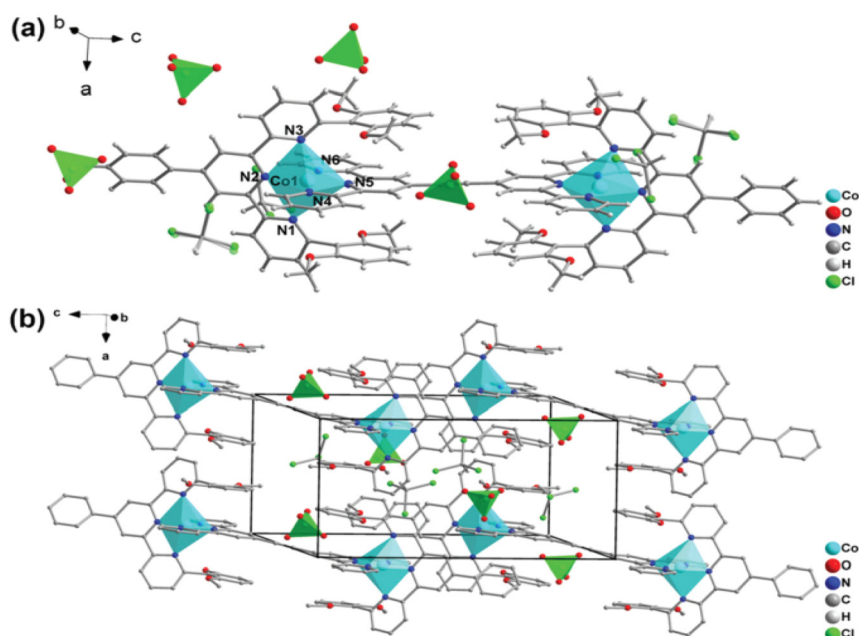


Figure 5: Mechanism. (a) The depiction highlights the SCXRD of (Co-1) (b) (Co-1) packing structure with b axis.⁵⁴

temperature of 120 K. At the same temperature it was seen that Co–N_{distal} distances (Co1–N3 = 2.259 Å, Co1–N1 = 2.241 Å, Co1–N6 = 1.969 Å and Co1–N4 = 1.972 Å) were greater than the axial Co–N_{central} distances (Co1–N5 = 1.859 Å and Co1–N2 = 1.936 Å). Furthermore, there is a noticeable Jahn-Teller extension across the N1–Co1–N3 path on the CoN₆ coordination sphere.⁷⁷ The characteristics of bond lengths and coordination distortion indicate cobalt(II) ion with $S = \frac{1}{2}$ which is common state (LS).⁷⁸ The chloroform molecules and the counter anions were observed in the space between the asymmetrical arrangement of dinuclear complexes in the lattice that is visible in Figure 5(b).

Transmission electron microscopy is used to observed the micro structure of the samples. TEM images of complex 1 for both samples doped 30 % with metals (Zn and Mn) and undoped are shown in (Figure 6). The structure of the films shows that the SCO crystals are growing regularly in granular form. The average particle size and shape of the various samples are approximately 300 nm, and metal dilutions have minimal impact on them. Mössbauer spectroscopy is helpful to examine the structure of compound and also the oxidation and spin states. In SCO complexes it is

utilized for the analysis of compounds which contain Fe in their structure. This technique is based on the Mössbauer effect in which a beam of gamma rays passes through the sample and the transmittance of beam after passing through the sample is measured. The Mössbauer spectra of [Fe^{III}₂Fe^{II}₂] was observed at temperature of 5 K (shown in Figure 7). This experiment was performed to observed the LIESST effect on SCO complexes. ⁵⁷Fe (95.5 %) was utilized as a stating material to prepare all samples. ⁵⁷Fe Mössbauer spectra highlights the confirmation of Fe^{II} LIESST effect when the green laser light irradiation of 532 nm was applied and the spin transition of Fe^{III} ions was due to red light irradiation at 808 nm. Measurements of magnetic susceptibility are an important method for describing spin-crossover complexes because they provide additional information on the magnetic transitions of various spin states. The data was collected on the magnetic susceptibility of [Fe^{II}₄] and [Fe^{III}₂Fe^{II}₂] to both light and heat stimulation. With regard to [Fe^{II}₄], the outcomes are shown as empty markers, where dark blue signifies the heating mode, while light blue the cooling mode, green the exposure to a 532 nm laser, and red the 808 nm laser irradiation. On the other hand, full markers

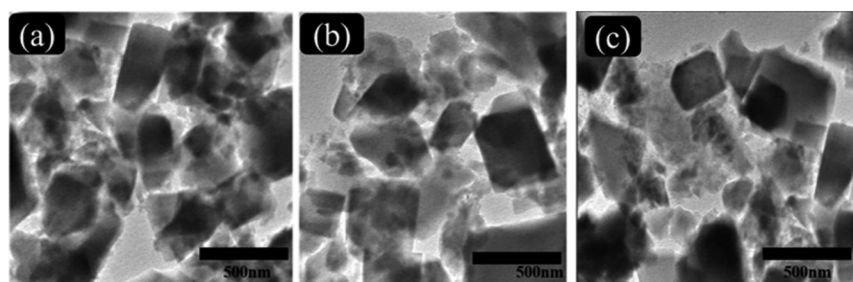


Figure 6: TEM images of SCO complex Fe(phen)₂(NCS)₂ (a) un doped (b) doped with metal (Zn) and (c) doped with metal (Mn).⁵⁵

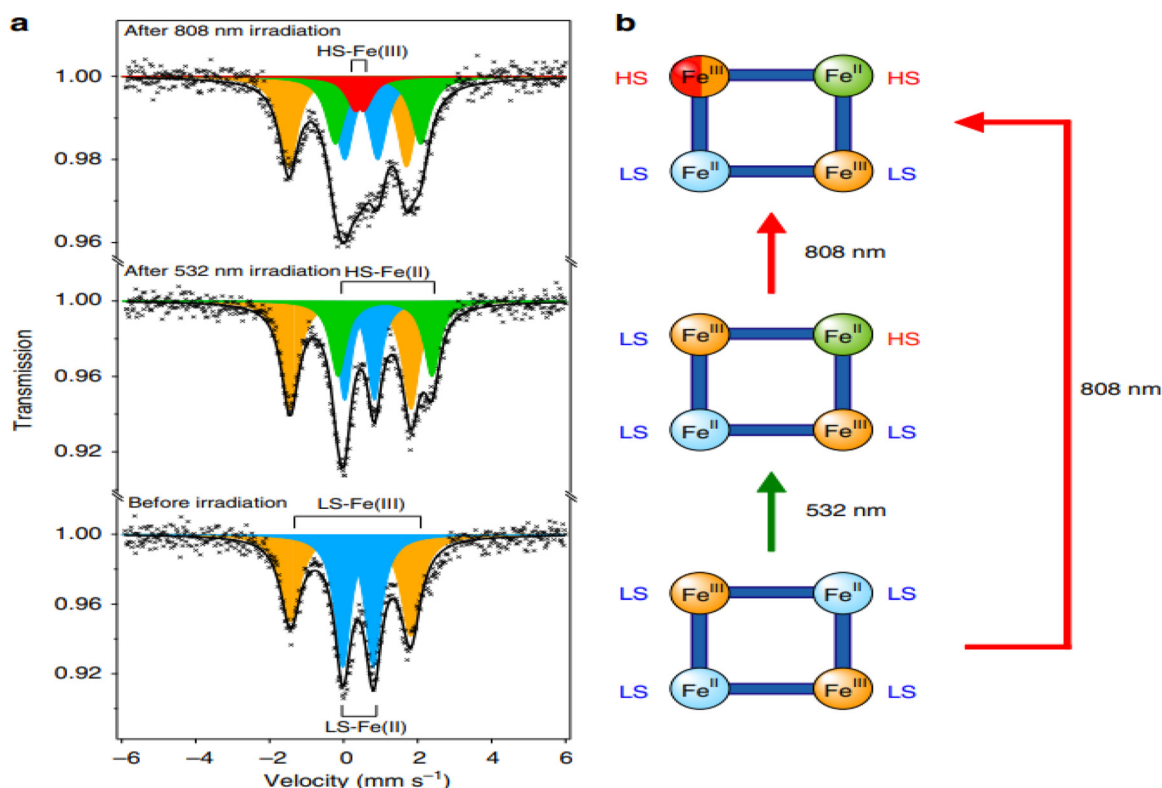


Figure 7: Mössbauer spectrum. (a) Showing the spectra of $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}_2]$ (b) ^{57}Fe Mössbauer spectra highlights the confirmation of Fe^{II} LIESST effect upon the irradiation of green and red light.⁷⁹

are used to display $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}_2]$ data; blue is used for heating, light blue for cooling, green is for 532 nm laser irradiation, and red is for sequential exposure to an 808 nm laser and a 532 nm laser. The complex $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}_2]$ showed minimal

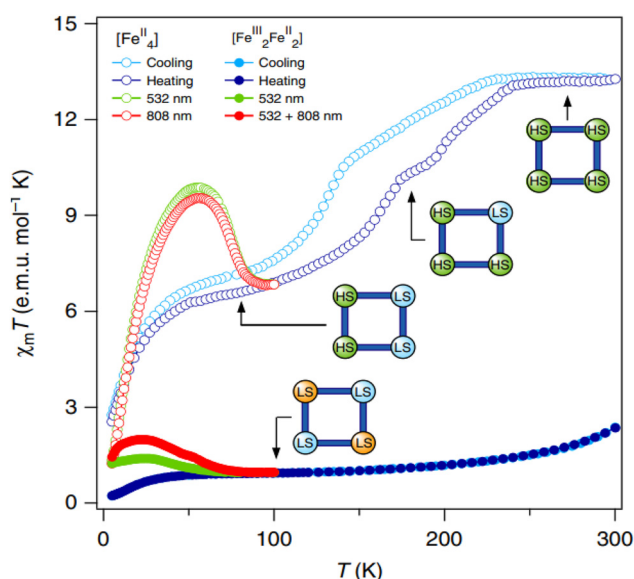


Figure 8: Magnetic susceptibility measurements obtained at the magnetic field of about 500 Oe.⁷⁹

thermal phase changes, however there were notable differences in the low-temperature $\chi_m T$ values after laser irradiation⁷⁹ (Figure 8).

