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On-surface synthesis of an imine based 2D-COF using the 2-in-1 strategy: Characterisation at multiple length scales

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In the wake of the "graphene rush", many two-dimensional materials (2DMs) caught attention because of their promising properties for various applications such as optics, catalysis, energy storage and (bio)imaging. Within those 2DMs, 2D covalent organic frameworks (2D-COFs) are interesting because of their straightforward synthesis by classical organic reactions and their easy tunability. Imine-based COFs, synthesised by the solvothermal method, are long-known but both the synthesis of high-quality monolayer 2D-COFs and the mechanism of their formation are not completely understood yet. For the on-surface synthesis of 2D-COFs, the concentration and the ratio of the precursors must be tuned carefully and the composition on the surface is often unknown.[1] To overcome these hurdles, we applied a monomolecular approach, using a pyrene-based two-in-one imine COF precursor.[2,3] After drop casting of a solution of the precursor onto highly oriented pyrolytic graphite (HOPG), scanning tunnelling microscopy (STM) at the liquid/solid interface revealed a densely packed self-assembled molecular network at higher concentrations, while small COF patches formed at lower concentrations (see figure). The kinetics of the imine COF formation were probed using UV-vis spectroscopy which allowed the extraction of the reaction rates and the activation energy. Comparison of the on-surface synthesised COF nanopatches with the solvothermally synthesised bulk 2D-COF using UV-vis spectroscopy and grazing-incidence wide angle X-ray scattering (GiWAXS) provided further insights into the formation mechanism. Lower precursor concentrations lead to better crystallinity on surface, as shown by STM for monolayer nanopatches and by GiWAXS for bulk 2D COFs. Together these results imply that imine formation occurs rapidly in acidic medium and low concentrations favour the formation of ordered structures, both in solution and on surface.

References

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Figures

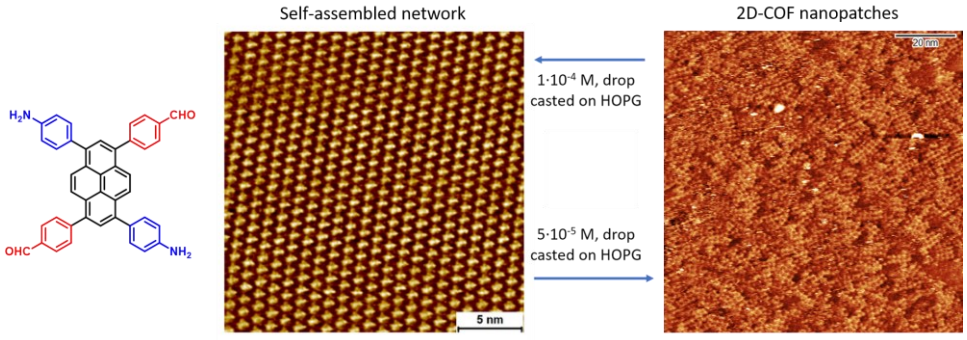

Figure 1: STM at the liquid/solid interface reveals the effect of the monomer concentration on the outcome of the on-surface synthesis of 2D-COFs: Higher concentrations lead to a densely packed SAMN, while lower concentrations favour the formation of 2D-COF nanopatches.