Application Note SMX038

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# SMX038 - Rigaku rotating anodes: powerful and reliable sources for seamless and high-throughput small molecule structure solution

## Introduction

Structural scientists often assume that rotating anode generators (RAG) are only useful for protein crystallography, while sealed-tube X-ray sources (and even more so *microfocus* sealed-tube sources that have become common in home laboratories in the past few years) are sufficient for the analysis of small molecule compounds. But contemporary small molecule crystallographers now often realize that the additional cost-of-ownership of RAGs is trumped by the greater power and versatility they offer. Indeed, the sheer power of RAGs not only enables a significant increase of crystal structure throughput in the laboratory, but also broadens the range of accessible crystals/compounds:

- Microcrystals
- Weakly diffracting crystals containing large voids filled with hosts/solvents, such as MOFs, COFs and sponge crystals
- Crystals unstable once taken out of their crystallization environment, which necessitate faster data collections
- Compounds going through a structural transition that require multiple data collections.
- Time-resolved crystallography studies
- Charge density experiments. Given the weaker flux of silver and molybdenum radiations, data collection with RAGs requires less time and yields stronger data at very high resolution.

Modern sealed-tube X-ray diffractometers often feature dual sources, allowing crystallographers to select the wavelength depending on the sample or the type of experiment they wish to perform. Rigaku manufactures the only RAGs that also offer this level of flexibility. A Rigaku dual-source rotating anode is built with two different metal targets and is coupled with two sets of mirrors specifically tuned to each wavelength. Users switch between the two sources with a button click, requiring no manual intervention.

## Small molecule crystallography in the world with Rigaku microfocus rotating anodes

Small molecule crystallography laboratories around the world currently use Rigaku RAGs. The rest of this document highlights interesting research performed in these laboratories. Rigaku offers two levels of RAGs, depending on the flux required. The XtaLAB Synergy-R and -DW are based on the world-renowned MicroMax-007 HF source and consume 1.2 kW. Installed in hundreds of laboratories across the world over the past 15 years, the robust MicroMax-007 HF has a proven record of performance and reliability. Rigaku also offers a top-tier RAG that uses a higher power (2.97 kW): the XtaLAB Synergy-Custom FR-X. Both feature a direct-drive rotating anode, improving reliability and up-time while reducing maintenance costs. And both types offer the choice of one or two wavelengths, among copper, molybdenum, and silver.

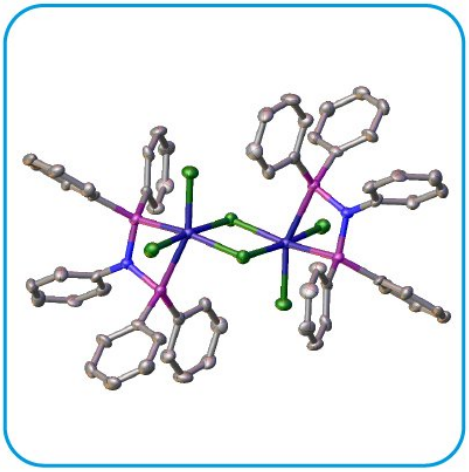
**Table 1**: Specifications for the XtaLAB Synergy microfocus rotating anode instruments.