In SCO complexes UV–VIS spectroscopy is essential to observed the electronic transitions with different spin change. As in SCO complexes spin state change by applying external pressure So, UV–VIS spectroscopy is helpful technique to monitor the difference in absorbance with regard to different spin states (LS and HS) by applying any external stimulus. In this evaluation we discuss UV–VIS spectra of the $\text{Fe}(\text{phen})_2(\text{NCS})_2$ thin film showing SCO behavior. At room temperature, data from a UV–vis spectrometer was used to monitor the thin films growth with the increase in their thickness. All films show a prominent absorption peak at about 530 nm, which is indicative of the $^1A_{1g}$ to $^1T_{1g}$ transition and gives the spin-crossover (SCO) complex violet color.^{80,81} For films varying in thickness from 20 to 300 nm, this absorbance remains unchanged, demonstrating that the films' electronic structure is unaffected by thickness (Illustrated in Figure 9).

Fourier transform infrared spectroscopy is used in the study of SCO complexes because it provides detailed information about the molecular vibrations mainly which involve on metal-ligand bond. Here FTIR spectra was used to elaborate the SCO complexes $[\text{Fe}(\text{phen})_3](\text{SCN})_2$ and

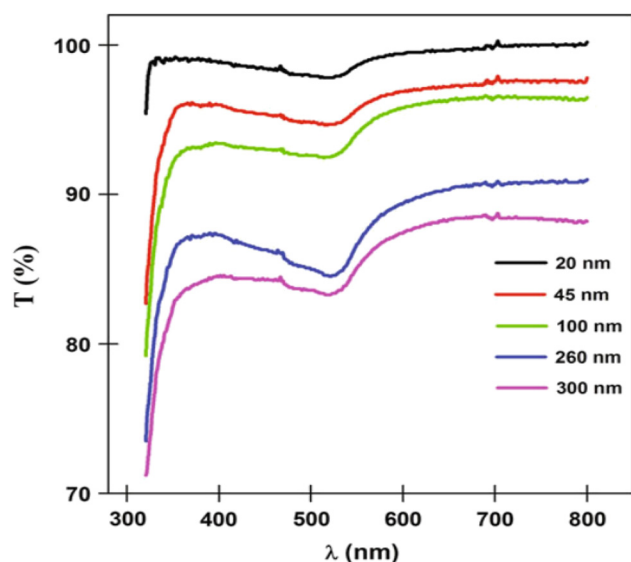


Figure 9: UV-vis spectra of $\text{Fe(phen)}_2(\text{NCS})_2$ with the thicknesses of thin films ranging from 20 to 300 nm.⁸⁷

$\text{Fe(phen)}_2(\text{NCS})_2$ (complex **1**) both in powder and film forms. The spectra were divided in three regions just to elaborate the weak bond. The stretching mode of N–CS was examined. The $[\text{Fe(phen)}_3](\text{SCN})_2$ powder shows a single band at 2048 cm^{-1} in the high energy region (Figure 10a). After pyrolysis, the $\text{Fe(phen)}_2(\text{NCS})_2$ powder exhibits a doublet at 2072 and 2058 cm^{-1} , corresponding to the asymmetric and symmetric stretches of the $(\text{NCS})^-$ ligands in a cis configuration. Vapor-deposited $\text{Fe(phen)}_2(\text{NCS})_2$ films show a single low-energy peak, same as $[\text{Fe(phen)}_3](\text{SCN})_2$, but with a slightly different shape. Upon annealing, the cis- $(\text{NCS})^-$ doublet reappears,

indicating similar ligand arrangements in both the purple films and the complex **1** powder. Small shoulders on the main peak are attributed to the naturally present isotopes. In the intermediate region illustrated in (Figure 10b). The phen ligands dominant in this location, which makes it less informative. With one exception of fluctuations in the peak's strength at approximately 1512 cm^{-1} and the peak shapes at $1,600\text{ cm}^{-1}$, all samples exhibit identical modes. These differences enable in discriminating complex **1** powder and purple films from $[\text{Fe(phen)}_3](\text{SCN})_2$ and the red films. In low energy region (depicted in Figure 10c) phen ligands ring deformation modes at $\sim 845\text{ cm}^{-1}$ and $\sim 723\text{ cm}^{-1}$ are the main characteristics. The relative intensities of various modes differ, even the positions remain unchanged. A well-resolved peak at 865 cm^{-1} is visible in the complex **1** powder and purple films, whereas weaker and less distinct peaks are seen in other samples. Although they are less noticeable in the purple films, the peaks at 804 and 794 cm^{-1} are associated with the NC–S stretch. Furthermore, in $[\text{Fe(phen)}_3](\text{SCN})_2$ samples, a shoulder at around 735 cm^{-1} may indicate the presence of uncoordinated thiocyanate.

Raman spectroscopy is used to characterize the thin films more efficiently. This technique is helpful to evaluate the effect of the metal dilution on structure of the complexes that are under research. It also examine how dopants break crystallographic symmetry in a crystal and alter the host crystal's lattice vibrational modes.⁸² Raman spectra of the SCO complex **1** was examined with both doped (Zn Mn) and undoped samples ambient conditions (Figure 11). The chemical shift in the doped sample either to higher or lower wave numbers in spectra is due to bond length of the molecules. The

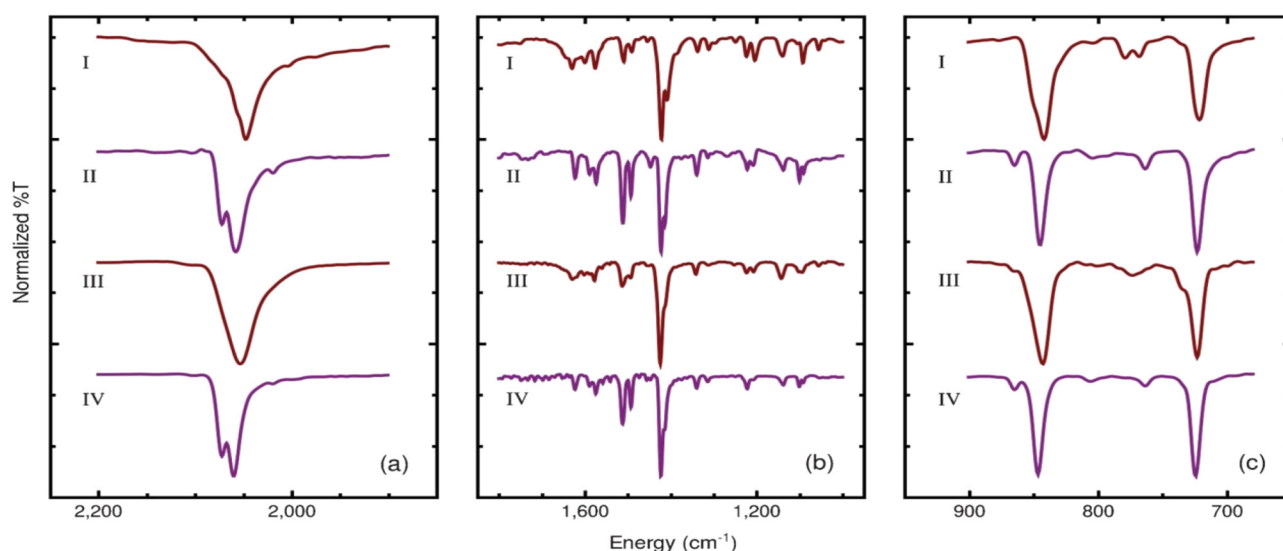


Figure 10: FTIR SPECTRA powder $[\text{Fe(phen)}_3](\text{SCN})_2$ (I). (II) The identical powder after it has been vacuum-annealed to become $\text{Fe(phen)}_2(\text{NCS})_2$. (III) A red layer that forms on KBr when $\text{Fe(phen)}_2(\text{NCS})_2$ is applied. (IV) An additional film made of $\text{Fe(phen)}_2(\text{NCS})_2$ was placed on KBr and vacuum-annealed at about 130°C .⁸³

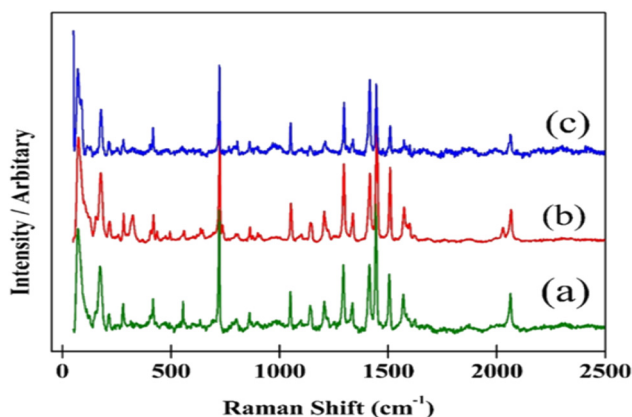


Figure 11: Raman spectra of $\text{Fe}(\text{phen})_2(\text{NCS})_2$ (a) un doped (b) Zn doped (c) Mn doped.⁵⁵

Longer wavelength cause shift to lower wave number and vice versa. The $\text{Fe}(\text{phen})_2(\text{NCS})_2$ (un-doped) exhibits peaks that can be attributed to different modes, including bending, torsion, deformation, stretching and the LS or HS states. The Fe–N bending and stretching mode has been given to the peak of pure $\text{Fe}(\text{phen})_2(\text{NCS})_2$ situated between 100 and 600 cm^{-1} . The symmetric FeN_6 bending and torsion modes of the Fe–NCS bonds are responsible for the peaks seen at 72 cm^{-1} , 215 cm^{-1} , and 280 cm^{-1} .^{83–85} Similar peaks can be seen in the Raman spectra of Zn-doped complex at 75 cm^{-1} , 218 cm^{-1} , and 281 cm^{-1} , and for Mn-doped at 71 cm^{-1} , 213 cm^{-1} , and 280 cm^{-1} , too. The undoped $\text{Fe}(\text{phen})_2(\text{NCS})_2$ peak at 722 cm^{-1} was due to the heterocyclic ring deformation. For Zn-doped SCO and Mn-doped samples, the peaks are apparent at 725 cm^{-1} and 723 cm^{-1} , respectively. At 862 cm^{-1} , the peak is ascribed to (NS)–S asymmetric stretching, while at 1335 cm^{-1} , it is attributed to (phen-) ring stretching. C–H in-plane bending is the cause of the peak at 1413 cm^{-1} and 1506 cm^{-1} . The Zn-doped compound at 865 cm^{-1} , 1337 cm^{-1} , 1416 cm^{-1} , and 1510 cm^{-1} and the Mn-doped compound at 1337 cm^{-1} , 1415 cm^{-1} , and 1509 cm^{-1} are found to have all these band locations with a minor positive shift. The doped crystal's spectra exhibits insignificant variations in peak locations and widths, which can be related to the crystal lattice deformation caused by Zn or Mn present in the $\text{Fe}(\text{phen})_2(\text{NCS})_2$.⁸⁶

This HS state identifying characteristic was also observed for Zn-doped at 2067 cm^{-1} and Mn-doped at 2063 cm^{-1} . When complex was doped with Zn (II) and Mn (II), the Raman peaks move as a result of the dopant's mass change and the varying amounts of micro-strain that the samples produce. Thus, the impact of the doping on bonding conditions for SCO in its HS state at ambient temperature was well illustrated by Raman spectra.

