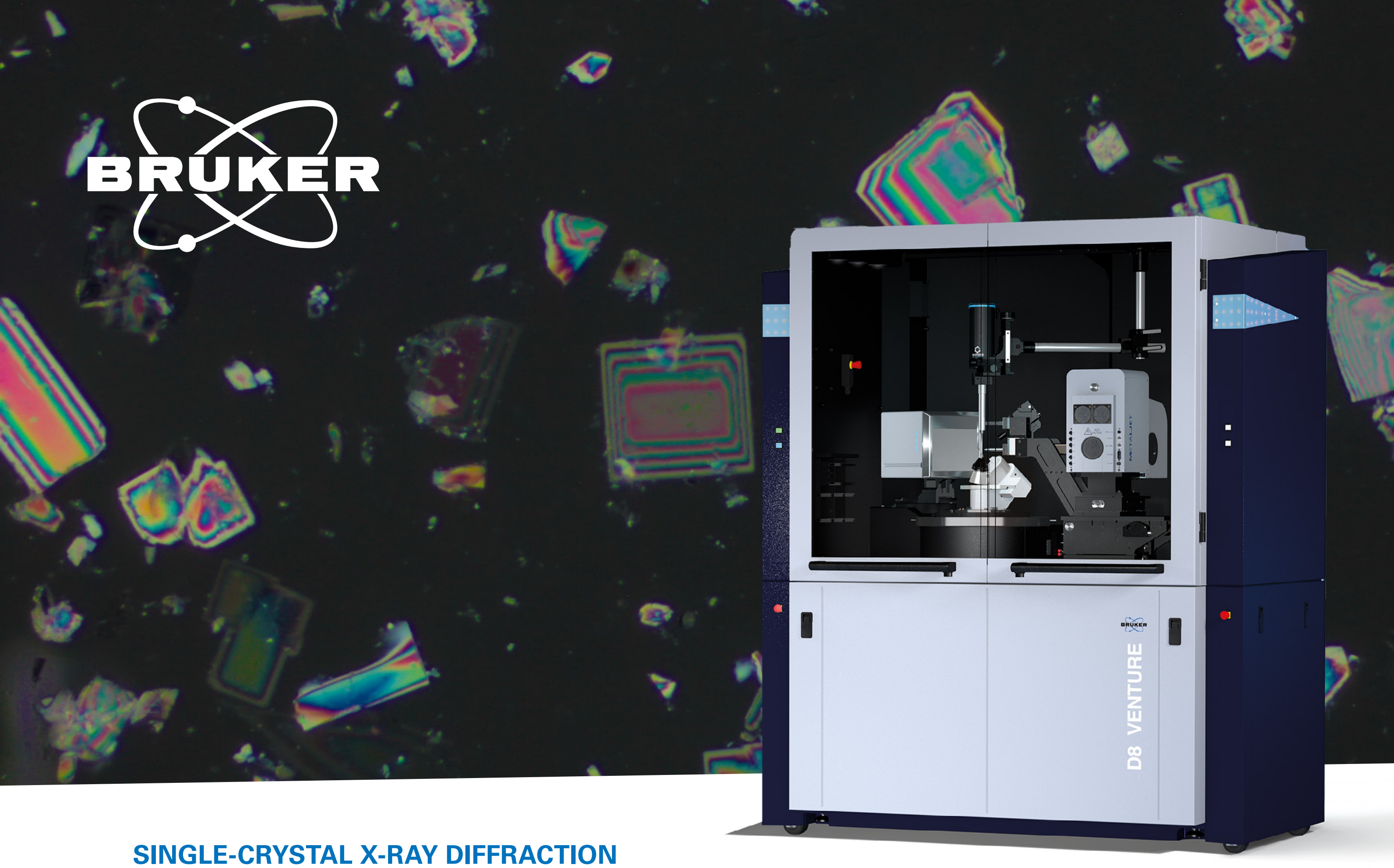

SINGLE-CRYSTAL X-RAY DIFFRACTION

A Bright Insight Into Functional Materials

The D8 VENTURE METALJET MC

Introduction

Functional materials are designed to achieve specific properties for advanced applications. Among these, supramolecular compounds formed through non-covalent interactions are a key category as they, for example, offer unique properties for environmental remediation applications such as contaminant detection and removal. Crystallography plays a vital role in the understanding and design of supramolecular compounds by revealing their atomic structure, which directly influences their properties and functionalities.