| | | **XtaLAB Synergy-R Single wavelength** | **XtaLAB Synergy-DW Dual wavelength** | **XtaLAB Synergy Custom FR-X Single wavelength** | **XtaLAB Synergy Custom FR-X Dual wavelength** |
|---|---|---|---|---|---|
| X-ray source | | MicroMax-007 HF Microfocus RAG Direct drive | | FR-X Microfocus RAG Direct drive | |
| Operating power | Cu | 40 kV x 30 mA = 1.2 kW | | 45 kV x 66 mA = 2.97 kW | |
| | Mo | 50 kV x 24 mA = 1.2 kW | | 45 kV x 66 mA = 2.97 kW | |
| | Ag | 50 kV x 16 mA = 0.8 kW | | 45 kV x 44 mA = 1.98 kW | |
| Wavelength | | Choice of Cu, Mo or Ag | Choice of Cu/Mo, Cu/Ag or Mo/Ag | Choice of Cu, Mo or Ag | Choice of Cu/Mo, Cu/Ag or Mo/Ag |
| Optics | | 1 set of λ-dependent confocal multilayered | 2 sets of λ-dependent confocal multi-layered with 1-click computer-controlled rotation | 1 set of λ-dependent confocal multilayered | 2 sets of λ-dependent confocal multi-layered with 1-click computer-controlled rotation |
| Goniometer Type | | Universal Goniometer 2 (UG 2): 4-circle Kappa geometry, kappa range: -179º to +179º | | | |
| Sphere of Confusion | | 7-10 µm | | | |
| Collection speed | | Up to 20º/sec (axis dependant) | | | |
| Detector options | | Rigaku Hybrid Photon Counting HyPix detectors:<br>• Flat HyPix-6000HE<br>• Curved HyPix-Arc 100°<br>• Curved HyPix-Arc 150°<br>Dectris Hybrid Photon Counting detectors<br>• Pilatus3 R 200K<br>• Pilatus3 R 300K<br>• Eiger R 1M | | Rigaku Hybrid Photon Counting HyPix detectors:<br>• Flat HyPix-6000HE<br>• Curved HyPix-Arc 100°<br>• Curved HyPix-Arc 150°<br>All Dectris Hybrid Photon Counting detectors | |

## Interesting structures from our users

Some of our RAG users have provided their peer-reviewed publications to show the range of samples that can analyzed and the diversity of research topics that can be addressed when using Rigaku microfocus rotating anode diffractometers. We provide a summary for each of them below. These results span the last 15-20 years, demonstrating that using RAGs for small molecule crystallography is not just a recent occurrence.

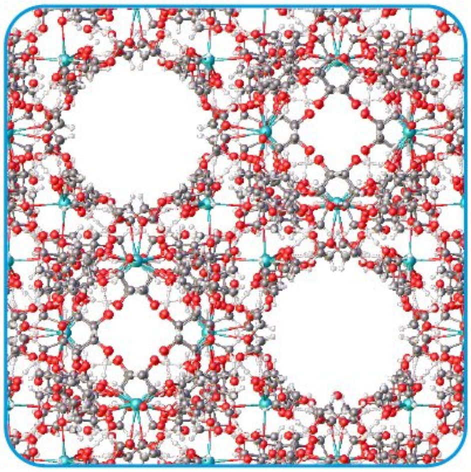
Ethylene Tetramerization: A New Route to Produce 1-Octene in Exceptionally High Selectivities, *J. Am. Chem. Soc.*, 2004, **126**, 45, 14712.



Annette Bollmann*, Kevin Blann, John T. Dixon, Fiona M. Hess, Esna Killian, David H. Morgan, Arno Neveling, Stefanus Otto, Hulisani Maumela, Matthew Overett, David S. McGuinness: Sasol Technology (Pty) Ltd., South Africa and U.K.; Alexandra M. Z. Slawin (crystallographer): University of St. Andrews, Scotland; Peter Wasserscheid and Sven Kuhlmann: University of Erlangen-Nuernberg, Germany

A new synthetic route to the synthesis of 1-octene with good selectivity of up to 70% via ethylene tetramerization was discovered. A complex of Cr(III) with diphosphinamine ligands $((R^a)_2P)_2$-$NR^b$ catalyzes the reaction . In addition to discussing the effect of the nature of the $R^a$ and $R^b$ substituents on 1-octene synthetic selectivity, the authors discovered that the catalyst didn't have to be synthesized in situ for the reaction to occur. Instead, they demonstrated that the catalytic reactions can also be conducted using a pre-synthesized Cr(III) complex. The unambiguous characterization of the catalyst formed in such a way came from X-ray analysis. The crystal structure of the derivative with Ra = Rb = phenyl was obtained and showed that it is a chlorine-bridged dimer $[Cr(((R^a)_2P)_2\text{-}NR^b)Cl_2(\mu\text{-}Cl)]_2$.