As the major focus of our review is on gas sensing properties of SCO complex so, here we will discuss the sample

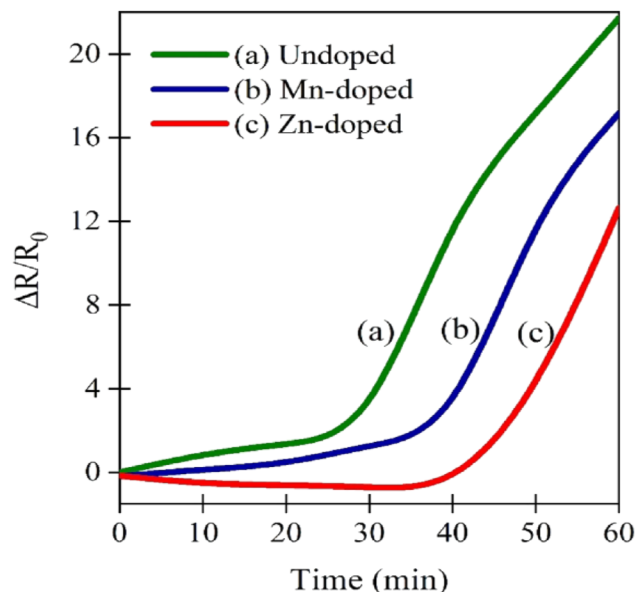


Figure 12: Graph is representing methanol sensitivity for SCO complex $\text{Fe}(\text{phen})_2(\text{NCS})_2$.⁵⁷

electrical resistance technique which was utilized for the analysis of SCO complex after the exposure of gas and volatile organic compounds. Initially the resistance R_0 of sample having $\text{Fe}(\text{phen})_2(\text{NCS})_2$ (complex 1) was measured at room temperature. After the exposure of methanol vapors to the sample a gradual change in resistance R was observed after 20–40 min. The sensitivity was measured by $\Delta R = (R - R_0)/R_0$ where R_0 was the electrical resistance of sample before exposure of methanol vapors and this is visible in (Figure 12). All of the samples respond the same way however undoped SCO films have better sensitivity than doped samples at any given moment in time. Additionally, the Mn-doped film exhibits a greater response compared to the Zn-doped film. The interaction between ethanol and topmost layer of SCO molecules may be the cause of slow response at initial stage. More methanol molecules were adsorbed by SCO complexes and they diffused through the pores of the sample at the surface as exposure duration increased hence increasing the effectiveness of the interactions. This leads to in a successful increase in the samples' resistance and also sensitivity.

4 Spin-crossover complexes in the field of gas sensing applications

Gas sensors play very important role to monitor environmental pollution. The hazardous gases are polluting environment day by day due to the increases in the number of industries. Since 1970 the research on gas sensors has gained

notable attention because of its practical applications in different fields. In past the sensors were made up of different material that had its own merits and demerits. In present era the researchers are making efforts to develop sensors with improved sensitivity, durability and accuracy so that can also be detectable even at low concentration. As the MOFs possess broad range of organized hybrid structures with mesoporous channels and cages, they are excellent materials for the flexible structure of complex assemblies.⁸⁸ So, by utilizing different methods like post synthetic and direct methods it is possible to alter its chemical composition. Due to structural and chemical flexibility MOFs are useful in different application like drug delivery, gas storage, catalysis and for separation techniques. Previously some MOFs were considered for the sensing of small molecules.⁸⁹ Research was reported on MOFs that could detect NH_3 at 100 °C based on changes in the corresponding luminescence, but no noticeable $\text{NH}_{3(g)}$ sensing results were obtained at room temperature. So, an alternative approach for the development of accurate sensing materials was the use of electronically bistable materials like SCO complexes. The switching process is followed by change in different physical properties like color, dielectric constant, magnetic susceptibility and many more. Due to these properties SCO materials were considered a good option for different technological application such as sensors, switches, actuators etc. The incorporation of gas or solvent molecules in the crystalline structure of the gas sensor devices in this framework allows for the adjustment of temperature, which makes their application significant from the perspective of sensing applications. This was observed that many of SCO compounds lack absorption properties due to its non-porous nature that is crucial for its sensing behavior. By considering the MOFs capacity to integrate different types of guest molecules the research was focused on the encapsulation of SCO complexes in the large water stable pores of MOFs.⁹⁰ This approach was expected to combine the absorption properties and stability of MOFs with sensing features of SCO complexes to make it useful in the application of gas sensor.²⁷ Recent studies have shown that SCO complexes can be successfully integrated with supramolecular structures and metal organic frameworks (MOFs) to create extremely sensitive and selective gas sensors. So here we will highlight the successful research that have been made on SCO complexes in gas sensing applications.

4.1 SCO complex (supramolecular $\text{Fe}^{\text{II}}_4\text{L}_4$) as ammonia (NH_3) gas sensor with fast analysis time

Ammonia is utilized in many fields like agriculture, medicines, industries and many more.⁹¹ Furthermore, NH_3 is a significant

component of volatile basic N_2 which is used as an indicator for the decomposition of protein enriched foods so, ammonia is utilized to monitor food safety.⁹² However, minimal amount of ammonia can cause serious health issues for humans and also affect the ecosystem and environment.⁹³ The U.S health administration set a limit for indoor exposure of NH_3 at 35 ppm for 10 min.⁵¹ Hence, for the sake of human health and with regard to its practical application researchers are trying to develop ammonia sensor with ideal features such as cost effectiveness, easy to use, timely and high-performance based sensors. Research was reported on a $\text{Co}^{\text{II/III}}$ (mixed-valence) MOF with excellent stability and reproducibility. However, the double colorimetric detection of H_2O and NH_3 vapors at room temperature makes this system inaccurate.⁹⁴ The complexes based on Fe^{II} have explored as excellent sensing materials as the coordination sphere of metal center is susceptible to minute changes imposed by the insertion of guest molecules. Furthermore, the spin state change modifies visual outputs which is helpful to understand sensing mechanism.⁹⁵ Two HS state mononuclear complexes were reported $[\text{Fe}^{\text{II}}(\text{trz-tet})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$, and $[\text{Fe}^{\text{II}}(\text{H}_2\text{btm})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ where (trz-tetH = 5-(4H-1,2,4-triazol-yl)-2H-tetrazole) and (H_2btm = di(1H-tetrazol-5-yl)methane), they were utilized as sensor for hazardous gases and different VOC_s at room temperature but the response for the sensing of ammonia gas was in significant.^{96–99} Furthermore, Iron based SCO hybrid materials with MOFs were also reported for the application in food industries and also as gas sensor (iodobenzene and H_2O).

Hence, to improve the stability and response time of such colorimetric sensor a research was made in which triazine-based ligands was introduced ($\text{L} = (1\text{E}, 1'\text{E}, 1''\text{E})\text{-N}, \text{N}', \text{N}''\text{-(1,3,5-triazine-2,4,6-triyl)tris(benzene-4,1-diyl)tris(1-(1-methyl-1H-imidazol-2-yl)methanimine))$ coordination with Fe^{II} to develop a polynuclear $\text{Fe}^{\text{II}}_4\text{L}_4$ (MOC-1) metal organic cage with an coordination environment of Fe-N_6 for ammonia sensing was based on these aspects a) in order to increase the selectivity and uptake ability of $\text{NH}_{3(g)}$ triazine-based ligands was introduced in MOC-1.¹⁰⁰ b) The porous structure can increase the sensitivity of sensor and improve the diffusion rate of ammonia. c) Utilizing the fast precipitation method to develop microcrystalline structures with increased surface area to improve the sensitivity of $\text{NH}_{3(g)}$. d) It is possible that guest NH_3 molecules will not be able to efficiently replace the FeN_6 coordination sphere in each Fe^{II} metal center, which provides endurance in comparison to reported Fe^{II} -based sensors where H_2O molecules was involved in coordination. MOC-1 was prepared by the reaction 2,4,6-tris-(4-aminophenyl) triazine (TATP), $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, and 1-methyl-2-imidazolecarboxaldehyde in acetonitrile. Diethyl ether was let to diffuse into the reaction solution and red block-like crystals was observed after few days. MOC-1 was responded quickly to $\text{NH}_3(g)$ as seen by the powder's color

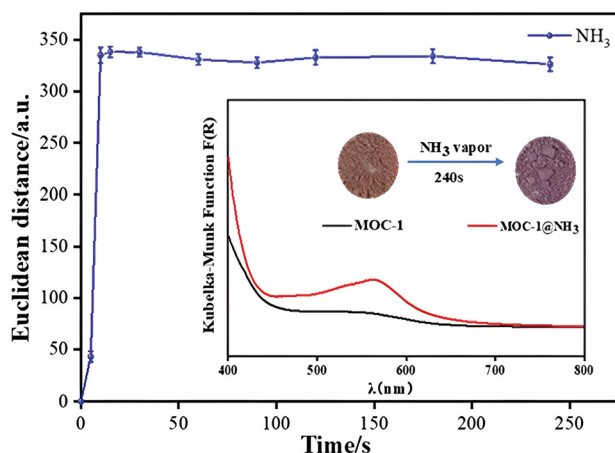


Figure 13: Metal organic cage-1 response time before and after ammonia exposure for 240 s.⁵¹

change within 10–240 s from light brown to purple color visible in (Figure 13).

