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Truncated conjugation in fused heterocycle-based conducting polymers: when greater planarity does not enhance conjugation.

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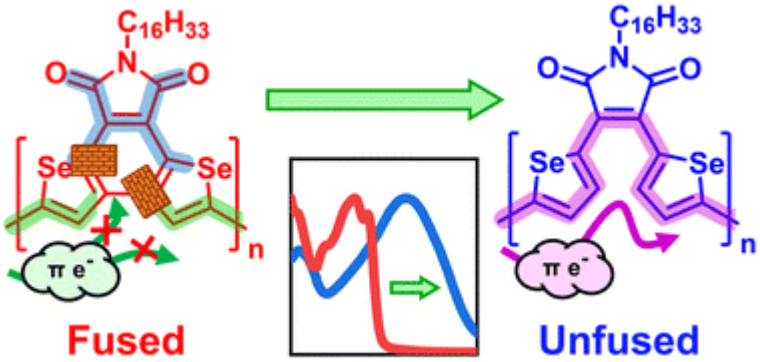
One of the main assumptions in the design of new conjugated polymer materials for their use in organic electronics is that a higher coplanarity leads to greater conjugation along the polymer backbone. Conventionally, a more planar monomer structure induces a larger backbone coplanarity, thus leading to a greater overlap of the carbon π-orbitals and therefore a higher degree of π-electron delocalisation. However, here we present a case that counters the validity of this assumption. Different diselenophene-based polymers were studied where one polymer possesses two selenophene rings fused together to create a more rigid, planar structure. The effects of this greater polymer coplanarity were examined using Raman spectroscopy and theoretical calculations. Raman showed a large difference between the vibrational modes of the fused and unfused polymers, indicating very different electronic structures. Resonance Raman spectroscopy confirmed the rigidity of the fused selenophene polymers and also revealed, by studying the excitation profiles of the different bands, the presence of two shorter, uncoupled conjugation pathways. Supported by Density Functional Theory (DFT) calculations, we have demonstrated that the reason for this lack of conjugation is a distortion of the selenophene rings due to the induced planarity, forming a new truncated conjugation pathway through the selenophene β-position and bypassing the beneficial α-position. This effect was studied using DFT in an ample range of derivatives with the substitution of the selenium atom with other heteroatoms whilst still maintaining the same unconventional conjugation-planarity relationship, confirming the generality of this phenomenon. This work establishes an important structure-property relationship for conjugated polymers that will help rational design of more efficient organic electronics materials.[1]



[1] **JM Marin-Beloqui,*** S. Gomez, H Gonev, M. Comí, M Al-Hashimi, TM Clarke*, *Chemical Science*, **2023**, *14*, 812-821.