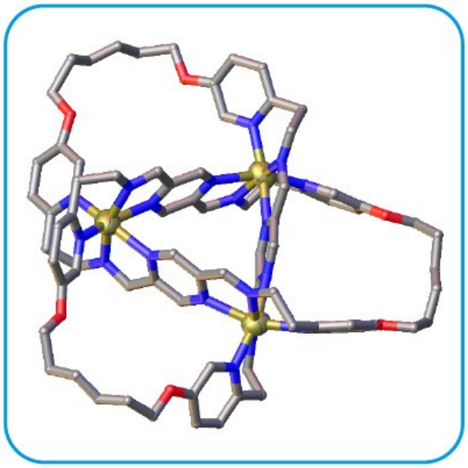
Metal–Organic Frameworks from Edible Natural Products, *Angew. Chem. Int. Ed.*, 2010, **49**, 8630.



Ronald A. Smaldone, Ross S. Forgan, Jeremiah J. Gassensmith, J. Fraser Stoddart*: Northwestern University, USA; Alexandra M. Z. Slawin (crystallographer): University of St. Andrews, Scotland; Hiroyasu Furukawa, Omar M. Yaghi: University of California Los Angeles, USA.

These authors report the successful synthesis of a Metal-Organic Framework (MOF) from a renewable, naturally available building block: γ-cyclodextrin (γ-CD), an additive commonly used in the food industry as well as a solubilizing and stabilizing agent in drug delivery. A series of CD-MOFs were synthesized, using various metals: $K^+$, $Na^+$, $Rb^+$ and $Cs^+$. The use of inexpensive, non-hazardous and readily available natural products aims to address the growing desire to avoid relying on organic building blocks derived from non-renewable petrochemical feedstocks. The CD-MOFs described in this work can be prepared entirely from edible ingredients: food-grade γ-CD, salt substitute (KCl) or potassium benzoate (food additive E212) in bottled water and Everclear® grain spirit (EtOH), making virtually edible MOFs. A detailed analysis of the crystal structure of the $K^+$ MOF derivative is used to explain the success of synthesizing and obtaining crystalline CD-MOFs. Additional structural analyses were performed on crystals of CD-MOFs soaked in the dye Rhodamine B. However, while the presence of the dye molecules was evident from the crystals turning red and was confirmed by $^1$H NMR, the crystal structures could not definitively reveal all counterions or guest molecules, indicating a likely heavy disorder of the guest molecules.

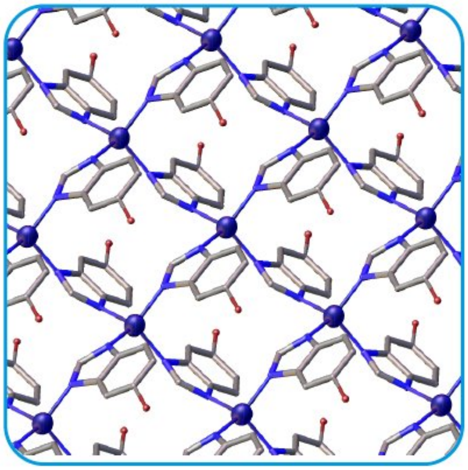
Molecular Trefoil Knot from a Trimeric Circular Helicate, *J. Am. Chem. Soc.*, 2018, **140**, 4982.



Liang Zhang, David P. August, Jiankang Zhong, George F. S. Whitehead (crystallographer), Iñigo J. Vitorica-Yrezabal, and David A. Leigh*: University of Manchester, U.K.