Application and legacy of perfluorinated alkyl acids

Perfluoroalkyl acids (PFAS) are a group of synthetic chemicals that have been widely used in various industrial and consumer products since the 1940s due to their unique properties such as resistance to heat, water and oil. Examples of products that may contain PFAS include non-stick cookware, food packaging, stain-resistant fabrics, firefighting foams and some cosmetics.

The resistance of PFAS compounds to degradation has led to their significant accumulation in the environment, with potential impacts on ecosystems and human health. This has led to intensive research and development of technologies to remove them from the environment or to enhance degradation processes.

Pillarenes

Pillarenes are a fascinating class of functional materials: synthetic macrocycles composed of hydroquinone or dialkoxybenzene units linked by methylene bridges at the para positions.

They are named for their cylindrical, pillar-like shape and are structurally similar to other macrocycles like cucurbiturils and calixarenes Pillarenes have unique properties that make them valuable in various fields, including host-guest chemistry, molecular recognition, and self-assembly. They can form strong association complexes with electron-poor species due to their electron-rich cavities.

Here we report on the structure determination of two complexes formed by Pillarene (P5) and PFDA and PFOA, respectively. Both belong to the PFAS as described above.

Crystallographic challenge of functional materials

Single crystal X-ray diffraction (SC-XRD) is the premier technique for determining the molecular and atomic structure with unprecedented accuracy, reaching sub-picometer precision. It excels at revealing intricate structural details that are critical to understanding the relationship between a material's structure and its properties. By providing precise atomic positions and bond lengths, SC-XRD delivers insights to researchers facilitating the design and optimization of advanced materials tailored for specific applications.

Functional materials–by design–often present challenges due to their structural flexibility leading to disorder, imperfect periodicity, high fragility. Often only tiny crystals are available. These challenges can be addressed with our state-of-the-art high-end in-house SC-XRD solutions, featuring a high intensity X-ray source with a beam diameter optimized to the small sample sizes, a precise goniometer, and advanced detector technology to facilitate rapid data acquisition.

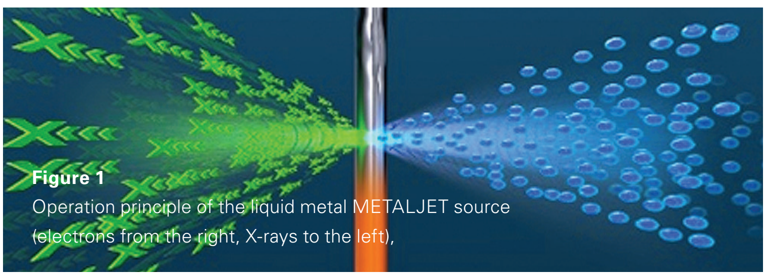

Figure 1
Operation principle of the liquid metal METALJET source (electrons from the right, X-rays to the left).

The METALJET MC

The Ga METALJET is undoubtedly the most brilliant X-ray source for in-house instrumentation. The intensity limitation of traditional solid metal targets is overcome by using a liquid Ga jet as a target (Figure 1). Furthermore, Ga radiation with a wavelength between Cu and Mo is the perfect choice for most SC-XRD applications. Dynamic beam adjustment further enhances brilliance and uptime. The recent introduction of the MC optics optimizes the METALJET beam for most tiny crystals.

This innovation increases the peak flux density of the METALJET by a factor of three and breaks the 10^{12} X-ray$\cdot s^{-1} \cdot mm^{-2}$ barrier. This makes the new METALJET MC the ideal solution for structure determination on weakly diffracting small crystals with dimensions even below 60 µm in size. Combined with the large active area PHOTON III detectors and the proven low sphere-of-confusion KAPPA goniometer, the D8 VENTURE MC (Figure 2) represents the most powerful in-house SC-XRD instrumentation.

