Bottom-up synthesis of crystalline 2-D polymers

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Scientists at the Center for Advancing Electronics Dresden (cfaed) at

TU Dresden have succeeded in synthesizing sheet-like 2-D polymers by a bottom-up process for the first time. A novel synthetic reaction route was developed for this purpose. The 2-D polymers consist of only a few single atomic layers and, due to their very special properties, are a promising material for use in electronic components and systems of a new generation. The research result is a collaborative work of several groups at TU Dresden and the Ulm University and was published this week in two related articles in the scientific journals *Nature Chemistry* and *Nature Communications*.

Ever since Hermann Staudinger discovered the linear polymers in 1920, it has been a dream of synthetic scientists to extend the polymerization into the second dimension. A two-dimensional (2-D) polymer is a sheet-like monomolecular macromolecule consisting of laterally connected repeat units with end groups along all edges. Given the enormous chemical and structural diversity of the building blocks (i.e., monomers), 2-D polymers hold great promise in the rational material design tailored for next-generation applications, such as membrane separation, electronics, optical devices, energy storage and conversion, etc. However, despite the tremendous developments in synthetic chemistry over the last century, the bottom-up synthesis of 2-D polymers with defined structures remains a formidable task.

Since 2014, a group of scientists from Technische Universität Dresden and Universität Ulm joined forces to pursue this intriguing yet challenging goal. The research team led by Prof. Dr. Xinliang Feng (TU Dresden) innovatively developed a novel synthetic route: using surfactant monolayer as a soft template to guide the supramolecular organization of monomers and the subsequent 2-D polymerization at an air-water interface. This synthetic methodology is now termed as surfactant-monolayer-assistant interfacial synthesis (SMAIS). By using the SMAIS method, Dr. Tao Zhang synthesized crystalline quasi-2-D polyaniline films with lateral size ~50 cm^2 and tunable thickness (2.6—30 nm).

The superior charge transport properties and chemiresistivity toward ammonia and volatile organic compounds render the quasi-2-D polyaniline films as promising electroactive materials for thin-film organic electronics. To further explore the potential of SMAIS, Mr. Kejun Liu, Dr. Tao Zhang, Dr. Zhikun Zheng and Dr. Renhao Dong achieved controlled synthesis of highly-crystalline few-layer 2-D polyimide and polyamide for the first time. The 2-D polymers have a thickness of only a few nanometers and can be readily transferred onto arbitrary substrates, opening up exciting opportunity for the integration of 2-D polymers into next-generation devices and systems.

Along with the pivotal developments on the synthesis front, the transmission electron microscopy group led by Prof. Dr. Ute Kaiser (Uni Ulm) provided another indispensable pillar of the joint research. Since the development of aberration correction, high-resolution TEM imaging has been a powerful technique in structural characterization down to the atomic scale. Yet, hydrogen-containing organic materials are extremely prone to structural disintegration under the electron beam, rendering HRTEM imaging of 2-D polymers a highly demanding mission. By utilizing the spherical-aberration-corrected HRTEM, Dr. Haoyuan Qi has successfully unraveled the micro-morphology, molecular structures, grain boundary and edge structures, of the synthetic 2-D polymers: an achievement which is rarely reported in literature.

The molecular structures and overall crystallinity have been further elucidated via synchrotron grazing-incidence X-ray scattering (cfaed Chair for Organic Devices, Prof. Dr. Stefan Mannsfeld, TU Dresden). The group of Prof. Dr. Thomas Heine (TU Dresden) provided density-functional tight-binding calculations which offers significant insights into the atomistic structures of the synthetic 2-D polymers.

More information: Tao Zhang et al. Engineering crystalline quasi-two-dimensional polyaniline thin film with enhanced electrical and

chemiresistive sensing performances, *Nature Communications* (2019). [DOI: 10.1038/s41467-019-11921-3](https://doi.org/10.1038/s41467-019-11921-3)

Kejun Liu et al. On-water surface synthesis of crystalline, few-layer two-dimensional polymers assisted by surfactant monolayers, *Nature Chemistry* (2019). [DOI: 10.1038/s41557-019-0327-5](https://doi.org/10.1038/s41557-019-0327-5)

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