A novel two-step synthesis of a molecular trefoil knot is described, based on the self assembly of a 12-component trimeric circular zinc helicate, followed by ring closing metathesis of six pendant alkene chains. Only three designed synthetic routes had been reported to date and they involved complex intermediates and lengthy syntheses. In contrast, this was one of the shortest and highest yielding designed routes to a trefoil knot developed to date. The crystal structure of the intermediate compound unambiguously established its trimeric circular zinc helicate nature and showed how the alkyl chains are well ordered in the solid state and positioned such that joining each of them to their nearest neighbor generates a trefoil knot. The crystal structure of the trefoil knot revealed an 84-atom-long closed loop that weaves a continuous path around the three zinc centers, with the strand crossing over or under itself at each zinc atom.

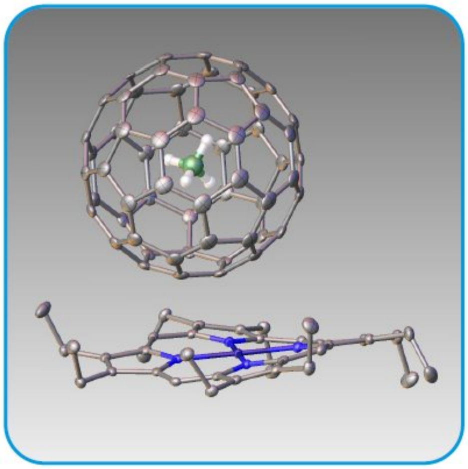
Isoreticular two-dimensional magnetic coordination polymers prepared through pre-synthetic ligand functionalization, *Nature Chemistry*, 2018, 10, 1001.



J. López-Cabrelles, S. Mañas-Valero, G. Mínguez Espallargas* and E. Coronado*: University of Valencia, Spain; I. J. Vitórica-Yrezábal (crystallographer): University of Manchester, U.K.; P. J. Bereciartua: Polytechnic University of Valencia, Spain; J. A. Rodríguez-Velamazá: Institut Laue-Langevin, France; J. C. Waerenborgh and B. J. C. Vieira: University of Lisbon, Portugal; D. Davidovikj, P. G. Steeneken and H. S. J. van der Zant: Delft University of Technology, The Netherlands

The authors describe a novel method to synthesize 2D materials with specific physical and chemical properties whereby organic ligands are covalently functionalized before the synthesis of the layered coordination polymers used in the preparation of 2D crystalline materials. Pre-synthetic ligand functionalization is a better way to preserve the long-range structural order of materials, unlike post-synthetic functionalization where molecules are anchored on a 2D crystal post-exfoliation to engineer their surface and tune their properties. A series of five isostructural layered magnetic coordination polymers between Fe(II) centers and different benzimidazole derivatives (bearing a Cl, H, $CH_3$, Br or NH2 side group) were prepared and used to produce the final material by mechanical exfoliation. The crystal structures of two of the compounds were determined from synchrotron data, while data collected on a Rigaku FR-X RAG led to the crystal structure of the other three. X-Ray analyses established the layered nature of the compounds, showed they were all isostructural and provided a path to explaining their magnetic properties.

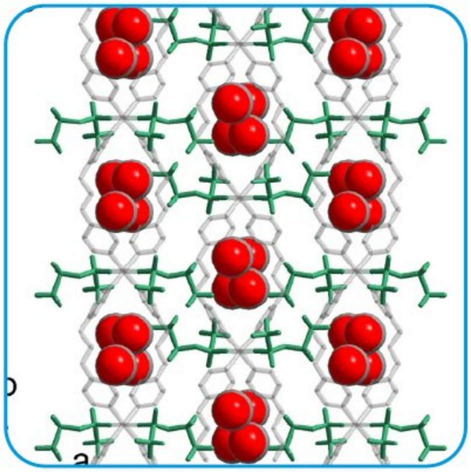
First Synthesis and Characterization of $CH_4@C_{60}$, *Angew. Chem. Int. Ed.*, 2019, **58**, 5038.



