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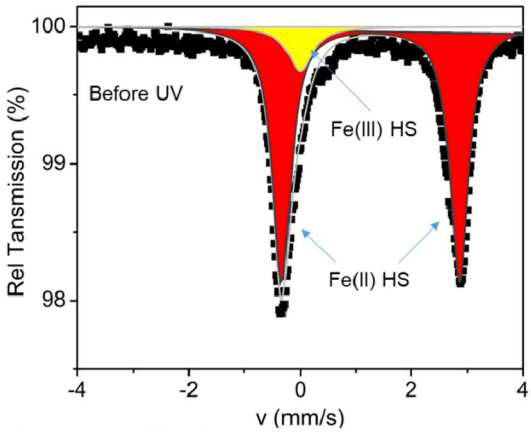

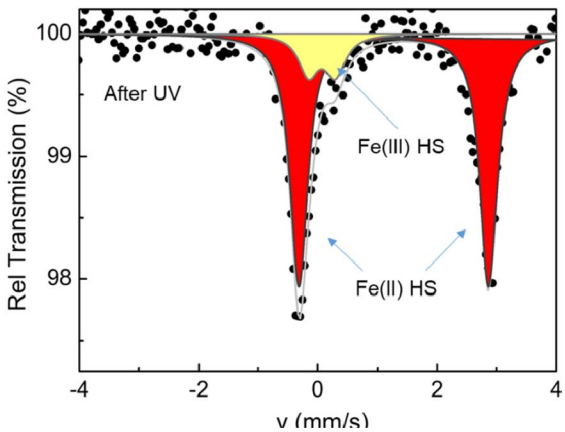

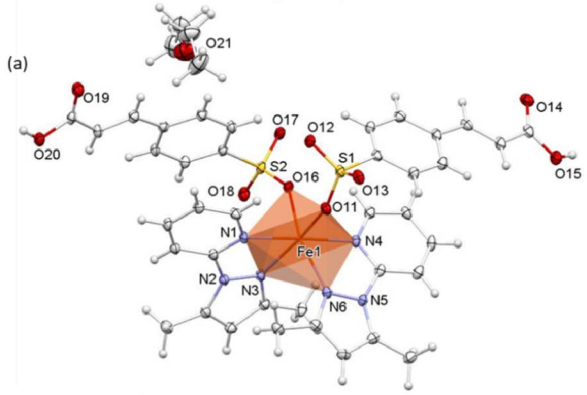

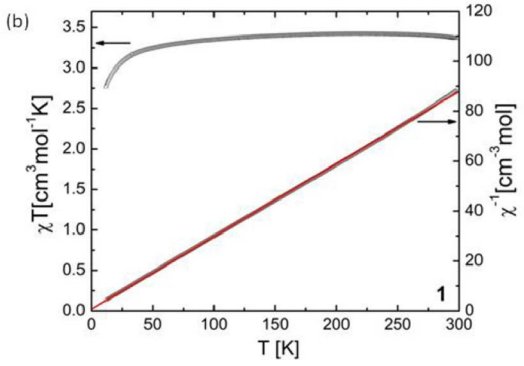

MÖSSBAUER SPECTROSCOPY
NEWSLETTER

July 2021

Anion Driven Light Induced Spin Crossover Systems: towards Multifunctional Coordination Compounds

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Dr. Varun Kumar

Dr. Varun Kumar was born on December 3rd, 1988 in Delhi, India. During his early education, he got fascinated by the role of chemistry in everyday life which led him to pursue a Bachelor's degree in Chemistry (Honors) from University of Delhi. Varun, then got himself enrolled in a Master's degree in Nanosciences which was a joint program between University of Delhi and Université Joseph Fourier (Grenoble, France). In France, Varun started his research career at Laboratoire National des Champs Magnétiques Intenses, CNRS where he worked on metal-radical compounds for the application of molecular magnetism. Varun later joined Prof. Yann Garcia's group as a PhD student at Université catholique de Louvain in Belgium in 2014 - 15 academic year. During his PhD, he worked on a novel approach called 'Anion driven light induced spin crossover' (AD-LISC) in which photo-responsive anions were incorporated into Fe(II) spin crossover compounds. Following a thorough study and rational strategic designing of molecules, Varun finally was able to find the very first evidence of AD-LISC effect in an Fe(II) coordination polymer, using ^{57}Fe Mössbauer spectroscopy. His thesis work will serve as the ground work for further development of the AD-LISC effect in the near future. Varun defended his thesis in March 2021 in front of a prestigious jury panel comprising of international scientists. He pursues his career at IPCMS Strasbourg, France working on hybrid multifunctional materials.