Furthermore, MOC-1 has outstanding selectivity for $\text{NH}_3(\text{g})$ and 12 other analytes, such as amines and common solvents. Five consecutive cyclic tests were used to examine the reproducibility. The sensing mechanism was investigated using ^{57}Fe Mössbauer spectroscopy, which showed that the Fe^{II} metal centers undergo to spin state transition after the adsorption of ammonia molecules shown in (Figure 14). Chemometrics and simple to use inexpensive smartphone-based analytical techniques were also employed to examine the sensing efficiency in order to replace the previous techniques such as spectrophotometry and gas chromatography that requires complex methodologies. In order to prove this concept that either MOC-1 is applicable to in-field applications an experiment was performed successfully to examine the spoilage of pork at 4 °C (Figure 15). The thermal stability was more than 200 °C of thermal stability. The mechanism of sensing was linked to the Fe^{II} ions' transition from HS to LS state, predicted for a ligand field strength that fulfills SCO requirements. These findings demonstrate the

great potential of MOC-1 as a cheap, efficient NH_3 gas sensor that may be applied to the inspection of food safety.

4.2 SCO hybrid with metal organic framework as gas sensor for different volatile organic compounds (chlorobenzene, iodobenzene, bromobenzene)

MOFs have been explored as emerging materials for the development of sensing devices. Such type of materials is formed when the flexible organic units are linked by the metallic center in order to design a variety of large modified structures. The reliable and versatile synthetic methods of such compound make them able to modify the porosity and also the MOF-host guest reactivity with the objective to improve its sensing features like response time, sensitivity and selectivity. Furthermore, recent research has shown the feasibility to obtain MOFs as nanopatterns and thin films.^{101,102} By the combination of physical and structural properties allows for the development of functional materials that absorb analytes while varying a certain physical property. Previously, gas molecules were detected using luminescence,¹⁰³ refractive index changes, and plasmonic magnetic resonance spectra.¹⁰⁴ As an example, in the analysis of plasmonic resonance spectra and refractive index or luminescence show modification after the absorption of guest molecules have been the most advanced transducing signal method as a sensor for gas molecules. However, any of the MOF property either (magnetic, electric) show modification after the uptake of any guest molecules and this principle can be utilized for sensing device. So, this is the point where MOF show SCO behavior. In short SCO process is switching of different transition states (LS to HS states) when an external stimulus like pressure, temperature, and light irradiation and specially uptake of guest molecules which was significant for this research.

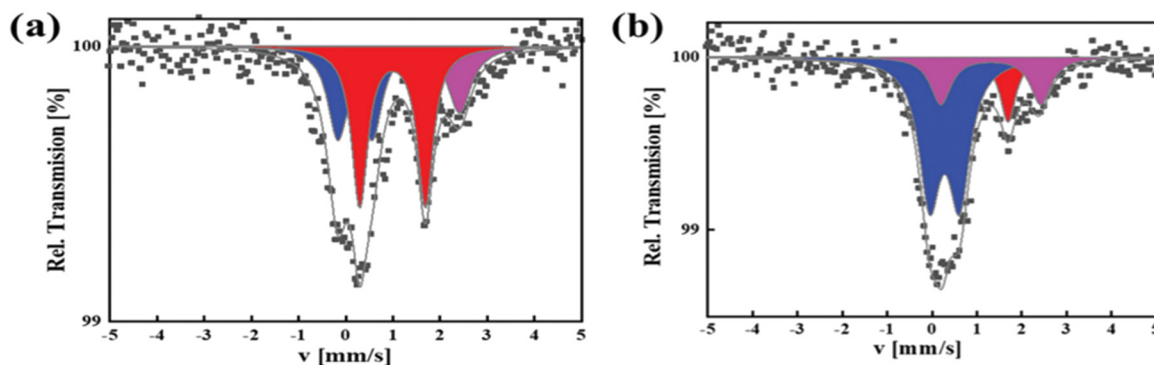


Figure 14: Mössbauer spectra of ^{57}Fe (a) metal organic cage -1 with ammonia (b) blue, red and magenta correspond to LS Fe^{II} , HS-1 , HS-2 respectively recorded at temperature 298 K.⁵¹

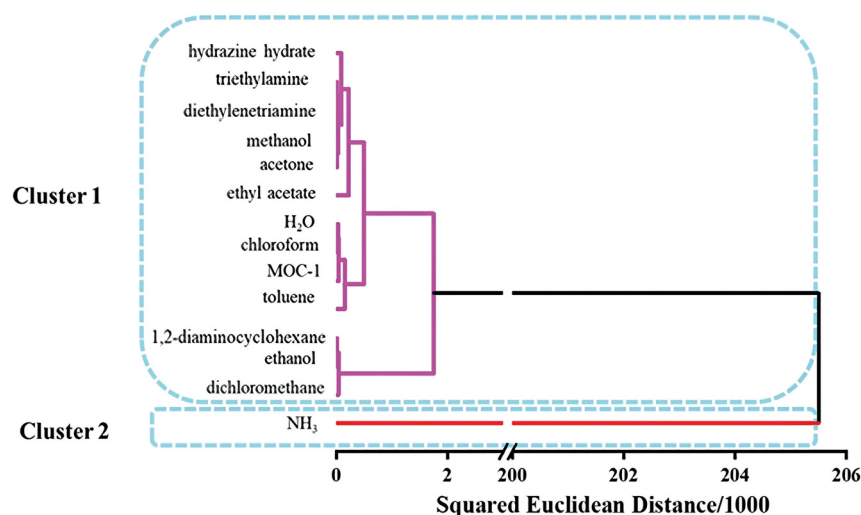
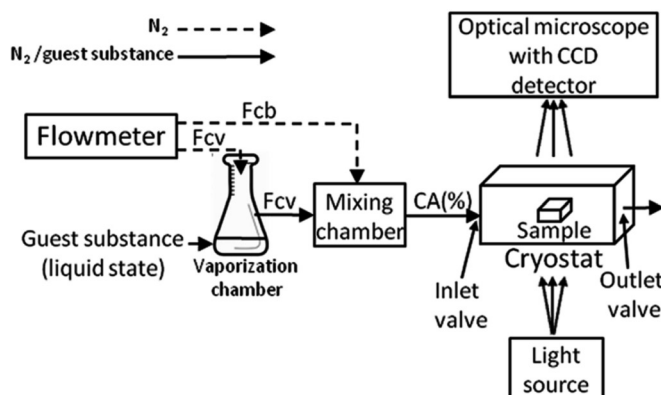


Figure 15: Hierarchical clustering analysis dendrogram for pork spoilage experiment performed under various time intervals.⁵¹

A research was made on a SCO complex $\text{Fe}(\text{pyrazine})[\text{Pt}(\text{CN})_4]$ which show change in its transition states from (LS to HS) and (HS to LS) after the absorption of guest molecules benzene and CS_2 .¹⁰⁵ Another research was also explored on a different SCO complex $[\text{Fe}(\text{NCS})_2(\text{bpbd})_2]$ (bpbd = 2,3-bis(4-pyridyl)-2,3-butanediol) here the transition was observed by absorption of different guest molecules methanol and ethanol.¹⁰⁶ The main step towards the gas sensing application of SCO complex is to develop a quantitative, sensitive and reliable signal transducing method. This is possible by monitoring the significant change in refractive index concerned with the change in spin transition after the uptake of guest molecules. This process can be done on nano and micro-patterned SCO molecules by optical diffraction.^{107,108} In this research spin transition of $\text{Fe}(\text{bpac})[\text{Pt}(\text{CN})_4]$ (complex 2) where (bpac = bis(4-pyridyl) acetylene) by diffraction grating was observed by the uptake of different VOCs like iodobenzene, chlorobenzene and bromobenzene. By the combination of two different methods layer by layer deposition and soft lithographic patterns the surface-relieve grating of complex 2 was fabricated.

The process was carried out by different steps **a)** an SU8 photoresist and a glass substrate coated in the metallic film of (5 nm Ti/15 nm Au) was exposed to ultra violet light through a photolithographic mask that displayed the grating patterns on it. **b)** To generate the patterns and eliminate the non-irradiated SU8, the photoresist was developed using a suitable solvent. **c)** Following the gold surface functionalization with thiol-type molecule, the substrate was constantly and repeatedly dipped in Fe^{2+} , $[\text{Pt}(\text{CN})_4]^{2-}$, and the bpac solutions (equivalent to one deposition cycle) to develop the complex 2 step-by-step. **d)** The final step in transferring SCO patterns was the lift-off procedure that was carried out in an acetone ultrasonic bath. The experimental setup shown in (Figure 16) was utilized for *in situ* diffraction gratings which is displaying the complete process of the absorption of guest molecules. The analytes concentration was monitored by the same process utilized for previous gas sensing research.¹⁰⁹ Nitrogen supply (Fcv) was provided via the vaporization chamber, which holds the liquid of the material which was utilized as a guest agent at room temperature. After being



$$CA(\%) = \frac{100F_{cv}P_a}{F_{cb}(P_b - P_a) + F_{cv}P_b}$$

$CA(\%) = \text{concentration of the guest substance}$
 $P_a = \text{Vapor pressure of the guest substance}$
 $P_b = \text{Room pressure}$

Figure 16: Schematic representation of the setup utilized for *in situ* diffraction measurements during the uptake of guest molecules.⁴⁹

saturated with the guest material, the nitrogen flow was fused with another flow of dry nitrogen (Fcb), which was sent directly towards mixing chamber. The resulting flow's concentration (CA%) can be controlled by adjusting the values of the Fcv and Fcb flows, which can be calculated by using the formula in (Figure 16). Thermal properties of SCO complex 2 was explored by the gratings. This was examined by first order of diffraction efficiency η_1 which was the estimate of temperature and any change in η_1 was related to change in refractive index that was modified with the change in spin states. The curve in (Figure 17) is displaying the SCO gratings behavior before the analyte's absorption (Open circles of grey color). The curve shifts towards the higher temperature after the exposure of iodobenzene vapors which was an indication of the absorption of iodobenzene by the complex 2 which modified its SCO behavior (closed circles of grey color). These results led to the concept that similar principal could be applied to other VOCs chlorobenzene and iodobenzene. The sensor was characterized by low limit of detection (approx. 30 ppm for iodobenzene), good reversibility, detection of linear dynamic range (300–1500 ppm) and also room temperature operation.