Sally Bloodworth, Gabriela Sitinova, Shamim Alom, Sara Vidal, George R. Bacanu, Stuart J. Elliott, Mark E. Light, Julie M. Herniman, G. John Langley, Malcolm H. Levitt, and Richard J. Whitby*: University of Southampton, U.K.

The first complete chemical synthesis of the endohedral fullerene $CH_4@C_{60}$ in which each $C_{60}$ fullerene entity encapsulates a single methane molecule, is reported. While the opening of a fullerene by a chemical route, to allow a small molecule to insert itself, was known, the critical step of suturing the fullerene to imprison the small molecule had remained elusive. This work describes the first successful closure of any $A@C_{60}$ compound, where A is methane, a molecule thought to be one of the largest possible guests for $C_{60}$. The crystal structure of the nickel(II) octaethylporphyrin/benzene solvate of $CH_4@C_{60}$ critically shows an additional spherical electron density blob inside $C_{60}$, demonstrating that methane has indeed been encapsulated. Moreover, a faint shell of electron density symmetrically distributed around the central carbon is also observed 1.03 Å away from it and attributed to the methane hydrogens,. This shell of electron density corresponds to the delocalized nuclear wavefunction of the methane hydrogens, as expected for a quantum description of the freely rotating molecule and as has been previously established for the analogous systems $H_2@$ $C_{60}$, $H_2O@C_{60}$, and $HF@C_{60}$.

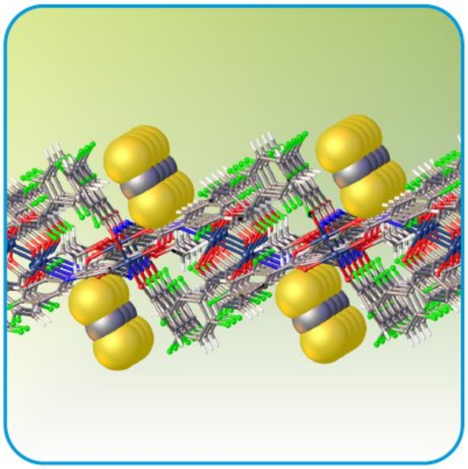
Understanding the interactions between the bis(trifluoromethylsulfonyl)imide anion and absorbed $CO_2$ using X-ray diffraction analysis of a soft crystal surrogate, *Commun. Chem.*, 2020, **3,** Article #143



Xin Zheng; Katsuo Fukuhara; Yuh Hijikata; Jenny Pirillo; Kiyonori Takahashi; Shin-ichiro Noro and Takayoshi Nakamura: Hokkaido University, Japan; Hiroyasu Sato: Rigaku Corporation, Japan.

In today's world where the threat from global warming increases rapidly, interests in ionic liquids (IL) has increased because of their capacity to selectively absorb carbon dioxide ($CO_2$). $CO_2$ absorption in ILs is known to be primarily dependent on the nature of the anion, where fluorinated anions have been identified as superior absorbers relative to those lacking that specific halogen. In that regard, the bis(trifluoromethylsulfonyl)imide (NTf2-) anion, made of two $CF_3SO_2$ moieties linked by a nitrogen center, has attracted much of the research effort. A clear understanding of the reasons for the superior $CO_2$ absorption capabilities remains elusive, given the lack of structural data on these liquid compounds. In this work, the authors propose to use soft crystals, materials that can switch between crystalline and soft states under the action of a chemical or physical stimulus, as solid-state models for ILs available for single crystal X-ray crystallography. They synthesized soft crystals of a ($NTf^{2-}$) salt of a $Cu^{2+}$ metal-organic cluster. The ligand on the $Cu^{2+}$ cation consists of two pyridyl groups linked by a propane chain similar to alkyl chains found in ILs. The crystal structure of the guest-free and $CO_2$-loaded species demonstrates how the compound switches from a closely-packed to an open, porous arrangement, principally due to a change of conformation of the ($NTf^{2-}$) moiety. Indeed, ($NTf^{2-}$) switches from a cis to trans conformation relative to the central S-N bond to form a cavity which encloses two $CO_2$ molecules. Additional structural and theoretical calculation details are provided, along with results from experiments that show that the soft crystals specifically absorb $CO_2$, but not nitrogen or argon gases.