Prof. Dr. Yann Garcia

Prof. Dr. Yann Garcia was born in Castres, France in 1972. He obtained his doctorate from the Université of Bordeaux at the Institute of Condensed Matter Chemistry of Bordeaux (ICMCB-CNRS) under the supervision of Prof. Olivier Kahn (academician) in Jan 1999. He then joined the Institute of Inorganic and

Analytical Chemistry of the University of Mainz (Germany) to work with Prof. Dr. Philipp Gütlich as a TMR EU post-doctoral fellow. While getting a permanent position at the CNRS (University of Paris VI), he was appointed assistant professor at the UCLouvain in 2001, associate Professor in 2004 and Professor in 2009. The research interests of Prof Garcia extend from photoswitchable coordination compounds, spin crossover materials to smart sensors, medicinal and environmental applications, where Mössbauer spectroscopy is considered as a key tool. Prof. Garcia has published more than 260 publications with several cover pages of top journals, book chapters, etc. Prof. Garcia is editorial board member of European Journal of Inorganic Chemistry (Wiley-VCH, Chemistry Europe) and associate editor of the Mössbauer Effect Reference Data Journal (Chinese Academy of Sciences). He is elected president of the French Speaking Mössbauer Society (GFSM, www.gfsm.fr) and international board member of the Applications of the Mössbauer Effect (IBAME, www.ibame.org). In 2009, he was selected among the next future leaders of Mössbauer spectroscopy by the Mössbauer Effect Data Center, located at that time in North Carolina University, just before moving to Dalian, China.

Introduction and context

The pursuit for new materials which can offer several functionalities is on the rise. Materials able to respond to external stimuli such that their properties can be controlled using these stimuli, are the advanced materials which emerge as the possibilities to combine various functionalities in one single compound. Fe(II) spin crossover (SCO) compounds belong to one such class of advanced materials, which exhibit remarkable change in magnetic and optical properties, and are thus lauded as potential candidates for various applications including data storage and display devices.[1] The most common approach to induce SCO has been to use temperature as external stimulus, but this is not very practical when imagining their uses in commercial devices. Alternatively, using light as a trigger to induce SCO presents a fascinating option as it provides the possibility for a faster spin transition and can be carried out remotely.[2] Till date, literature has reported cases of two types of light induced spin transition in Fe(II) coordination compounds depending on the component of coordination compound targeted by light irradiation. Inducing spin transition through selective light irradiation of Fe(II) ions is called LIESST effect (Light Induced Excited Spin State Trapping),[3] whereas selective light irradiation of ligands is called LD-LISC effect (Ligand Driven Light Induced Spin Change).[4] The LIESST effect, still poses a major limitation regarding its use in commercial devices that it can still be initiated at very low temperature (~20 K). On the other hand, the LD-LISC effect uses photo-responsive ligands to target to induce spin transition in Fe(II) ions. The principle behind LD-LISC effect is to alter the ligand field strength around the metal center through photoisomerization of ligand by light irradiation which in turn results in change in spin state of Fe(II) ions.[5] The observation of LD-LISC effect in solid state at room temperature would be of great significance in the sense of utilizing LD-LISC effect in commercial devices, which was not yet achieved due to several factors. Because of these existing limitations, there is a need for an alternative approach in order to have an efficient light induced spin transition so that the enticing properties of Fe(II) SCO compounds can be exploited for application purposes.

In the doctorate thesis of Varun Kumar performed at UCLouvain under the supervision of Prof. Yann Garcia, we have developed a novel approach to address the light induced spin transition at room temperature and in solid state. To reach this target, we have incorporated photo-responsive anionic organic molecules in Fe(II) systems. This insertion would not only introduce additional photo-responsive properties to the targeted Fe(II) SCO compounds but could also result in a light induced spin transition upon light irradiation. We termed this new phenomenon as 'Anion Driven Light Induced Spin Change' (AD-LISC) as the spin transition would be induced by photo-responsive changes occurring in anions. The idea behind this 'anion-driven' approach is similar to the one with LD-LISC, *i.e.* to irradiate the compound and observe the changes in magnetic properties of the coordination compound. We expect SCO to ensue in synergy with photo-switching of non-coordinated anions because non-coordinated anions may modulate the ligand field strength and intermolecular lattice pressure, therefore, causing a significant change in SCO characteristics such as $T_{1/2}$ (transition temperature where HS and LS are equally populated), different transition curves etc.

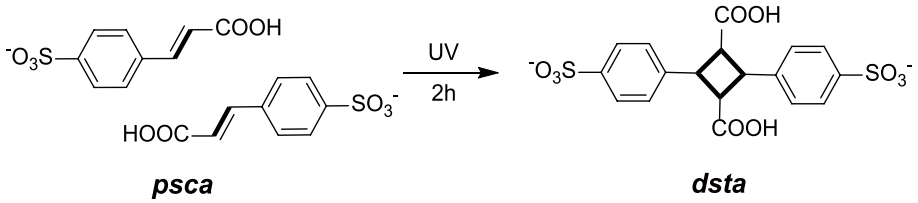
There are several reported cases which show that even subtle changes in non-coordinated anions (e.g. Cl^-, Br^-, …) can result in different SCO behavior, while the same structural unit is maintained.[6-10] The term 'AD-LISC' was first tossed few years ago as a concept by our research team.[11] In the thesis of Dr. Varun Kumar, the goal was to observe it experimentally. The thesis was defended online in March 2021 using Microscoft Teams service due to the pandemic situation in front of several international scientists including Dr. Pierre Rabu (IPCMS Strasbourg), Dr. Valérie Marvaud (Sorbonne université, Paris) and Dr. Mathieu Surin (UMONS, Belgium).[12]