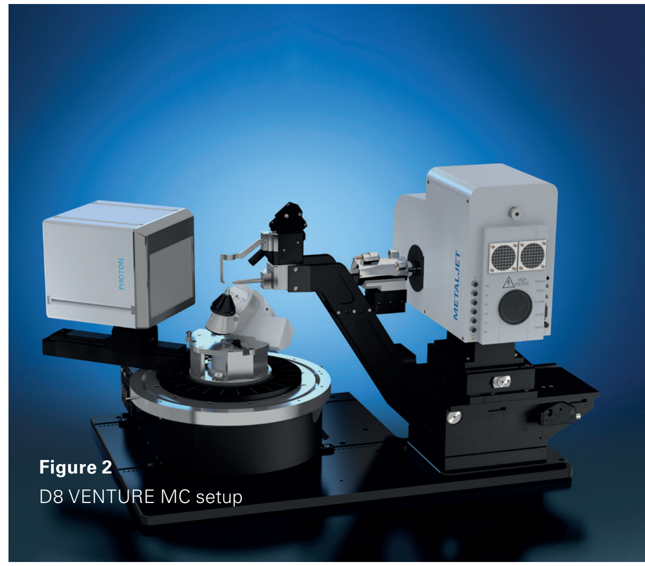

Figure 2
D8 VENTURE MC setup

Experimental

Colorless plate-like crystals of P5-PFDA of (120 × 85 × 30 μm^3) and P5-PFOA (120 × 100 × 60 μm^3) were mounted on a D8 VENTURE system equipped with a METALJET MC (Ga, $K\alpha$ = 1.34139 Å), a KAPPA goniometer and a PHOTON III 28 detector.

All data were processed, and the structure solved and refined using the APEX software suite.[3] As expected for such flexible structures, the lack of strict long-range order and hence the lack of high resolution diffraction.

Therefore, even with the high intensity instrumentation used, the crystals diffracted relatively poorly and hardly any reflection visible beyond 0.95 Å could be observed. The rather poor crystallinity manifests itself in the abundance of disorder, much of which could be resolved thanks to the relatively high data quality.

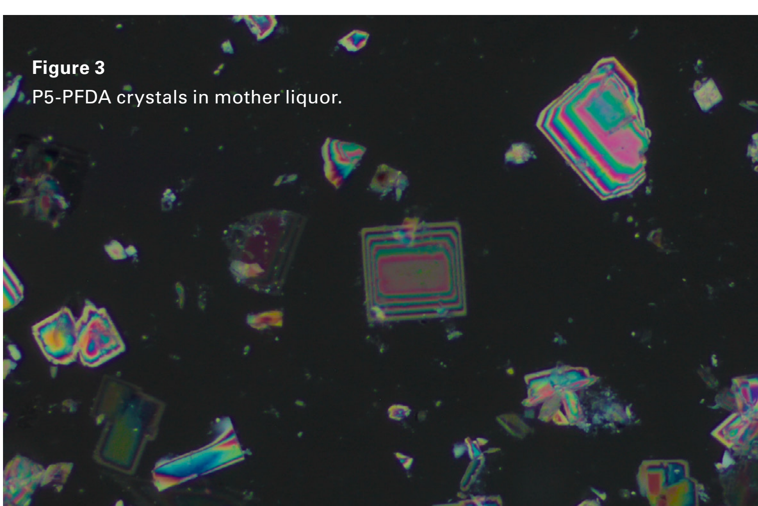

Figure 3
P5-PFDA crystals in mother liquor.

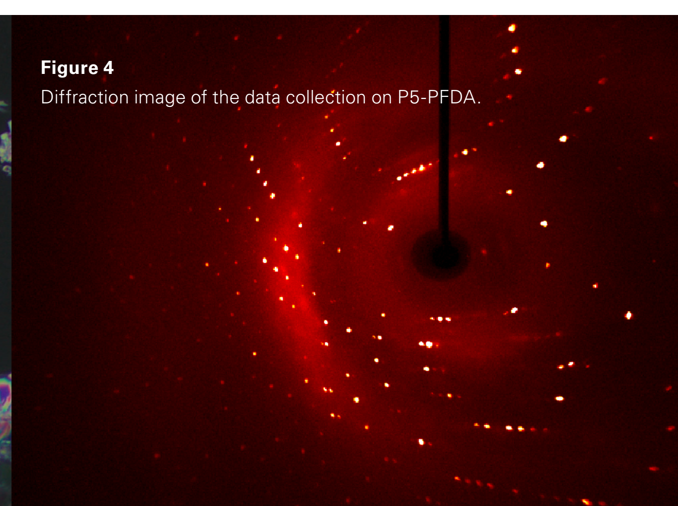

Figure 4
Diffraction image of the data collection on P5-PFDA.

