Electron diffraction for the promotion of stable and green metal-organic frameworks

E. Svensson Grape[1], T. Hidalgo[2], P. Horcajada[2], I. A. Ibarra[3], A. K. Inge[1]

[1] *Stockholm University, Stockholm, Sweden,*
[2] *IMDEA Energy, Madrid, Spain,*
[3] *Universidad Nacional Autónoma de México, Mexico City, Mexico*

andrew.inge@mmk.su.se

Metal-organic frameworks (MOFs) have become one of the most widely studied nanoporous materials of the past two decades. Single crystal X-ray diffraction still remains as the preferred method for structure determination, but requires sufficiently large crystals. Still predominantly to this day, MOFs are prepared using synthesis conditions that are optimized for producing larger single crystals, which often includes dissolving starting materials with polar organic solvents followed by heating under solvothermal conditions.

With the emergence of fast 3D electron diffraction (ED) techniques such as MicroED, solving crystal structures from nano-sized crystals has never been easier for crystals with organic constituents that traditionally were considered too beam sensitive [1-2]. This provides opportunities to easily study MOFs that can only be synthesized as small nanocrystals. Many of the more stable MOFs have a tendency to form as smaller crystallites, which can now be conveniently studied by ED. This makes it easier to study MOFs made using less typical synthesis conditions which may be less hazardous, more environmentally friendly and require less energy input.

Access to fast ED has allowed us to focus on the development of new stable MOFs prepared under green synthesis conditions. SU-101 was prepared using nonhazardous and edible starting materials which were stirred in water at room temperature without any other energy input [3]. The reaction starts and ends as a suspension in water, resulting in phase pure MOF. Scaling up the synthesis of SU-101 was easily achieved. For the first time in a MOF, ellagic acid was used as the organic linker. Ellagic acid is one of the building units of naturally occurring polyphenols and is a well-known antioxidant found in fruits, berries, nuts, and wine. Unlike many MOF linker molecules, ellagic acid does not contain carboxylic acids groups but instead has multiple phenol groups which can chelate to metal cations forming strong bonds and hence robust framework structures. SU-101 demonstrates excellent stability in organic solvents and water even at elevated temperatures. SU-101 has one of the highest uptake capacities for hydrogen sulfide among MOFs. Due to the stable structure, the lack of heating during synthesis and the use of a poor solvent (water), SU-101 was synthesized as small nanocrystals. The crystal structure of SU-101 was nonetheless solved by ED with ease.

The advent of fast ED techniques and the relative ease now in solving structures of nanocrystals with organic components, has changed our habits in the chemistry laboratory regarding the synthesis of novel crystalline materials. Significantly less time is now required for synthesis optimization. Rather than by default using organic solvents, elevated temperatures and pressures, we now focus on utilizing greener chemical reagents and ambient synthesis conditions directly from the early stages in the development of novel biocompatible and stable MOFs.

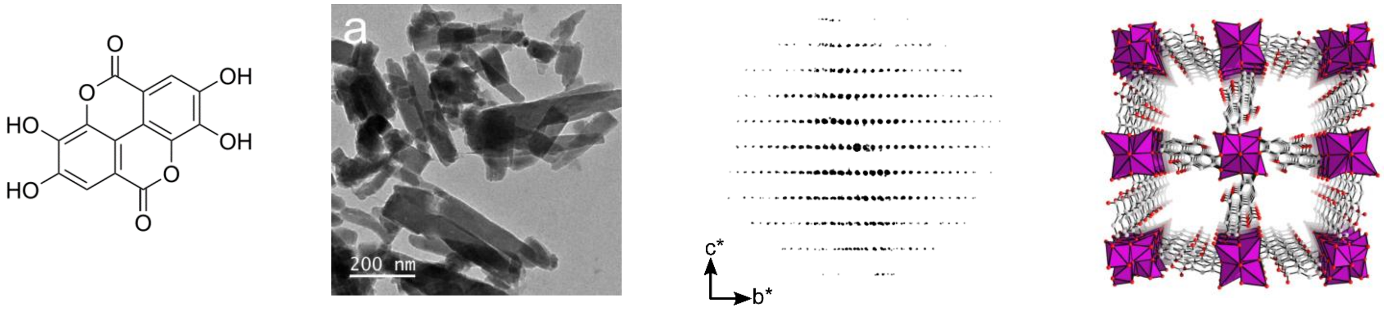

Figure 1. (From left to right) Ellagic acid; crystals of SU-101; ED data on SU-101; and the crystal structure of SU-101. [3]

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