The photo-responsive anion: *psca*

To realize AD-LISC at ambient conditions, we needed such a photo-responsive anion which could undergo photo-switching at room temperature in solid state without requiring large spatial voids for photo-switching. In this context, we successfully synthesized and studied a photo-responsive anion, *para*-sulfocinnamic acid (***psca***). Two molecules of ***psca*** undergo [2+2] photodimerization from the vinyl bond in solid state when irradiated with UV-light to give 4,4'-disulfonate-truxillic acid (***dsta***) as shown in Scheme 1.[13] The [2+2] photodimerization of ***psca*** follows Schmidt's topochemical rules of [2+2] photodimerization which states that the photodimerization will only take place if, (i) the distance between the two vinyl bonds to be dimerized is $d \leq 4.2$ Å, and; (ii) the two vinyl bonds are parallel to each other in order to have a good overlap of the π-orbitals.[14]

The [2+2] photodimerization of ***psca*** is an irreversible reaction. The irreversible photoswitching of ***psca*** would sustain the changes in properties of the coordination compounds, in contrast to reversible photoreactions where natural light usually interferes with the photoswitching of the molecules and makes it difficult to follow the changes in detail.[15]

In our recent publication,[13] we reported the detailed characterization of ***psca*** and ***dsta***, along with the kinetic study of the photo-conversion from ***psca*** to ***dsta***. The photoreaction was monitored with time using ^{13}C solid state NMR spectroscopy. NMR spectra of the photoreaction with respect to time are given in Figure 1(a). The degree of conversion and time plot were



Scheme 1: [2+2] photodimerization of two molecules of ***psca***. The photodimerizable vinyl bonds and cyclobutane ring thus formed are emphasized as bold bonds.[13]

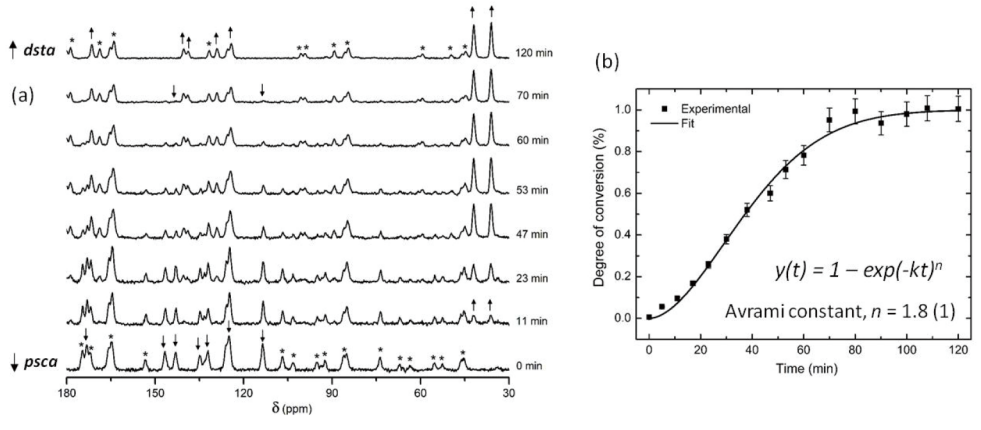


Figure 1: (a) Solid state ^{13}C CP-MAS (cross-polarization magic angle spinning) NMR spectra of photoconversion from ***psca*** to ***dsta*** recorded at different irradiation time. The symbols (↓) and (↑) represent signals from ***psca*** and ***dsta*** respectively, whereas the asterisks (*) represents the spinning sidebands. The irradiation time is written beside each spectrum; (b) Degree of conversion plot with irradiation time to explain [2+2] photoconversion kinetics from ***psca*** to ***dsta***. The curve is fitted according to JMAK model of nucleation and growth.[13]

used to explain kinetics of the photoreaction are shown in Figure 1(b). The kinetics results were interpreted on the basis of JMAK model of nucleation and growth which revealed that ***psca*** gets converted into ***dsta*** through 1-D heterogeneous growth.

Fe(II) ion and *psca* together in a single compound: $[Fe(H_2O)_6](psca)_2 \cdot 2H_2O$

After asserting the photo-properties of ***psca***, the next step towards AD-LISC was to combine ***psca*** and Fe(II) ions in a single compound. It was done by synthesizing a hexaquairon(II) complex, **$[Fe(H_2O)_6](psca)_2 \cdot 2H_2O$** in which six water molecules were coordinated to Fe(II) ions and two ***psca*** molecules remained outside the coordination sphere as non-coordinated anion. **$[Fe(H_2O)_6](psca)_2 \cdot 2H_2O$** is an iron precursor to synthesize different coordination complexes where H_2O ligand molecules can be easily replaced by heterocyclic ligands. A new *in-situ* synthesis procedure was devised to obtain hexaquairon(II) complex with aromatic sulfonate anions which we nicely reported in our recent publication.[13] Crystal structure of **$[Fe(H_2O)_6](psca)_2 \cdot 2H_2O$** shown in Figure 2 revealed that the distance between the concerned vinyl bonds to be dimerized was 3.6 Å, and the two bonds were also parallel to each other. Thus, ***psca*** molecules were arranged in favorable arrangement for photodimerization reaction in the lattice of **$[Fe(H_2O)_6](psca)_2 \cdot 2H_2O$** according to Schmidt's topochemical rules. Hence, we proceeded to irradiate **$[Fe(H_2O)_6](psca)_2 \cdot 2H_2O$** with UV light in solid state at room temperature and found that ***psca*** got partially dimerized in **$[Fe(H_2O)_6](psca)_2 \cdot 2H_2O$**.

