In-operando Spectroelectrochemistry Applied to Molecular Semiconductors: the Case of Odd [n]Cumulenes

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Abstract

Charge transfer processes can induce substantial modifications in the electronic structure of molecules, which can be understood by probing both electronic and vibrational transitions. This work focuses on doping phenomena in *sp*-carbon chains with cumulated double bonds (i.e. cumulenes). Together with their counterparts showing alternating single and triple carbon–carbon bonds (i.e. polyynes), *sp*-carbon atomic wires (CAWs) represent an exciting platform for future organic electronics. Indeed, their energy gap can be easily tuned by adjusting just two structural parameters: length and termination [1]. This has recently led to the demonstration of CAW-based electronic devices in the form of field-effect transistors [2] and electrochemical supercapacitors [3].

The multi-spectroscopic approach presented in this work aims to address two major shortcomings in CAW research: little is known about the structural modifications induced by the presence of free charge carriers in these materials. Studies that have attempted to address this issue have relied on chemical doping [4] or nanoparticle interactions during surface-enhanced Raman spectroscopy measurements [5] to achieve charge transfer. Both techniques do not allow the investigation of the intrinsic properties of charged molecules. By achieving doping in solution through an electrochemical setup, charged cumulenic CAWs are studied by means of Raman and UV–visible spectroscopy in a simpler environment, as isolated species in solution.

To validate this method, we present a study on phenyl-terminated cumulenes with three and five double bonds ([3]Ph and [5]Ph). Electronic absorption spectra clearly show a reduction in the energy of the lowest allowed transition for both p- and n-doping. Low-energy polaronic features can be ascribed to the phenyl termination based on measurements conducted on tetraphenylethylene, which acts as a purely sp^2 reference. Raman spectroscopy unveils a substantial stiffening of the collective vibration along the *sp*-carbon chain, possibly linked to a shift of the charge density toward the molecular backbone. This study opens new possibilities for the investigation of molecular semiconductors, shedding light on the deep link between the electronic and structural evolution of active materials under device-relevant conditions.

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References

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