Results

The D8 VENTURE MC produced exceptional high quality data down to atomic resolution from both samples. This allowed both structures to be solved and refined using routine methods[3], giving detailed insight into the molecular packing.

The quality of the data even allowed the disorder present in the perfluorated alkyl moieties to be modeled to an extraordinarily large extent.

A large number of other less-populated conformations cause ubiquitous diffuse disorder background that cannot be described by an atomistic model. It should be pointed out that the instrumentation used allowed a fast and accurate experiment, which was crucial treating the samples rapid decomposition even at 100 K.

The refined models led to the conclusion that the remarkable self-assembly of these compounds is driven by electrostatic host-guest attractions combined with strong fluorophilic interactions.

In general, pillarenes feature a well-defined cavity size (4.7Å)[4] featuring the ability to incorporate a wide range of molecules, as e.g. can be used for drug delivery[5]. Interestingly, in both structures discussed herein, the pillarene cavity is left empty. Other than expected for such a system, no laminar structure is formed, although it combines strong hydrophobic and hydrophilic units.

Instead, a smectic-like structure of fluorous and pillarene phases is observed, with an unprecedented PFAS to pillarene ratio of 5:1 (PFDA) and 10:1 (PFOA), respectively. The chessboard arrangement in one direction indicates a size-matching effect of the structural building blocks.

The exceptionally high affinity, capacity and speed of PFSA capture by the pillarene studied herein makes this system a very promising candidate for the filtration of contaminated water. Initial tests have already demonstrated the efficient removal of PFAS from water in a manner orthogonal to the in-cavity complexation of common organic molecules[2].

The orthogonal behavior can be easily correlated to the structural differences between a typical pillarene arrangement and the one found for P5. The example highlights the absolute necessity of detailed structure determination.