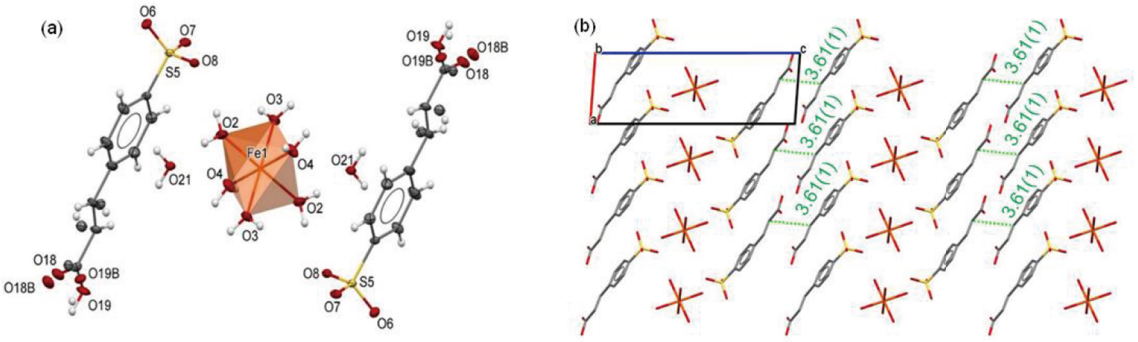


Figure 2: Crystal structure of **$[Fe(H_2O)_6](psca)_2 \cdot 2H_2O$**. *(a)* Formula unit, showing thermal displacement ellipsoids at the 30% probability level. The disorder of the vinyl and carboxylic group is shown by the corresponding atom color. *(b)* crystal packing when viewed along the *b*-axis. Hydrogen atoms and solvent molecules are removed for clarity. Color code: Fe (orange), C (dark grey). O (red), S (yellow), H (light grey).[13]

To observe the difference in magnetic properties before and after UV irradiation, **^{57}Fe Mössbauer spectroscopy** was used as it can efficiently give a compositional analysis of iron based compounds. ^{57}Fe Mössbauer spectra of **$[Fe(H_2O)_6](psca)_2 \cdot 2H_2O$** before and after UV irradiation were fitted to the sum of Lorentzian lines by a least-squares refinement using Recoil 1.05 Mössbauer Analysis Software (Table 1).[16] The spectra were recorded at ambient conditions and are shown in Figure 3. In each Mössbauer spectrum, a doublet (highlighted in red) at isomer shifts of δ = 1.26 mm/s (before UV irradiation) and 1.28 mm/s (after UV) was observed. These doublets in both spectra show a quadrupole splitting of ΔE_Q = 3.18 mm/s, which is characteristic of Fe(II) high-spin (HS) ions. Alongside the doublet shown in red, another doublet, highlighted as yellow with an isomer shift, δ = 0.14 mm/s and quadrupole splitting of ΔE_Q = 0.43 mm/s was also observed in both spectra. The parameters obtained for the doublets highlighted in yellow correspond to the presence of Fe(III) HS ions[17] and suggested that **$[Fe(H_2O)_6](psca)_2 \cdot 2H_2O$** tends to oxidize over time. After irradiation, the Fe(III) HS content was found to increase to 15% because the UV irradiation and Mössbauer measurements were performed at ambient conditions. As expected with the weak ligand field strength exerted by H_2O ligands on iron ions, **$[Fe(H_2O)_6](psca)_2 \cdot 2H_2O$** was found to be a complete HS compound. Because of the weak ligand field strength of H_2O molecules, UV irradiation also did not have any effect on the spin state properties of Fe(II) ions and it remains HS after irradiation. Most interestingly, the hyperfine parameters show similar values

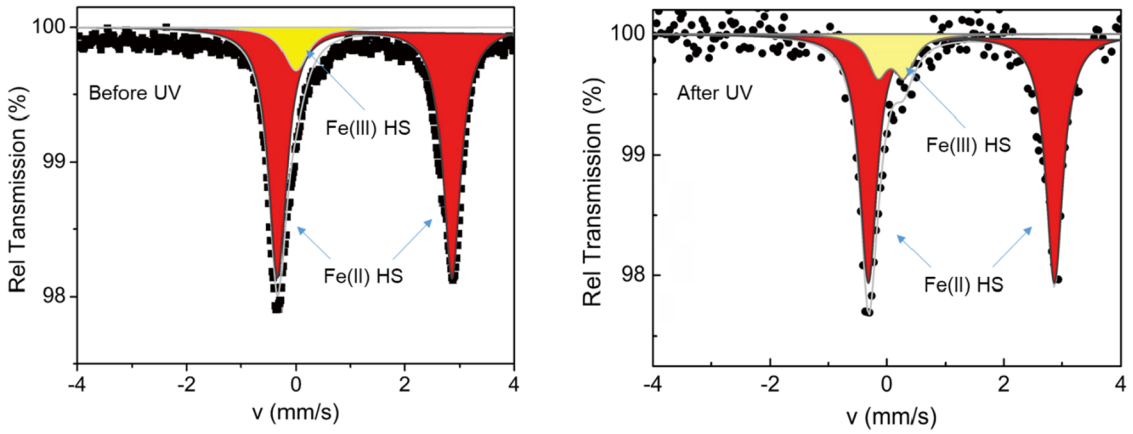


Figure 3: Room temperature ^{57}Fe Mössbauer spectrum of **$[Fe(H_2O)_6](psca)_2 \cdot 2H_2O$** before irradiation (left) and after irradiation (right).[12]

