1478
doi:10.1017/S1431927619008122
Microsc. Microanal. 25 (Suppl 2), 2019

A Scanning Tunneling Microscopy Study on Surface-Supported Imine-Based Covalent Organic Frameworks: a New Design for Robust 2D Materials.

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Two-dimensional covalent organic frameworks (2D COFs) are bidimensional sheets of ordered crystalline porous material that stack and form a layered eclipsed structure with periodically aligned columns[1]. By decreasing their thickness down to the monolayer, an atom-thick sheet of crystalline organic material can be achieved. In this manner, graphene properties can be targeted, while maintaining COF advantages (*e.g.* chemical versatility). In order to achieve single-layer COFs, one possibility is to exfoliate the 2D bulk material. Alternatively, a bottom-up approach can be followed and use a surface to template the synthesis of the COF. By using a conductive substrate such as highly oriented pyrolytic graphite (HOPG), the on-surface synthetic process can be followed *in situ* by scanning tunneling microscopy (STM). This microscopy technique rises as a powerful tool to carefully scrutiny the reaction product.

Because of their potential applications, single-layer COFs are been widely investigated[2,3]. Nevertheless, achieving stable 2D polymers displaying long-range order, remains a challenge. The reversibility of the dynamic covalent reaction, necessary to assure crystalline and defect-free COFs, is also the reason of their limited stability when exposed to specific conditions. The Schiff-base condensation reaction between an amine and a aldehyde works well on the surface[4,5]. However, the stability of the material is compromised by the easy hydrolysis of the imine bond in the presence of ambient moisture.

In this work, we present the on-surface condensation between 3,5-triformylphloroglucinol (**TFP**) and two different aromatic diamino compounds, namely 1,4-diaminobenzene (**DAB**) and 4,4''-diamino-*p*-terphenyl (**DATP**) (Figure 1a). In the design proposed, the initial step consists on a reversible Schiff base reaction that yields an imine-enol moiety that, once formed, undergoes tautomerization to the more stable keto-enamine form[6]. The first step runs under thermodynamic equilibrium and is thus useful for correcting potential defects in the larger structure. The second tautomerization step is irreversible, and hence, the final product is expected to display higher stability than related imine-based COFs.

Different on-surface synthetic protocols were tested, and the concentration of the molecular precursors, solvent systems, deposition methods, reaction times and temperatures were optimized. By drop-casting **TFP** and **DAB** 10^{-4} M solutions in dichloromethane (DCM) onto two separate HOPG substrates, placing one on top of the other with a droplet of heptanoic acid (HA) in between, and then, heating this "sandwiched" sample to 150 ºC for 1 h, an extended and ordered porous sCOF could be imaged by STM (Figure 1b).

In conclusion, an extended and crystalline network of a sCOF with improved stability could be prepared on the surface. This two-step reaction proved to be highly challenging and produce most times disordered inter-linked networks. We believe the second irreversible step occurs very fast and limits the self-correcting ability of the dynamic covalent Schiff-base first step process.

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[7] Funding from the E.U. (Horizon 2020 – MSCA-IF - Project ID 741384, CustomCOF) is gratefully acknowledged.

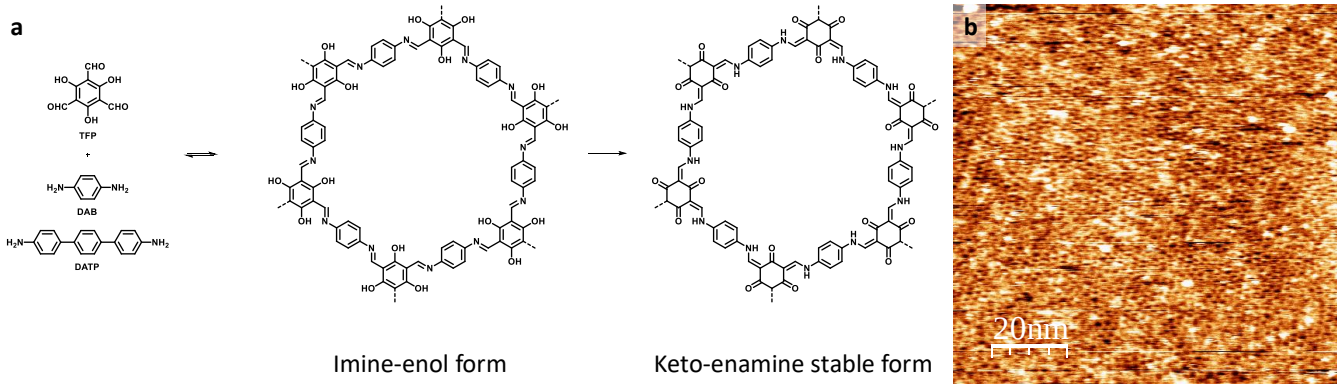

Figure 1. (**a**) On-surface chemistry towards robust sCOF materials. (**b**) STM image at the solid-liquid interface of a sCOF prepared from **TFP** and **DAB**. Scanning conditions: (a) I_{set} = 0.030 nA, V_{bias} = -0.900 V.

https://doi.org/10.1017/S1431927619008122 Published online by Cambridge University Press