4.3 SCO based thin films for the sensing of methanol vapors

Methanol is a commonly used organic solvent with a wide range of uses, including power sources, perfume, industrial manufacturing, medicine preparation, and many more. The development of a highly sensitive methanol sensor is

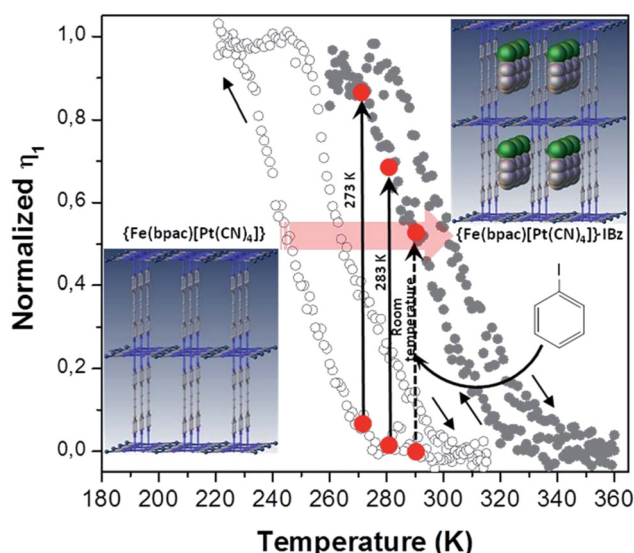


Figure 17: Temperature dependence of η_1 (normalized) on both cooling and heating moods before and after uptake of iodobenzene. The arrows connecting the red points show the variations in the value of η_1 among the loaded and empty gratings at the temperature of 273, 283 K, and at r.t.⁴⁹

essential due to its extremely poisonous properties, which can cause lethal effects in humans or atmospheric pollution. SCO sensor materials work on the principle of modulating spin states to produce detectable signals when they interact with external stimuli such as alcohol, gas, and vital parameters. In this research the SCO complex 1 was utilized to monitor the methanol sensing behavior with the doping of metals such as Mn and Zn. These metals were selected because of their paramagnetic and diamagnetic properties. Their crystal structure is the same as the corresponding ferrous complex. Due to Fe(II) comparable ionic radius to Mn(II), and Zn(II), the ferrous ions can be replaced iso-structurally. In this research the chemical wet technique was utilized to synthesize the desired complex which has already discussed in the previous discussion (synthesis of SCO complex). The crystal structure was examined by TEM and synchrotron XRD (Figure 18). Due to diffraction peaks all the SCO complexes have crystalline structure. The peak shift after metal doping was observed Fe²⁺ (76 pm) was replaced in its lattice site by dopant ions. Zn²⁺ ion (73 pm) has small ionic radius as compared to Fe²⁺ while Mn²⁺ ion (83 pm) has large ionic radius as compared to Fe²⁺. SXR peaks shift to higher and lower angle for Zn and Mn doped complexes. The sensitivity of methanol was observed by UV–VIS spectra. Furthermore, the sensing behavior of methanol was observed by measurement of electrical resistance and this technique has already discussed in the discussion of characterization techniques shown in (Figure 12). Charge distribution in SCO material occurs via polaron hopping between the two adjacent atomic sites.¹¹⁰ The mechanism that was related to the methanol sensing was based on difference in electrical conduction. The resistance is observed to be altered by variations of frequency, polaron hopping length, and mobility in the presence of polar methanol molecules. It is possible that the partial replacement of Mn or Zn for Fe in

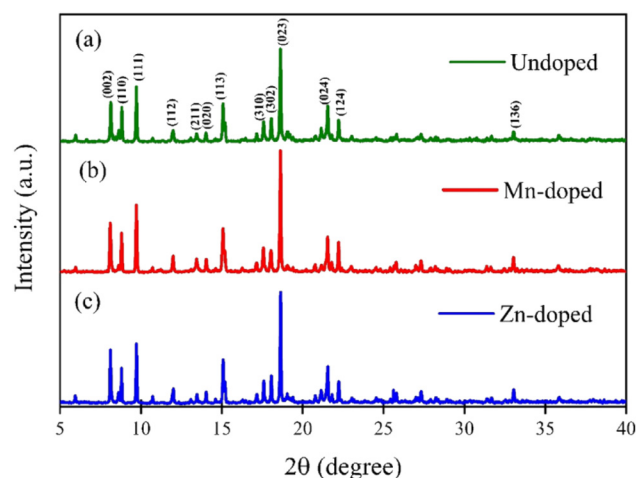


Figure 18: XRD pattern of Fe(phen)₂(NCS)₂ at room temperature.⁵⁷

the SCO affects the connectivity of center metal. Zinc is more electroconductive and electronegative than Mn, on other side methanol gas is electron donor and polar. Zn or Mn atoms will drag lone pair of electrons bound to the oxygen atom in the –OH- group hence, increasing the positive charge density and conductivity of the SCO backbones overall. This explains methanol vapors interaction with SCO complex and the measured sensitivity data is shown in (Figure 19). The research proved that SCO films exhibit high sensitivity to methanol exposure, and SCO material may play a significant role in the manufacturing of future smart gas sensors.

4.4 SCO complex as multi-modal sensor for ethanol and methanol vapors

Due to the unique properties related to different spin transitions and their response to the external stimulus SCO complexes offer a rare opportunity as multi modal sensor. Research was made on multi-model sensing potential of a neutral SCO complex was utilized as a selective sensor for ethanol and methanol. The sensing behavior of SCO complex observed that was due to insertion of VOCs in crystalline structure of complex. In this research the complex **3** [Fe(L)₂] (LH: (2-(pyrazol-1-yl)-6-(1H-tetrazol-5-yl)pyridine) which is a neutral molecule and can show different transition states at room temperature was utilized whose synthesis and characterization was reported in previous researches.¹¹¹ Complex **3** is a neutral compound that crystallizes into block-shaped crystals with 10 methanol molecules and eight complex units [Fe(L)₂] in each unit cell. The crystals grown in CH₂Cl₂/CH₃OH

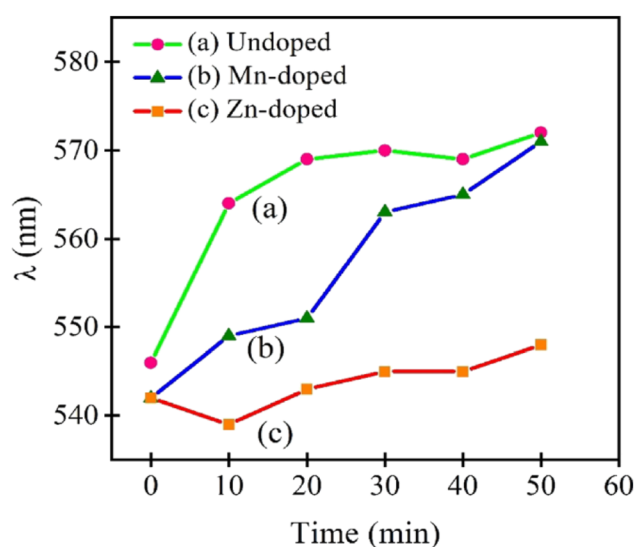


Figure 19: Modification in optical absorption of band wavelength on methanol vapors interaction at room temperature.⁵⁷

solution was yellow in mother liquor and turned red after evaporation of surrounding solvents. The magnetic characterization of the complex **3** depicted in (Figure 20) which displays a transition temperature that was centered at 295 K with hysteresis of about 5 K that arises after first thermal cycle.

The spin transition can be observed by polarized optical microscopy and Raman spectroscopy. Below transition temperature the powder form of the complex **3** was prepared from the red crystals of the size range from a few diameters to up to 100 μm. After heating to 300 K spin state of powder change from LS to HS observed by the change in colored from red to orange/yellow. the transition is related to the fragmentation of crystals likely due to the change in the structure of crystals in HS and LS states. Figure 21 shows the birefringence evolution and color difference after thermal cycling. It was observed by optical microscopy (OM) that the crystals were dark in LS state (absence of birefringence) while strongly colored in HS state (show birefringence). When the sample was cool down below its transition temperature the crystals (fragmented) restore to red color and lose its birefringence.

After magnetic characterization and optical microscopy (OM) Raman spectra was observed at different temperature. As in (Figure 20) displays the complete transformation of complex **3** in LS at 280 K and HS state at 328 K. The experiment was performed on single crystal at 294 K then cooled down to 160 K and then increasing up to 328 K and finally it was cool down to 280 K again. The Raman spectra was reversible on thermal cycling. The spin state of the molecules has significant impacts on the overall Raman spectrum, which has multiple distinct (diagnostic) peaks that are mainly centered in the 400–1100 cm⁻¹ region. Figure 22 depicts the Raman spectra of specific crystals at different

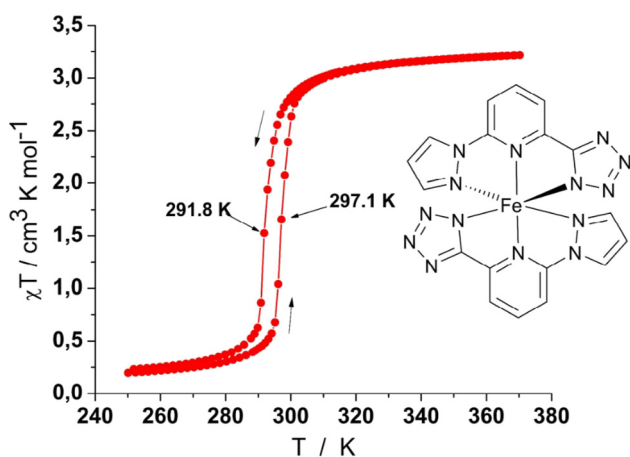


Figure 20: Magnetic characterization of complex [Fe(L)₂] with its structural formula.⁵²

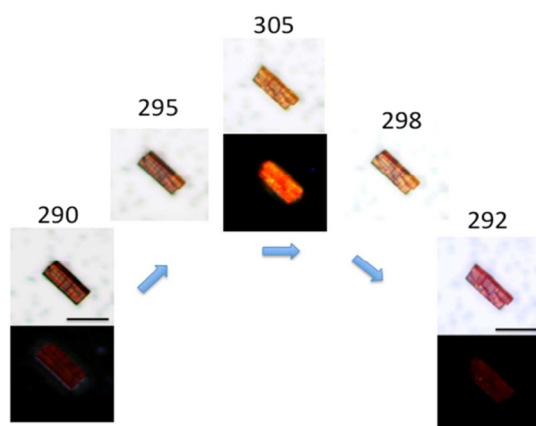


Figure 21: Visualization of optical and the cross-polarized images of SCO crystals deposited on the silicon upon a thermal cycle of 290 K $\rightarrow$ 305 K $\rightarrow$ 292 K.⁵²

temperatures (328 K and 280 K) showing HS and LS states respectively.