Table 1: ^{57}Fe Mössbauer parameters **$[Fe(H_2O)_6](psca)_2 \cdot 2H_2O$** at room temperature before and after irradiation. Isomer shifts (δ) are given with respect to metallic α-Fe. $\Gamma/2$ = half width of the lines.[12]

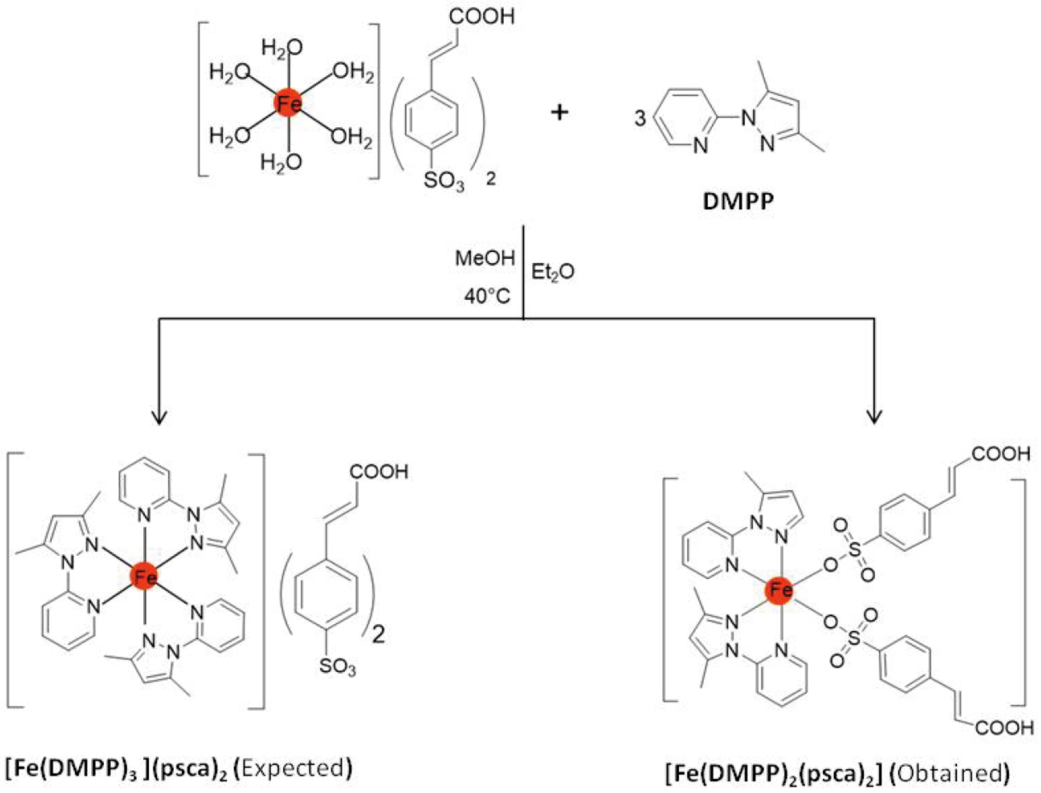
$[Fe(H_2O)_6](psca)_2 \cdot 2H_2O$	Sites	δ (mm/s)	ΔE_Q (mm/s)	$\Gamma/2$ (mm/s)	Fraction (%)
Before UV irradiation	Fe(II) HS	1.26(2)	3.18(4)	0.20(1)	91
	Fe(III) HS	0.14(1)	0.43(4)	0.19(1)	9
After UV irradiation	Fe(II) HS	1.28(2)	3.18(3)	0.18(2)	85
	Fe(III) HS	0.07(1)	0.45(2)	0.20(2)	15

before and after UV irradiation which implied that partial photodimerization of ***psca*** did not cause any damage to the coordination spheres, $[Fe(H_2O)_6]^{2+}$. This information held a good perspective for Fe(II) compounds with heterocyclic ligands and psca as counter-anions in terms of observing AD-LISC.

Mononuclear complex of Fe(II) with DMPP and *psca* ligands

After successfully synthesizing and studying **$[Fe(H_2O)_6](psca)_2 \cdot 2H_2O$**, the next step towards AD-LISC was to replace all H_2O ligands in **$[Fe(H_2O)_6](psca)_2 \cdot 2H_2O$** by a heterocyclic nitrogen donor ligand of suitable ligand field strength to obtain a Fe(II) SCO compound. Following this, the final SCO compound would be irradiated with UV light to observe any changes in the magnetic and optical properties.

