CASE STUDY

Bruker's D8 VENTURE with METALJET enabled us to obtain structural data on small, weakly diffracting crystals composed of ionic porphyrin synthons with unprecedented resolution. These π-conjugated supermolecular assemblies are promising electron delivery systems for photovoltaics and energy storage devices.

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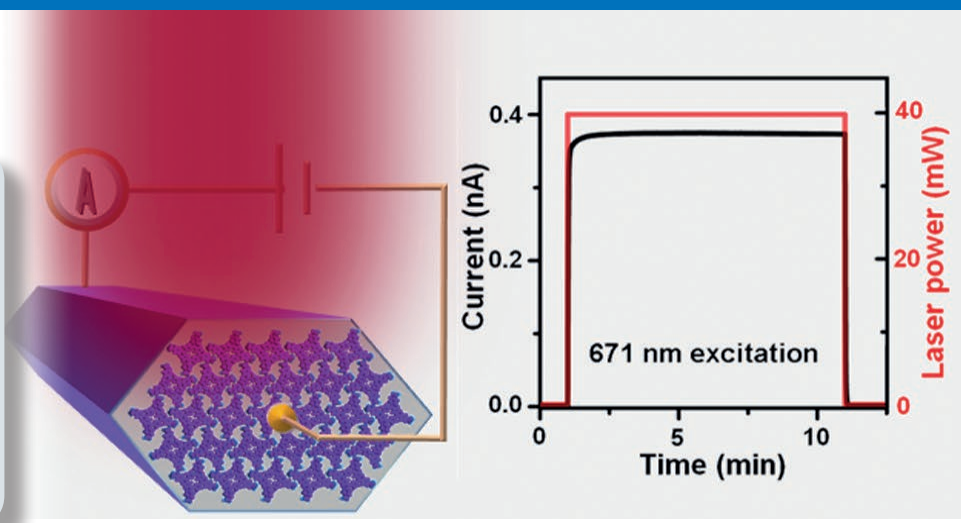

Case Study 5
Three-dimensional structures of supermolecular materials provide insight into their function

Structure – property relationship

Harnessing porphyrin superstructures for optoelectronic device applications requires accurate knowledge and control of the charge carriers and their concentration. Central to these efforts is a fundamental understanding of the relationship between structural organization of the chromophores and their optoelectronic behavior.

Challenge

Binary ionic porphyrins are generally nanocrystalline with a thickness of a few micrometers. This makes it usually impossible to obtain the so much needed crystal structure from these samples.

Solution and findings

With the aid of D8 VENTURE equipped with the strong METALJET source we were able to determine, for the first time, the molecular organization of a binary ionic porphyrin crystalline solid and combine this result with electronic structure and photoconductivity measurements in a unified manner.

- In TMPyP:TSPP crystals the ionic tectons are arranged in an alternating fashion forming coherent columns in the direction normal to the crystallographic *a* axis; electrostatic and π bonding play dominant roles in the molecular organization.
- The conduction process is one dimensional, proceeds along the porphyrin synthons stacking direction in the crystal and is facilitated by π-π interactions.
- TMPyP:TSPP is a direct band gap n-type photoconductor.

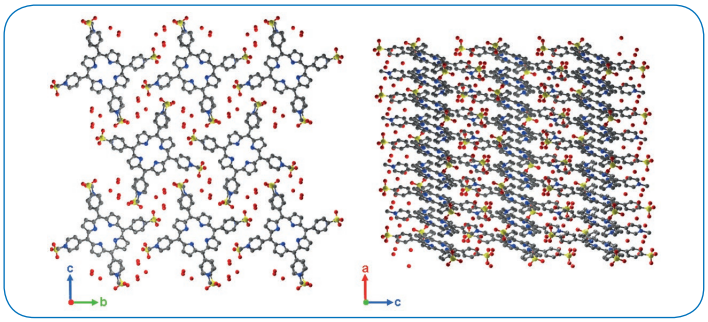

Figure 1. Crystal structure of tetra-methylpyridyl porphyrin4+ and tetra-sulfonatophenyl porphyrin4- (TMPyP:TSPP).

Combining structural geometry and computational modeling

Quantum mechanical calculations can provide insights into the properties of porphyrin materials and help develop predictive algorithms to optimize their electrical and optical responses. The structure we obtained from the D8 VENTURE is a prerequisite for these studies.

Combined results from structural and theoretical studies and their correlation with function opens the road to the engineering of highly-organized functional materials.

Literature

Adinehnia, M.;.Borders, B.; Ruf, M.; Chilukuri, B.; Hipps, K.W.; Mazur, U. J. Mater. Chem. C, ***2016,*** *4, 10223 (hot paper).*

Borders, B.; Adinehnia, M.; Rosenkranz, N.; van Zijll, M.; Hipps, K. W.; Mazur, U. J. Porph. Phthal. ***2017****, 21, 569.*