From the above data it was concluded different spin transition states can be analyzed by color, Raman spectra and birefringence in which weak birefringent state and red color relates to low spin state while the highly birefringent state and yellow color corresponds to high spin state. By taking influence from the observation that the crystals of $[\text{Fe}(\text{L})_2]$ show yellow color in HS state in mother liquor that was utilized in its synthesis and turned to red when the solvents were evaporated the research was made to observe the switching effect of SCO complex under different physical properties as a multi modal sensor for ethanol and methanol. Complex **3** was exposed to ethanol and methanol at r.t then the crystals turned from red to yellow same as in case of

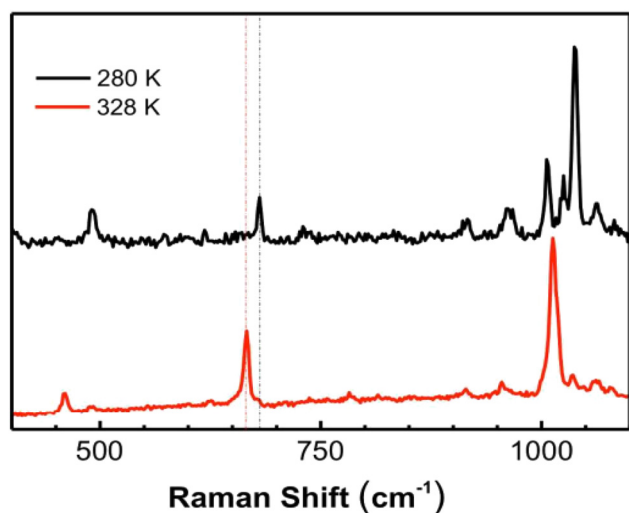


Figure 22: Raman spectra of complex $[\text{Fe}(\text{L})_2]$ at different temperatures (280 K and 328 K).⁵²

thermal spin transition. The effect name solvatochromic change of spin state has been already observed for different magnetic materials, SCO complexes and mainly efficient in the neutral compounds. The spin transition occurred in vapor environment it took few secs for methanol while few minutes for ethanol. The crystals that were exposed to methanol return back to their original state (red color) when they were removed from solvent (methanol) while remain stable for few minutes for ethanol. No noticeable effect was observed after exposure to other alcohols like chloroform, dichloroethane and acetone (likely due to steric hindrance). It is important to remember that when crystallites were taken out of the alcohol atmosphere, a nucleation and growth mechanism leads to the shift from HS to LS. Within 10 s, the nucleation expands along the entire crystal from one side. No fragmentation was seen after 10 repetitions of the methanol vapor's exposure. However, when ethanol was used, the behavior of complex **3** following solvent exposure more closely resemble to thermal cycle, and crystals begin to fragment after few cycles of solvent exposure (Figure 23).

In this research the crystals thermal behavior under methanol atmosphere was observed by Raman spectra while

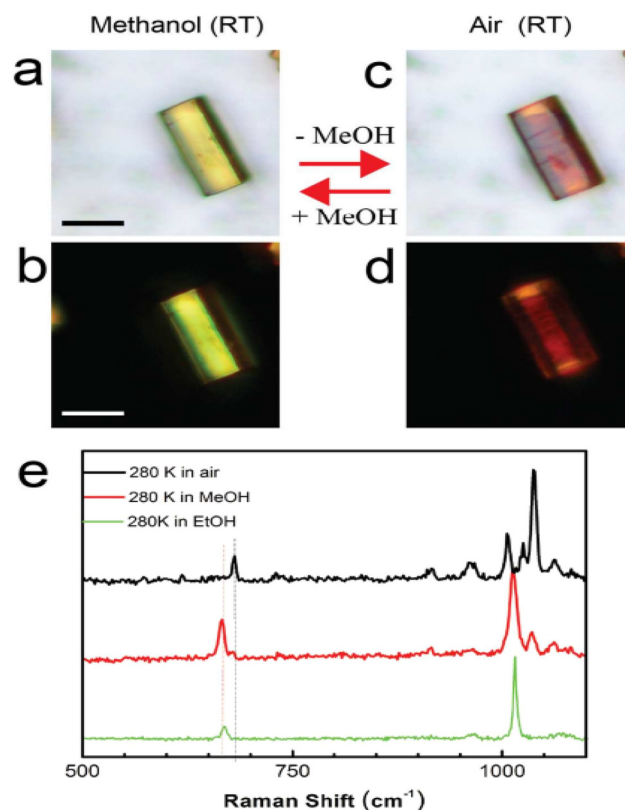


Figure 23: Depicts the behavior of crystals in both air and methanol by polarized OM and comparison of Raman spectra for air, ethanol and methanol.⁵²

for ethanol it was not feasible use Raman spectroscopy to monitor thermal behavior due to ethanol condensation on sample surface during cooling stage. To obtain detailed information on sensing behavior XRD was performed on the bigger crystals that was suitable for synchrotron XRD. To monitor multi sensor behavior the same setup was utilized that has already been used for TAG time temperature integrators the devices that are used to record thermal history.¹¹² A commercial CCD was used to record cross polarized and optical images at r.t and at thermal treatment under ethanol and methanol atmosphere. Figure 24 depicts the color counts of blue(B), green (G) and red(R) as function of temperature. The RGB color combination was itself away to monitor whether the crystals were exposed to ethanol or methanol and it was further confirmed by monitoring the crystals thermal behavior. The CCD interprets the spin transition as a dramatic change in the green component, whereas the red component displays a mean constant decrease throughout the cooling. Both the crossed-polar and

bright field visuals clearly indicate the transition as for the crystals exposed to ethanol and methanol, it happens around 270 ± 3 K and 256 ± 3 K, respectively. Hence it become easy to clearly distinguish between methanol and ethanol because to the difference in transition temperatures. This research illustrates a significant advancement in the field of SCO complexes offering a valuable insight for its application as multi modal sensor.

4.5 SCO complex ($\text{Fe}^{\text{II}}\text{L}_2$ and $\text{Fe}^{\text{II}}4\text{L}_6$ cage) as ammonia gas sensor with high nuclearity and tuneable porosity

NH_3 , a common environmental contaminant, has been identified as it is produced on a daily basis in a number of industrial sectors, such as manufacturing, agriculture, and the synthesis of chemicals. Excessive inhalation of this unpleasant and hazardous gas can result in respiratory system