In this context, we chose a bidentate ligand, **DMPP** (3,5-dimethyl-1-(2'-pyridyl) pyrazole) which is known to give Fe(II) SCO mononuclear complexes having the coordination sphere $[Fe(DMPP)_3]^{2+}$.[18] The mononuclear complexes of Fe(II) with **DMPP** ligand can be synthesized by usual complexation reaction, where Fe(II) precursor and **DMPP** ligand are mixed in 1:3 molar ratio.[18] Following the standard protocol, we performed the reaction of **$[Fe(H_2O)_6](psca)_2 \cdot 2H_2O$** and **DMPP** ligand in 1:3 molar ratio to obtain **$[Fe(DMPP)_3](psca)_2$**. However, the homoleptic coordination complex **$[Fe(DMPP)_3](psca)_2$** was found to be unstable at ambient conditions and could not be isolated as solid phase. To counter this problem, diethyl ether (Et_2O) was diffused into the complexation reaction to isolate **$[Fe(DMPP)_3](psca)_2$** in single crystalline or at least in powder form. Interestingly, we ended up with single crystals of heteroleptic complex **$[Fe(DMPP)_2(psca)_2]$**, in which two ***psca*** molecules were found to be coordinated to Fe(II) centers along with two **DMPP** molecules. Upon investigating the heteroleptic formation further we figured out that it was Et_2O which caused this heteroleptic coordination layout. The whole process of expected and obtained complexes is summed up in Scheme 2.



Scheme 2: Complexation reaction scheme of **$[Fe(H_2O)_6](psca)_2$** with **DMPP**, showing the expected and obtained coordination complexes.[19]

We further ascertained the role of Et_2O in dictating the heteroleptic coordination layout by replacing ***psca*** anion by other similar aromatic sulfonate anions namely, ***ps*** (phenyl sulfonate), ***tos*** (*p*-toluenesulfonate), ***nitps*** (*m*-nitrophenylsulfonate) in the complexation reaction. Interestingly, all the complexation reactions developed exactly in the same manner and yielded heteroleptic coordination complexes *viz*. **$[Fe(DMPP)_2(ps)_2]$**, **$[Fe(DMPP)_2(tos)_2]$**, and **$[Fe(DMPP)_2(nitps)_2]$** in which the sulfonate anions were found to coordinated to the Fe(II) ions along with two **DMPP** molecules. The crystal structure of **$[Fe(DMPP)_2(psca)_2]$** is shown in Figure 4(a), two ***psca*** molecules can be seen coordinated to Fe(II) centre through SO_3 groups. The susceptibility measurements revealed that all the complexes remained HS at all temperature range because the aromatic sulfonate anionic ligands contribute towards weaker ligand field strength. The susceptibility measurement of **$[Fe(DMPP)_2(psca)_2]$** against temperature is shown in Figure 4(b). In Figure 4, the results of only one complex are shown because the results of all the synthesized complexes were found to be similar.[19]

^{57}Fe Mössbauer spectra of all the complexes were found to be in accordance with the susceptibility measurements and are collectively shown in Figure 5. A red doublet is detected in each spectrum, centered around an isomer shift of δ = 1.1 - 1.2 mm/s with a quadrupole splitting in the range ΔE_Q = 2 - 3 mm/s, which is characteristic of Fe(II) HS ions. Mössbauer spectra confirm that complexes **$[Fe(DMPP)_2(psca)_2]$**, **$[Fe(DMPP)_2(ps)_2]$**, and **$[Fe(DMPP)_2(nitps)_2]$** exist as whole Fe(II) HS compounds. However, an additional yellow doublet was observed in the spectrum of **$[Fe(DMPP)_2(tos)_2]$** centered at δ = 0.14 mm/s with a quadrupole splitting of ΔE_Q = 0.51 mm/s which corresponds to HS Fe(III) ions.[17] The absence of any Fe(III) HS in SQUID measurement leads to the conclusion that **$[Fe(DMPP)_2(tos)_2]$** was synthesized as an Fe(II) HS compound but got partially oxidized to Fe(III) over a period of time needed to record the Mössbauer spectrum, which was performed at ambient conditions. The reason that only **$[Fe(DMPP)_2(tos)_2]$** got partially oxidized with time and not the other complexes was attributed to the degree of distortion of Fe(II) octahedral geometries. As a matter of fact, quadrupole splitting in Mössbauer spectra can also provide information about the degree of distortion. For similar ferrous compounds, the higher the distortion degree, the lower

is the quadrupole splitting, due to the lattice contribution to the electric field gradient,[20] which is indeed the case with **[Fe(DMPP)$_2$(tos)$_2$]** as can be seen in Table 2. Regarding the photodimerization in **[Fe(DMPP)$_2$(psca)$_2$]**, the psca molecules in **[Fe(DMPP)$_2$(psca)$_2$]** do not meet the Schmidt's topochemical criteria for [2+2] photodimerization[14] because the concerned vinyl bonds were found to be pointing away in opposite directions from each other (Figure 4a). Therefore, the synthesized complex **[Fe(DMPP)$_2$(psca)$_2$]**, was acknowledged as non-photoresponsive complex. However, on the positive side, this study allowed us to establish a new procedure to synthesize heteroleptic complexes of Fe(II) with **DMPP** and aromatic sulfonate ligands.[19]