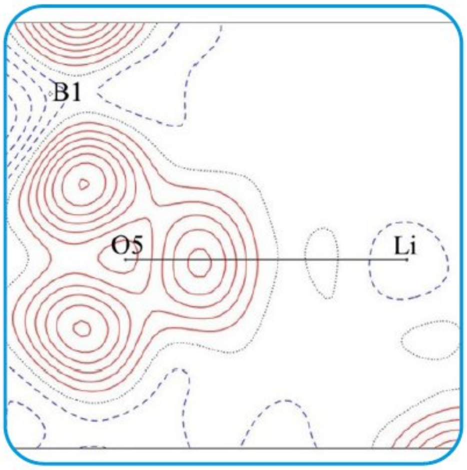
Magnet Creation by Guest Insertion into a Paramagnetic Charge-Flexible Layered Metal–Organic Framework, *J. Am. Chem. Soc.*, 2021, **143**, 7021.



Jun Zhang, Wataru Kosaka, and Hitoshi Miyasaka*: Tohoku University, Japan; Hiroyasu Sato: Rigaku Corporation, Japan

Three collaborating groups at Tohoku University in Japan propose to chemically alter the magnetic properties of molecular materials through the lens of Metal-Organic Frameworks (MOFs). First, they synthesized a MOF where Ru-based clusters are linked by single molecules of tetracyanoquinone(TCNQ)-ether, forming a 2D-layered framework. The solvent-free paramagnetic MOF compound is a charge-transfer complex which undergoes an electron transfer from the electron-rich TCNQ moiety to the electron-accepting Ru cluster at 380 K via a structural transition. Then, the authors were able to initiate the same electron transfer and trigger a non-magnetic to magnetic transition at temperatures between 70 K and 92 K by inserting molecules of various organic solvents into the MOF. Remarkably, they were able to tune the magnetic properties of the solvated compounds to ferrimagnetic or antiferromagnetic upon inserting guest molecules of benzene, xylene, dichloroethane and dichloromethane vs. carbon disulfide, respectively. High-quality rotating anode data were collected on the non-solvated and solvated crystals at various temperatures and allowed for the careful analysis of the crystal arrangements as well as relevant interatomic distances, such as the C-N triple bonds of the TCNQ moiety, to estimate the electronic charge borne by various parts of the MOF. X-ray data and results from differential scanning calorimetry, infrared and Raman measurements are used to discuss in detail the structure-properties relationships in this charge-flexible MOF material.

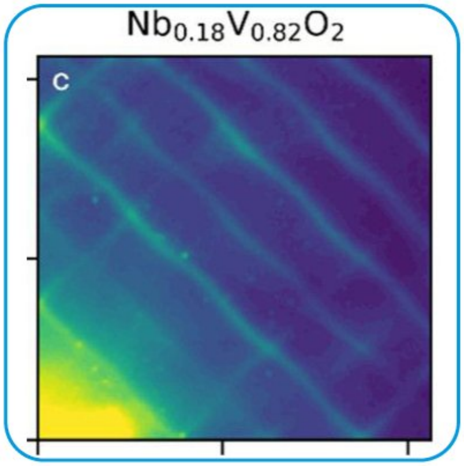
Uncovering a Functional Motif of Nonlinear Optical Materials by In Situ Electron Density and Wavefunction Studies Under Laser Irradiation, *Angew. Chem. Int. Ed.*, 2021, **60**, 11799.



