Nanospectral Imaging of a Two-dimensional Polymer Monolayer with Tip-enhanced Raman Spectroscopy

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Two-dimensional polymers (2DPs) are covalently linked monomolecular networks with periodic bonding and repeat units that show in-plan, large-range order [1]. Compared to graphene, 2DPs are expected to offer better flexibility in composition, porosity, modifiability and other physicochemical properties, which should enable applications in optoelectronic devices, separation membranes, surface catalysis, and molecular sensing [2]. Although diverse strategies have emerged to synthesize and characterize 2DPs, an in-depth understanding of the structure of 2DPs has proven challenging. To achieve this, it would be particularly useful to record chemical “fingerprints” down to an individual monolayer with sub-nanometer thickness [3].

Tip-enhanced Raman spectroscopy (TERS) integrates scan probe microscopy (SPM) for nanoscale spatial resolution with Raman spectroscopy for chemical characterization, and can simultaneously provide topography and chemical fingerprints of such samples.

Here, we synthesized a new 2DP monolayers from rigid aromatic amine and aldehyde building blocks through dynamic imine chemistry at a water/air interface by the Langmuir–Blodgett method. Taking advantage of the high sensitivity and high spatial resolution of TERS, we investigated a single 2DPs sheet by using TERS to obtain further understanding of planar network information of 2DPs, such as the used end groups, newly formed covalent bonds, molecular orientations, and nano-defect domains.

[1] W. Dai, F. Shao, J. Szczerbiński, R. McCaffrey, R. Zenobi, Y. Jin, A. D. Schlüter, W. Zhang, *Angew. Chem. Int. Ed.* **2016**, *55*, 213-217.
[2] Boott CE, Nazemi A, Manners I. *Angew. Chem. Int. Ed.* **2015**, 54(47): 13876-13894.
[3] Colson JW, Dichtel WR. *Nat. Chem.* **2013**, 5(6): 453-465.