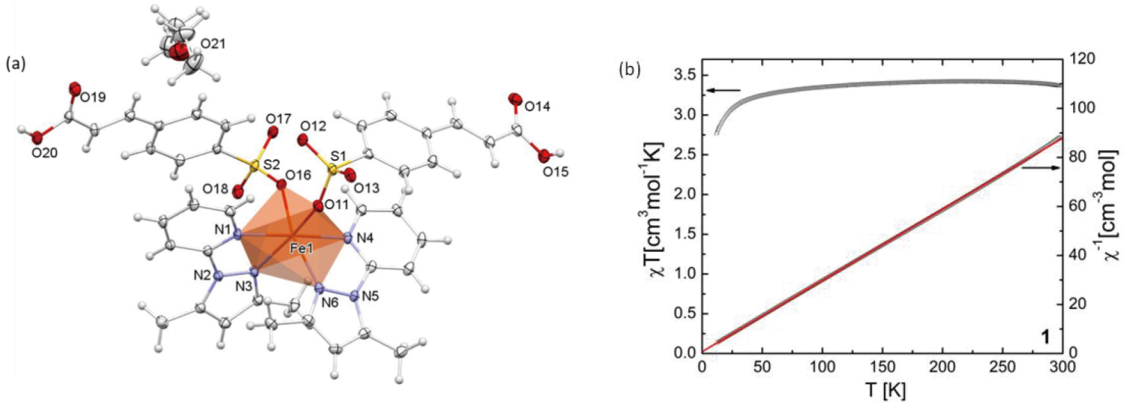


Figure 4: (a) Asymmetric unit of **[Fe(DMPP)$_2$(psca)$_2$]**, showing thermal displacement ellipsoids at the 30% probability level. Color code: Fe (orange), N (blue), C (grey), H (light grey), S (yellow), O (red); (b) χT *vs.* T, and χ^{-1} *vs.* T plots of **[Fe(DMPP)$_2$(psca)$_2$]**. The red line represents a Curie-Weiss law fit of the magnetic data.[19]

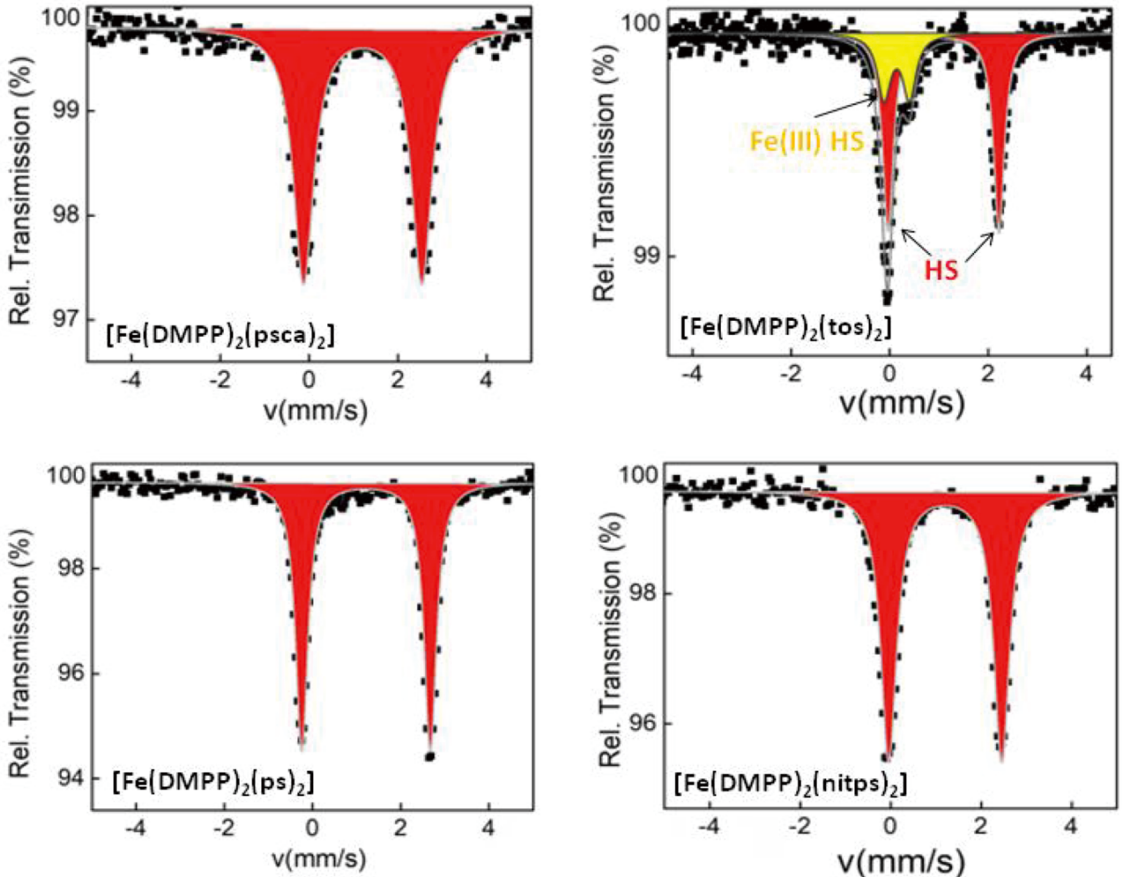


Figure 5: Room temperature ^{57}Fe Mössbauer spectra of **[Fe(DMPP)$_2$(psca)$_2$]**, **[Fe(DMPP)$_2$(ps)$_2$]**, **[Fe(DMPP)$_2$(tos)$_2$]**, and **[Fe(DMPP)$_2$(nitps)$_2$]**.[19]