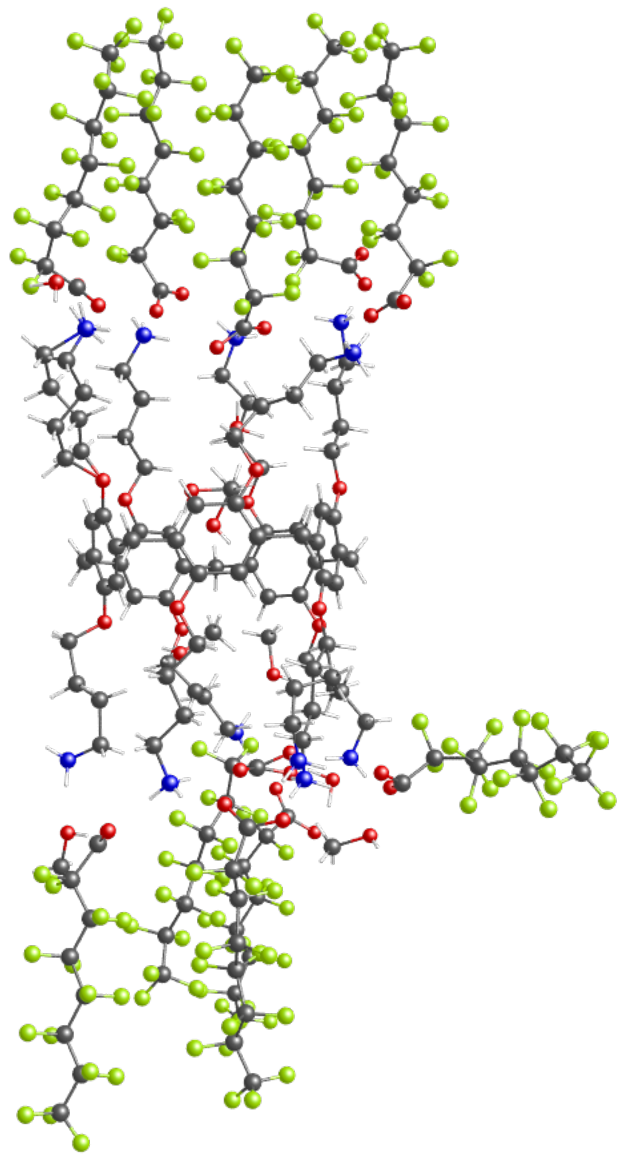

Figure 5
Structure of the pillarene – PFSA assembly in C5-PFOA.[2]

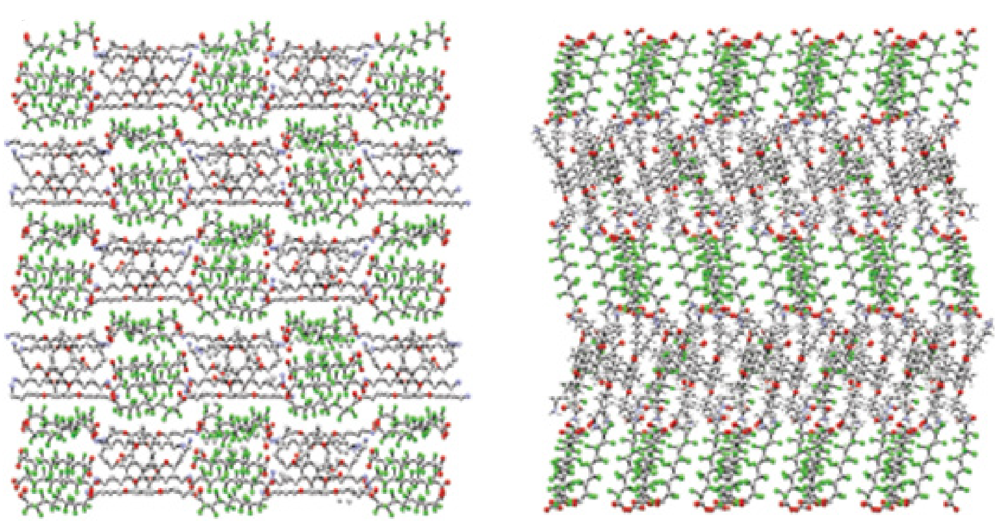

Figure 6
ac- and bc plane of the structure of P5-PFDA.[1]

Conclusions

Functional materials play a key role in modern industrial and environmental processes. A clear understanding of the structure-property relationship is essential and demands a fast and accurate structure determination. On the other hand, these materials notoriously feature limited crystallinity. Maximum brilliance microfocus sources combined with a single-photon sensitivity detector are crucial for the success of the investigation.

The D8 VENTURE MC is the most powerful in-house single-crystal X-ray diffraction instrument. The tiny highly intense X-beam in combination with the PHOTON III 28 renders the D8 VENTURE MC the ideal system for these challenging compounds. The structure determination of P5-PFOA and P5-PFDA, has been made possible due to the outstanding performance of the D8 VENTURE MC.[1],[2]

Acknowledgement

Samples of the compounds P5-PFOA and P5-PFDA were provided by the University of Wageningen. We are grateful for the opportunity to contribute to the fruitful collaboration which resulted in two notable publications in renowned journals.[1],[2]

References

1. *Adv. Sci.* **2024**, 2401807, https://doi.org/10.1002/advs.202401807, CC BY 4.0

2. *Angew. Chem. Int.* Ed. **2024**, 63, e202403474, CC BY-NC 4.0

3. APEX4 2022.1-1 with SAINT 8.40B and SADABS 2016/2, Shelxl-2019/2

4. *J. Am. Chem. Soc.* **2008**, 130, 5022

5. *J. Am. Chem. Soc.* **2013**, 135, 10542–10549.

Authors

Dr. Tobias Stürzer,
Bruker SC-XRD Application Laboratory,
Bruker AXS SE, Karlsruhe, 2024

Bruker AXS

info.baxs@bruker.com

bruker.com