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The role of Raman spectroscopy in the investigation of the π -conjugation properties of halogenated Carbon Atomic Wires

Carbon atomic wires in the form of polyynes are linear sp-hybridized carbon chains made of an alternation of single and triple bonds [1]. These systems possess a strong π -electron conjugation and outstanding optical, mechanical, and electrical properties that can be modified by changing the length of the chains and their termination groups [1]. In this framework, it is crucial to better understand the effect that the variations in the structures of these systems can have on the modification of their properties to develop in the next years polyynes-based tunable devices. To accomplish this, Raman spectroscopy is one of the most used characterization techniques since polyynes present a characteristic peak (i.e., Effective Conjugation Coordinate, ECC) from whose frequency it is possible to extrapolate important information on the electronic properties of these systems [2]. In this work, we studied a class of polyynes (Fig. 1a) with different halogen terminations (Cl, Br, and I) and with different lengths (2,3, and 4 C=C bonds) [3]. Combining DFT calculations and experimental FT-Raman spectroscopy, we compared the extent of the tuning given by an increase in the length of the sp-chain and by a variation in the halogen end group. Both increasing the length or the size of the halogen, we observed an increase in the π -conjugation of the chains but with different magnitudes: a strong modulation (coarse tuning) is observed in the first case while a smoother change (fine tuning) is present in the second case (Fig. 1b). Moreover, by comparing the spectra of powders and solutions, we investigated the aggregation state of halogenated polyynes identifying some important features in the normal modes ascribed to a passage from an “isolated molecule” configuration to a “crystal” configuration in which we recognize strong halogen bonding between adjacent molecules. In this work, Raman played a crucial role in determining how halogens can affect the tunability of polyynes, thus paving the way for the use of halopolyynes in future developments of materials with tunable properties.

References

- [1] Casari et al., MRS Commun., 8 (2018) 207-219
- [2] Milani et al., Beilstein J. Nanotechnol., 6 (2015) 480-491
- [3] Pigulski et al., Cryst. Growth Des., 19 (2019) 6542-6551

Figures

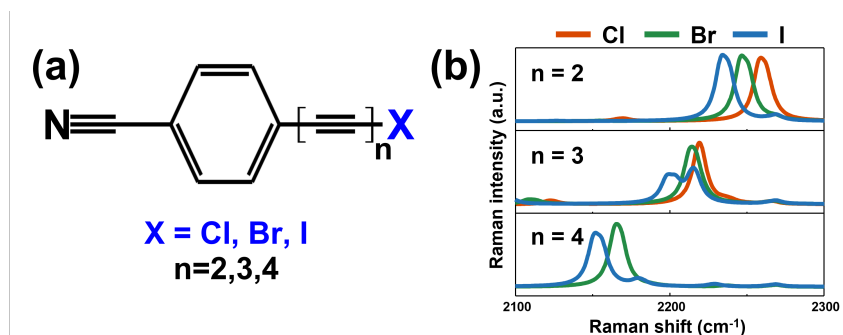


Fig 1: (a) Chemical structure of the halogenated polyynes characterized in this work. (b) Effect of the chain length and of the halogen termination on the modulation of the ECC peak frequency and of the electronic properties of halopolyynes.