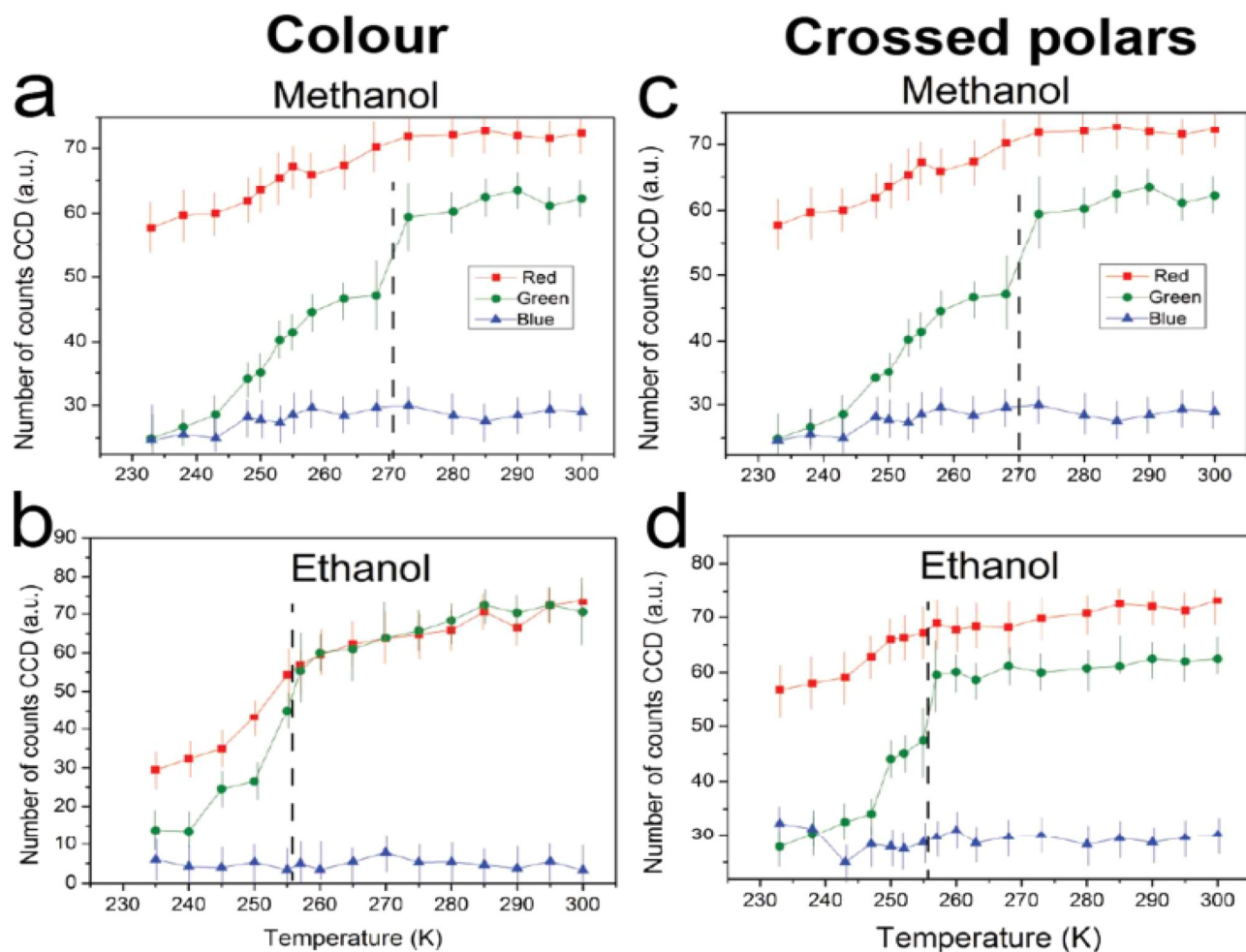


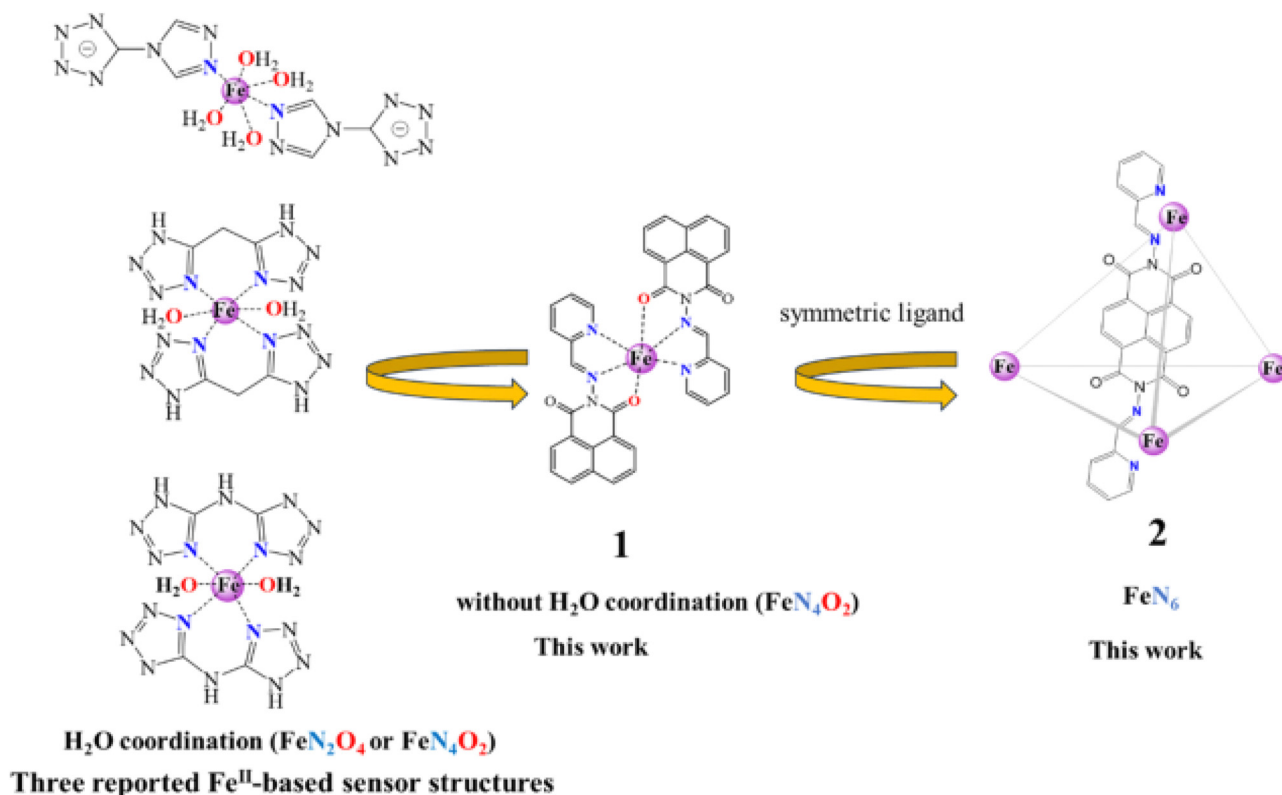
Figure 24: Optical images of CCD recorded data for different environments (ethanol and methanol).⁵²

damage, lung swelling, and even fatality. Continuous exposure of $\text{NH}_3(\text{g})$ traces to an atmosphere will also be detrimental to the health and growth of livestock. Therefore, there is a great need for research into inexpensive, highly effective, and simple-to-use $\text{NH}_3(\text{g})$ sensor materials for both environmental protection and human health.^{113–115}

The chemi-resistive gas sensors based on metal oxides and conjugated conducting polymers have been the subject of numerous studies due to their great sensitivity and ease of manufacture. However, their broad application is still limited due to their high operating temperature (150 – 500 °C.), low selectivity, and requirement for a constant energy source, for example in food quality inspection and environmental monitoring.¹¹⁶ Different researches have been made on ammonia sensing utilizing MOFs and other materials that has already discussed in this review with the advantages as well as limitations of these methods. In this research two complexes HS complex a mononuclear(**cage 1**) ($\text{Fe}^{\text{II}}\text{L}_2(\text{BF}_4)_2$, $\text{L}_1 = (\text{E})\text{-}2\text{-}((\text{pyridin-2-ylmethylene})\text{amino})\text{-}1\text{-H-benzo[de]isoquinoline-1, 3(2H)-dione}$) and tetranuclear SCO edge bridge (**cage 2**) ($\text{Fe}^{\text{II}}_4\text{L}_2\text{L}_6$, $\text{L}_2 = 2,7\text{-bis}(((\text{E})\text{-pyridin-2-ylmethylene})\text{amino})\text{-benzo[lmn][3,8] phenanthroline-1,3,6,8(2H,7H) tetraone}$) (depicted in Scheme 3) by symmetric modification of

ligands. to cage 1, cage 2 responds to $\text{NH}_3(\text{g})$ more quickly, and both exhibit different color changes during their sensing processes. Cage 1 was synthesised by the sub-component self-assembly of 2-formylpyridine, $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, and N-amino-1,8-naphthalimide in acetonitrile solution in a 2:1:2 stoichiometry. Red rod-shaped single crystals of cage 1 were created by diffusing diethyl ether into purple solution that was left over after filtering for a duration of two weeks. Cage 2 was synthesised by stirring of N,N-diaminonaphthalene-1,4,5,8-tetracarboxydi-imide, $\text{Fe}(\text{BF}_4)_2\text{H}_2\text{O}$ and 2-formylpyridine in a CH_3CN solution under $\text{Ar}(\text{g})$ at 65 °C. Using the slow vapor diffusion approach, a single crystal was grown.¹¹⁷ Rapid precipitation was used to create microcrystalline powder by adding diethyl ether straight into the reaction solution.

Cage 1 and 2 possess FeN_4O_2 and FeN_6 coordination modes respectively without any solvent molecules in their coordination unlike some sensors that have been previously reported.¹¹⁸ They show distinct sensing characteristics at room temperature for $\text{NH}_3(\text{g})$ molecules in addition to having a high thermal stability (500 K). The transition from reddish brown (cage1) and light purple (cage2) to dark gray can be used as a colorimetric indicator of the sensing process. Compared to 1 (8 min), cage 2 (90 s) responds more



Scheme 3: Structures of 3 previously reported Fe(II) based sensor and newly designed complexes (cage 1 and 2).¹²⁰

quickly because of the hollow structure and its large surface area. Different characterization techniques like SXRD and ^{57}Fe Mössbauer spectroscopy was used to analyze sensing mechanism. Furthermore, cage 2 has remarkable selectivity to $\text{NH}_3(\text{g})$ in a variety of amines and solvents. The partial oxidation of Fe^{II} to Fe^{III} and the replacement of O-donors of L1 with $\text{NH}_3(\text{g})$ molecules are the two mechanisms responsible for the sensing mechanism of cage 1. $\text{NH}_3(\text{g})$ sensor with a FeN_2O_4 core and no water molecules in its coordination sphere is an innovative example. The sensing behavior of 2 also show distinct features as compared to the previous findings with a spin state switch from HS to LS triggered by the formation of FeN_6 center and the unusual solid-state production of NH_4BF_4 . Furthermore, the ammonia sensing process for both 1 and 2 is irreversible due to alterations in the sensor structure. This characteristic is advantageous in colorimetric sensing array as for ammonia sensing because the most of the arrays are disposable.¹¹⁹ This research provides a new core for exploring and designing new Fe^{II} -based SCO complexes as a potential for NH_3 gas sensor taking advantage from a variety of multinuclearity, tuneable porosity and ligand system.

4.6 SCO based research to capture small hazardous gas molecules mainly CO_2

A major area of research these days is the development of effective materials for absorbing hazardous gasses, particularly CO_2 has become significant research due to increasing concerns to climate changes. The high surface area and microporous structure of MOFs make them promising materials in a variety of significant applications such as energy sensing,¹²¹ energy storage,¹²² separation,¹²³ catalysis,¹²⁴ health¹²⁵ and hazardous gas degradation and adsorption.¹²⁶ Moreover, MOFs with (OMS) offer the potential to create suitable porous magnetic materials in addition to the conventional gas separation and storage methods.¹²⁷

Regarding this (OMSs) Open metal sites incorporating in (MOFs) have become attractive choices in this field. In this research SCO was explored as an effective method for controlling gas molecules captured on MOFs having OMSs. The cationic and neutral forms of $\text{M}_2(\text{BTC})_4$ ($\text{M} = \text{Ni}$ and Cu) was utilized as models for the paddlewheel building units DUT8 and HKUST-1 respectively. Using first-principal computations, the interaction between $\text{M}_2(\text{BTC})_4$'s magnetic characteristics and its adsorption behaviors toward six small gas molecules (H_2 , N_2 , CH_4 , CO_2 , H_2S and CO) was examined. It was observed that gas adsorption is more favorable thermodynamically in (LS) state of copper and