Guo-Cong Guo, Xiao-Ming Jiang, Shu-Juan Lin, Chao He and Bin-Wen Liu: Fujian Institute of Research on the Structure of Matter, China

Thanks to their capabilities to generate tunable laser sources via second harmonic generation, nonlinear optical materials (NLO) are of great interest for a wide range of applications in medicine, the military, and in communication networks. Understanding the mechanisms leading to NLO activities, and thus designing better materials, resides upon the identification of the Functional Motif (FM) responsible for the optical response and upon the study of how its molecular topology and electronic structure may change under the stress of external fields. The authors of this work set out to achieve, for the first time, the experimental identification of the FM of a NLO material. To that effect, they selected the archetypical NLO material $LiB_3O_5$ and used the Mo radiation of their rotating anode diffractometer to collect very high-resolution single-crystal X-ray diffraction data, both in the dark and under a laser beam with wavelength of 360 nm or 1064 nm at 85 K. The systematic study of the topological changes in the electron density distribution and wavefunction of $LiB_3O_5$ established that laser irradiation significantly alters the atomic and bond properties of the $[B_3O_5]$- unit, due to electron movement from oxygen atoms to boron atoms. As it is fully in line with what was known about $[B_3O_5]$- being the FM of NLO material $LiB_3O_5$, it is hoped that this work represents a new method to determine the structural origin of optical efficiency in NLO materials.

Geometric Frustration Suppresses Long-Range Structural Distortions in $Nb_xV_{1-x}O_2$, *J. Phys. Chem. C* 2022, **126**, 2049–2061.



Top B. Rawot Chhetri, Tyra C. Douglas, Matthew A. Davenport, Stephan Rosenkranz, Raymond Osborn, Matthew J. Krogstad and Jared M. Allred: University of Alabama, USA.

Certain transition metal dioxides, such as $VO_2$ and $NbO_2$, undergo simultaneous structural and electronic transitions, inducing a metal-to-insulator transition (MIT) at 340 K and 1073 K respectively for $VO_2$ and $NbO_2$. The dependency of the MIT temperature on pressure and on small amounts of other metals such as Nb (for $VO_2$), Mo, W, Cr and Al makes these materials good candidates as temperature sensors, optical switches, memory devices, smart windows, etc. However, the forces driving the MIT transitions are not well misunderstood. So, researchers at the University of Alabama undertook the determination of the phase diagram for the alloy $Nb_xV_{1-x}O_2$ using total X-ray scattering and 3D-difference pair distribution function (3D-ΔPDF) methods. In their total X-ray scattering experiments, they used the power of the Rigaku dual source Cu/Mo rotating anode in the Mo Kα mode and the extremely low electronic noise and high sensitivity of the Hybrid Photon Counting detector HyPix-6000HE to study the weak, but obvious, diffuse scattering features present across all samples and temperatures, albeit at varying levels of intensity and complexity. They discovered two separate short-range ordered phases, one of which has not been observed before. These short-range orders, probably both two-dimensional, suggest that the MIT mechanism is likely related to the geometric frustration of displacement models, suppressing long-range structural order in these materials.

## Related products

### EIGER2 R series

High-resolution X-ray detectors for X-ray diffractometers from DECTRIS.

### HyPix-6000HE

Extremely low noise detector based on direct X-ray detection technology.

### HyPix-Arc 100°

A curved detector based on direct X-ray detection technology with the highest 2θ range at a single position available for the home lab.

### HyPix-Arc 150°

A curved detector based on direct X-ray detection technology with the highest 2θ range at a single position available for the home lab.

## XtaLAB SynergyCustom

A bespoke, extremely high-flux diffractometer with custom enclosure and the flexibility to utilize both ports of the rotating anode X-ray source.

## XtaLAB Synergy-DW

Spectacular performance combined with dual wavelength versatility, provides the perfect answer for high-capacity Chemical Crystallography labs or for X-ray facilities that support Chemical Crystallography and Protein Crystallography.

## XtaLAB Synergy-R

Our most popular diffractometer for Protein Crystallography, configured with a high-flux rotating anode X-ray source and an extremely low noise direct X-ray detection detector.

## MicroMax-007 HF

Microfocus rotating anode X-ray generator