Table 2: ^{57}Fe Mössbauer parameters of **[Fe(DMPP)$_2$(psca)$_2$]**, **[Fe(DMPP)$_2$(ps)$_2$]**, **[Fe(DMPP)$_2$(tos)$_2$]**, and **[Fe(DMPP)$_2$(nitps)$_2$]** at 298K. Isomer shift (δ) are given with respect to metallic α-Fe. $\Gamma/2$ = half width of the lines.[19]

Compound	Sites	δ (mm/s)	ΔE_Q (mm/s)	$\Gamma/2$ (mm/s)	Fraction (%)
[Fe(DMPP)$_2$(psca)$_2$]	Fe(II) HS	1.20(1)	2.50(1)	0.21(1)	100
[Fe(DMPP)$_2$(ps)$_2$]	Fe(II) HS	1.20(1)	2.66(1)	0.27(1)	100
[Fe(DMPP)$_2$(tos)$_2$]	Fe(II) HS	1.09(1)	2.25(1)	0.13(1)	72
	Fe(III) HS	0.14(2)	0.51(5)	0.16(3)	28
[Fe(DMPP)$_2$(nitps)$_2$]	Fe(II) HS	1.21(1)	2.91(1)	0.16(5)	100

Coordination polymers of Fe(II) with *psca* as non-coordinated anions

After not being able to attempt AD-LISC with **[Fe(DMPP)$_2$(psca)$_2$],** we dropped the idea to insert ***psca*** into mononuclear complexes, and instead tried to incorporate it in a more confined space where ***psca*** molecules can be close to each other for photodimerization. In this regard, we chose a series of Fe(II) coordination polymers in which suitable insertion was carried out. As a first positive sign of structural change, the color of our coordination polymers changed from pink to brown after ~12 h of irradiation in solid state. Photodimerization reaction of ***psca*** in coordination polymer was followed using diffuse reflectance spectroscopy, and most of all changes in magnetic properties were followed using ^{57}Fe Mössbauer spectroscopy at ambient conditions. A clear evidence of the AD-LISC effect was observed. A complete report will soon be submitted.[21]

Acknowledgements

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Position of Talented Young Scientists Program of MOST of China

Position: Composited Materials Postdoctoral Researcher

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Description of the organization.

Dalian Institute of Chemical Physics-Chinese Academy of Sciences(DICP-CAS) founded in 1949, the key disciplines are catalytic chemistry, chemical engineering, chemical lasers and molecular reaction dynamics and modern analytical chemistry and biotechnology. DICP-CAS has two national key laboratories, a number of national science and technology innovation platform, a number of laboratories, and a number of international research institutions. The Mössbauer Effect Data Center is a research center of the DICP-CAS.

Responsibilities and description of the project.

Research fields of Junhu Wang's group (DNL2005, Mössbauer Functional Materials Research Group): 1) Novel and highly efficient environmental & energy catalytic materials; 2) Novel and highly efficient reactive adsorbents; 3) advanced spectroscopies.The candidate will independently carry forward the project study of "**Development and Spectroscopic Studies of Prussian Blue Analogues and Apatite Nanocomposites for Efficient Cs^+ Removal**" which is financially supported by National Natural Science Foundation of China.

Description of the project: It is an important and urgent issue to research and develop advanced treatment and purification technology for radioactive waste water with ^{137}Cs. By carefully investigating the possible routes of Cs^+ fixing into the structures of Prussian blue-based (PBA) and apatite-based (AP) sorbents, the new Cs^+ sorbents of a series of soluble and insoluble hexacyano cobaltate(III) iron(II), hydroxyapatite and fluorapatite will be separately synthesized by co-precipitation, ion-exchange and intercalation methods. Based on the characterization results of regular and in-situ ^{57}Fe Mössbauer spectroscopy, Cs L_{III} edge X-ray absorption fine structure spectroscopy, the Rietveld structural refinement and other various advanced techniques for the prepared materials, the relationships will be made clear between their Cs^+ sorption capabilities and their various physical and chemical properties, the reasonable Cs^+ sorption mechanism will be explored systematically. Beyond these above mentioned researches, the PBA and AP novel nanocomposite sorbents with different mole radio and architectures will be developed by using the established methods of chemical precipitation and simulated body fluid, their chemical compositions, structures, Cs^+ sorption properties and mechanisms will be further studied. The Cs^+ sorption properties can be improved and their mechanical stabilities can be enhanced by compositing the selected high efficient PBA and AP sorbents with defined composition and structure. Through the deep understanding of the structure-activity relationships and mechanisms of PBA, AP and their composited sorbents, we aim to develop novel nanocomposited Cs^+ sorbent with stable composition and structure, provide a theoretical basis and help for their industrial applications. Advantage of this project is realized the monitor of the real-time status of Cs^+ in and out of the sorbent structures by the utilization of the in-situ spectroscopic characterizations and a variety of conventional techniques. The project is multidisciplinary, its goal is to design novel kinds of highly efficient sorbent materials for removal radioactive Cs^+ pollutants from waste aqueous solution, furthermore, exploring out of their sorption mechanisms.

Requirements for applicants.

1) In accordance with the basic conditions of the Ministry of science and technology of China on the Talented Young Scientist Program.

(http://www.tysp.org/English/Details/d6145a24-c766-4f17-b2cf-d60ffff35b1e#a2).

2) The applicant should be an excellent young scientist, having the research background in the fields of nano-composite materials and advanced spectroscopies, and already published more than 3 papers in high level journals.