Conjugated polymers by ESD-STM: a pathway to understanding defects

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Conjugated polymers are promising materials for modern organic electronics, as they combine structural and electronic adaptability to deliver smart, efficient, low-cost and environmentally friendly devices [1,2]. Existing applications for these polymers include organic photovoltaics (OPVs), organic light-emitting diodes (OLEDS), organic field effect transistors (OFETs) and biochemical sensors [3,4]. The molecular-scale characterisation of conjugated polymers is, however, still unsatisfactory, as analytical techniques that can reliably provide high-resolution information on the structure and composition of polymers are scarce.

Here, we report an innovative approach to study conjugated polymers, namely the combination of ultrahigh vacuum (UHV) electrospray deposition (ESD) with low-temperature scanning tunnelling microscopy (LT-STM) [5]. UHV-ESD is used for intact deposition of thermally fragile macromolecules onto atomically flat and clean single-crystal surfaces under extremely controlled conditions. This allows for characterisation of the adsorbed macromolecules at the ultimate spatial resolution of UHV-STM, thereby shedding light on the fundamental properties of these materials, such as self-assembly, length distribution, polymer sequence and exact chemical structure, including the presence of defects.

The precise identification and analysis of polymerisation defects is of fundamental importance to the field of conjugated polymers, as structural modifications to the sequence of a polymer have been predicted to alter the charge-transport properties and overall assembly order of the material [6]. While these defects are mostly elusive to traditional characterisation techniques such as NMR, mass spectrometry and chromatography, ESD-STM gives unique insight into them. Understanding if and how a polymer includes defects will provide feedback to synthetic processes and, for the first time, allow reliable experimental-based structure-function relationships in materials to be established.

The current study utilises a simple yet fully representative model system for conjugated polymers based on the structure of widely used diketopyrrolopyrrole (DPP) donor/acceptor polymers, which has been synthesised, UHV-deposited by ESD on Au(111) and characterised by LT-STM. In particular, the polymer was synthesised by direct-arylation polymerisation (DArP), a recently developed approach that provides a greener alternative to standard polymerization techniques [2], but still suffers from reduced performance in optoelectronic devices. Unprecedented information about the presence of polymerisation and conformational defects has been revealed by STM, and the exact nature and frequencies of these defects have been ascertained. Accordingly, a new hypothesis for the formation of branching defects [6] has been proposed, and new insight into the relationship between branching defects and conduction properties of polymers has been attained.

[1] Pankow R.M. et al., *Polymer* **2020**, *207*, 122874.
[2] Pankow R.M. et al., Polym. Chem. **2020**, *11*, 630-640.
[3] Leclerc M. et al., *Polym. J.* **2020**, *52*, 13-20.
[4] Aldrich T.J.et al., Chem. Mater. **2019**, *31*, 11, 4313-4321.
[5] Warr D.A. et al., Sci. Adv. **2018**, *4*, 6, 9543.
[6] Aldrich T.J.et al., Macromol. **2018**, *51*, 22, 9140-9155.