(HS) state of nickel. For cupric systems, the variations in the adsorption enthalpies on the LS and HS states are negligible, but for nickel centers, these differences can exceed more than 150 kJ mol^{-1} (Figure 25). According to these findings it was observed that all the gas molecules undergo a transition from chemisorbed to physisorbed in the LS state after becoming highly adsorbed at the high spin state of nickel center. Based on these results, in this research $\text{Ni}_2(\text{BTC})_4$ was proposed as a material for controllable CO_2 capture through spin crossover at the nickel center, marking the first time this approach has been suggested for CO_2 capture and release technology. Although the findings of this study were encouraging, there are still several intriguing unexplained topics that require further investigation. As an example, more research is needed on the adsorption behavior of MOFs containing OMS against paramagnetic species like O_2 and NO . The gas molecules utilized in this research were diamagnetic, with the magnetically active MOFs. By using the same theoretical procedures as those were used in this research to examine the capture and release process of paramagnetic species across magnetic MOFs would also be an important research in future.¹²⁸

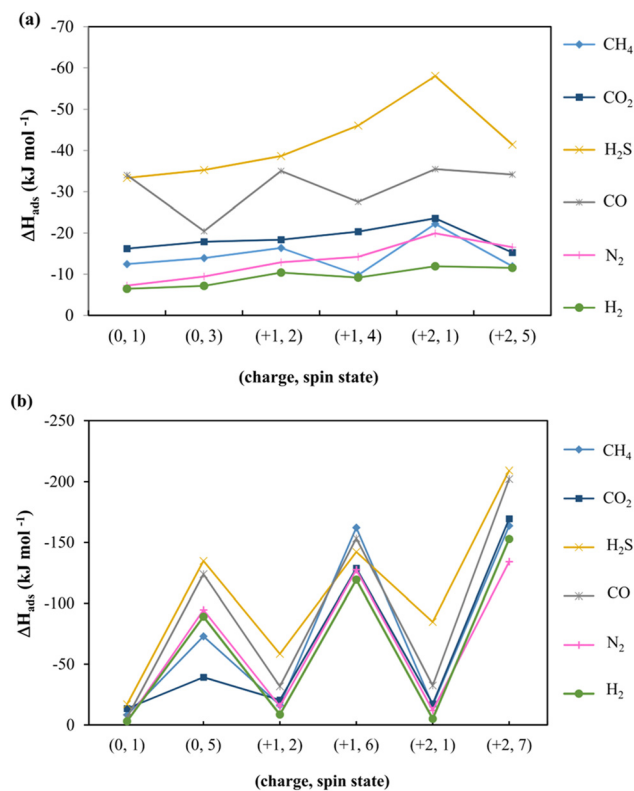


Figure 25: The variations in the adsorption enthalpies with spin state and charge of (a) $\text{Cu}_2(\text{PhCO}_2)_4$ and (b) $\text{Ni}_2(\text{PhCO}_2)_4$.¹²⁸

4.7 Characterization of SCO based MOFs by computer simulations for the application in gas and chemical sensing

Computer simulations are particularly relevant in this context because they can offer fundamental conclusions that are challenging, if not impossible, to achieve from experimentation. Previous research has indicated that the SCO properties of complex $\{\text{Fe}(\text{pz})[\text{Pt}(\text{CN})_4]\}$ could be accurately replicated by combining ligand-field molecular mechanics (LFMM) with hybrid Monte Carlo/molecular dynamics (MC/MD) simulations on adsorption of pyrazine and water. The underlying chemical processes that stabilize the LS state of complex upon guest adsorption, however, are still unknown. Using hybrid MC/MD simulations, this study first monitored the molecular-level changes in the SCO behavior of $\{\text{Fe}(\text{pz})[\text{Pt}(\text{CN})_4]\}$ following the adsorption of CS_2 , CO_2 and SO_2 . So, it was discovered that the MOF pores having CO_2 content had little effect on $T_{1/2}$, both CS_2 and SO_2 were able to stabilize LS state (Figure 26). A clear correlation between particular host-guest interactions and SCO behavior is subsequently deduced from the simulation findings. Ultimately, expanding on this study, $T_{1/2}$ projections for this complex after it has adsorbed different harmful gases are presented, indicating that $\{\text{Fe}(\text{pz})[\text{Pt}(\text{CN})_4]\}$ might be used as a nano porous material for detection and gas sensing. A thorough examination of the anisotropy and strength of the interactions between the guest molecules and the framework demonstrates a clear relationship among the rotational mobility of the pyrazine rings of structure, the mobility of

the guest molecules inside the MOF pores, and the stabilization of material's LS state. Detailed molecular criteria was developed based on these correlations to predict the spin state upon guest adsorption. Furthermore, estimations of the SCO temperature following the adsorption of several hazardous gases show that *in silico* modeling can offer essential perspectives and design guidelines for the creation of SCO-MOFs for use in chemical sensing and gas detection applications.

4.8 Gas sensing with SCO complexes for alcohol detection: mechanistic insights from single-crystal-to-single-crystal transformation (SCSC)

SCSC transitions, which occur when small molecules migrate across a lattice (desorption, exchange or absorption), are becoming increasingly important in multiple fields. These applications include separation, storage, heterogeneous catalysis, gas absorption, detection and chemical sensing. These transformations are prominent in porous materials like (MOFs), but are less common in molecular crystals due to their packed structures. However, they have potential in fields like sensing and pharmaceuticals, where shifts in properties, such as magnetic or optical changes, may act as detection signals. Spin-crossover (SCO) transitions are an excellent approach for such sensing application. In this process certain d-block metal ions undergo a reversible transition process between two attainable spin states, induced by external stimuli like pressure or temperature variations.

In this research Fe^{II} molecular material $[\text{Fe}(\text{bpp})(\text{H}_2\text{L})](\text{ClO}_4)_2 \cdot \text{C}_3\text{H}_6\text{O}$ where (bpp and H_2L are 2,6-bis(pyrazol-3-yl)-pyridine type ligands) was utilized having their lattice acetone molecules which were replaced by the selective alcohols like (methanol, ethanol or n-propanol but not iso-propanol), resulting in a spin transition and color shift of crystals. The signalling complex's magnetic response was determined by the length of the alcohol chain, allowing for the selective detection. These SCSC transformations make it possible for comprehensive structural evaluation of resulting compounds using SCXRD. The magnetic and thermal properties of the material can indicate the type of alcohol absorbed. Solvent exchange results in HS-to-LS spin switching, followed by HS-to-LS conversion at higher temperatures due to the combination of solvent extrusion and SCO processes, each having a unique characteristic temperature. SCXRD was used to study the process of removing n-propanol from its host lattice at different stages. This disclosed important data about the mechanism of the transformation.¹²⁹

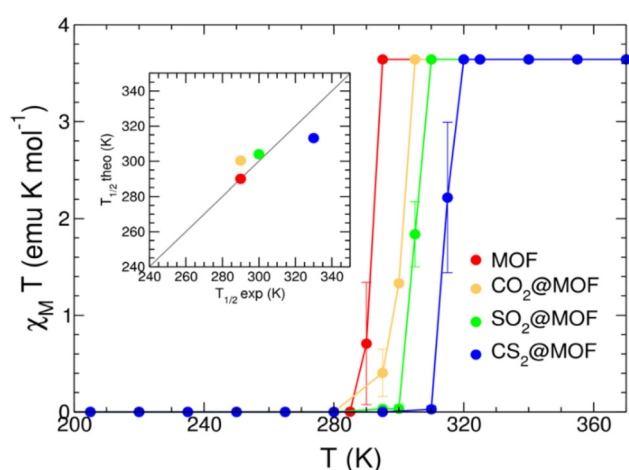


Figure 26: The temperature dependence of $\chi_M T$ was determined using MC/MD simulations of $\{\text{Fe}(\text{pz})[\text{Pt}(\text{CN})_4]\}$, both in absence of adsorbed guest molecules (MOF) and after the adsorption of SO_2 , CS_2 and CO_2 . The experimental and theoretical values of SCO temperature ($T_{1/2}$) are highlighted in this figure.⁵³

5 Concluding remarks and future perspectives

Spin crossover complexes a class of coordination compounds exhibit reversible spin transitions when exposed to external stimulus such as temperature, pressure, light, or gas molecules. These unique properties make them valuable in the fields like spintronics, actuators and sensing. This review highlights the synthesis and structural elucidation of SCO complexes with its application as gas sensor in the sensing of hazardous gases for environmental safety. Different synthesis method can be utilized to synthesize such complexes such as hydrothermal, solvothermal, solid-state method, mechanochemistry, solution-based methods, direct synthesis and wet chemical technique. Similarly different characterization techniques like SCXRD, UV–VIS spectroscopy, Raman spectroscopy, IR, Magnetic susceptibility measurements and Mössbauer Spectroscopy can be employed for structural elucidation of SCO complexes. Gas sensors are crucial for monitoring environmental pollution as industrial activities increase hazardous gas emission. The reversible spin transition behavior analyzed by the change in color or optical properties when gas molecules are exposed to SCO complexes make them suitable to act as gas sensor. When integrated with MOFs which provide porosity and structural stability these properties are enhanced allowing for improved gas absorption and sensitivity. The combination of SCO-MOF leads to the development of highly effective sensors capable of detecting different gases. The application in this review includes the key points of the researches that have been made from past few years on the sensing of ammonia, carbon dioxide, and different VOCs (methanol, ethanol, iodobenzene, alcohol). Different techniques like electrical resistance, UV–VIS spectroscopy and magnetic susceptibility measurements can be efficiently utilized during gas sensing. To advance the detection of hazardous gases in the environment substantial efforts should be directed towards optimizing SCO complexes for enhanced gas sensing applications. Future research should focus on the advancement in synthesis techniques such as green chemistry and mechanochemical approaches. Because it avoids the use of harmful solvents and could reduce the production cost making these materials environment friendly and commercially more applicable. Efforts should focus on improving gas selectivity, response time, operational stability and sensitivity under diverse conditions. Enhancing their sensitivity towards the sensing of selective gases especially in trace amount is another crucial area where the advancements could make SCO materials more competitive for environmental and industrial applications. Furthermore, as SCO complexes possess the reversible switching capabilities the

speed of these transitions should be optimized for real-time sensing devices. Achieving faster response time without compromising the structural durability could be great research in gas sensing applications by providing a way for their commercialization in the areas such as industrial safety and environmental monitoring.

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Use of Large Language Models, AI and Machine Learning

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