

Organic mixed ionic–electronic conductors progress at pace



A synthesis method for large-scale conjugated polymers as well as studies under operational conditions show that research on organic mixed ionic–electronic conductors continues to progress.

Organic semiconductors have potential for a wide array of applications. One materials class, organic mixed ionic–electronic conductors (OMIECs)¹, has garnered considerable interest due to the controllable carrier properties by electrochemical gating. But the transport behaviours are complex, involving ion movements, electron (hole) movements and ionic–electronic couplings. Owing to this inherent complexity, a comprehensive understanding of the processes, particularly the transient processes under operational conditions, in OMIEC devices remains elusive. In addition, it remains challenging to synthesize one of the key material ingredients of OMIECs, π -conjugated polymers (hereafter CPs), free from structural defects at large scale.

Traditionally, a Suzuki–Miyaura polymerization process is favoured for the synthesis of CPs, but this approach involves high temperatures that often result in structural imperfections and complex protocols that lead to low batch-to-batch uniformity. In an [Article](#) in this issue of *Nature Materials*, Haigen Xiong and colleagues introduce a modified room-temperature Suzuki–Miyaura-type polymerization, which not only achieves high-quality, large-molecular-mass CPs without structural defects, but also high batch-to-batch uniformity and scalability (more than 100 g). This method, validated by synthesizing 24 different CPs and workable with a plethora of substrates with different electronic properties, has broad applicability. The resulting polymers exhibit improved performance in devices. In an accompanying [News & Views article](#), Mario Leclerc and Serge Beaupré point out that the main improvement of this method over traditional Suzuki–Miyaura polymerization is that it uses a toluene-only system instead of the usual biphasic polymerization reaction

to achieve defect-free CPs. This simplified process is also more convenient to enable industrial applications.

When polymers are made into devices, it is crucial to understand device characteristics under operational conditions. In another [Article](#), Ruiheng Wu and colleagues explore the internal strain and mesoscale dynamic properties of OMIECs by using operando X-ray photon correlation spectroscopy. They observe large structural changes, which are mostly reversible under electrochemical cycling. A more striking observation is the path-dependent and long-lived non-equilibrium dynamic polaronic states (a polaron is a quasiparticle resulting from the coupling of electrons or holes with ionic vibrations), implying a coordinated motion of solvation shells, ions and electrons in equilibrium. The insights provided in this work may help in the design of new materials and device functionalities through engineering the dynamic properties of OMIECs.

At the device level, an organic electrochemical transistor (OECT), that is, a transistor that uses electrochemical gating to modulate the bulk conductivity of an organic semiconductor channel², uses OMIECs as channel active layers, and the coupling between the ionic and electronic carrier species can result in distinctive operational performances compared with conventional transistors that only have electronic carriers. Notably, while the channel current of OECTs in steady-state operation is relatively well studied, and the product of the electronic mobility and volumetric capacitance, μC^* , has been recognized as a figure of merit, knowledge of OECT transient behaviours is still limited. For example, the switching speed for OMIECs with identical μC^* can be quite different³. A recent study⁴ reveals that the electrochemical doping speed of a polythiophene electrode can be limited by poor hole transport, leading to a much slower switching speed. This is in stark contrast to the commonly held view that the slow ionic movement is the primary origin of slow switching behaviour. In another [Article](#), Jiajie Guo and colleagues study the switching kinetics in operational OECTs and provide insights on the asymmetric switching speed between turn-on and turn-off by using operando optical

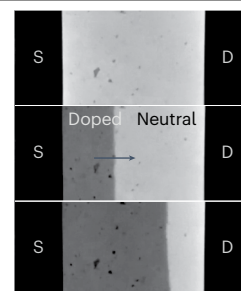


Fig. 1 | Turn-on kinetics of an OECT device visualized by operando optical microscopy. S, source; D, drain. Figure adapted with permission from the [Article](#) by Guo and colleagues, Springer Nature Ltd.

microscopy (Fig. 1). They uncover a two-stage turn-on process and a single-stage turn-off process. They identify factors that determine the rapid turn-off behaviour including fast dedoping kinetics of CPs, channel geometry and carrier-density-related mobility, and highlight ion transport as the limiting factor to device kinetics. In an accompanying [News & Views article](#), Hang Yu and Jenny Nelson comment that the use of operando optical microscopy enables the transient (de)doping processes to be visualized, showing its promise for wider application to many other electronic devices.

This recent progress in the field of OMIECs represents just a few examples of the rapid development of organic semiconductor research. Such development involves the rational design and synthesis of polymers with better performance by further understanding structure–function relationships; advances in in situ and operando measurements to improve the stability and lifetime of devices; and ability to be manufactured by various fabrication techniques to facilitate applications. The studies highlighted here also demonstrate the importance of interdisciplinary efforts in driving advances in technologies.

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