Investigation of the Long Effective Conjugation Length in Defect-Free Insulated Molecular Wires

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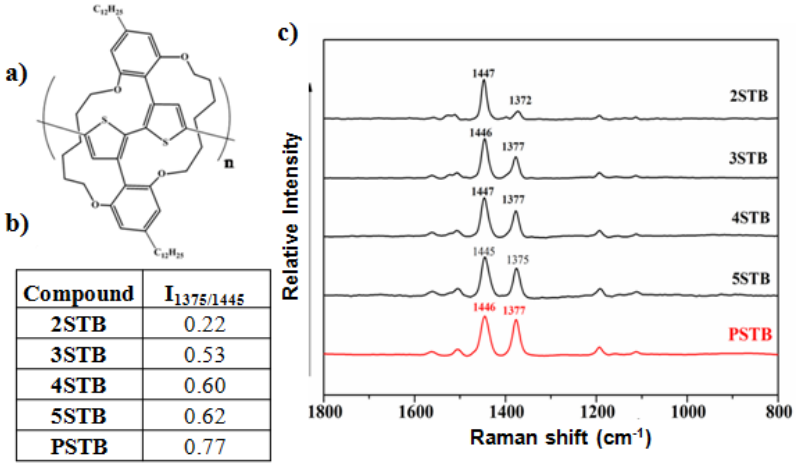
Due to the "insulation" of the π-conjugated backbones, insulated molecular wires (IMWs) are expected to be applied to various optoelectronic applications and nanotechnology.[1] Recently, Kazunori *et al* have succeeded in the synthesis of a self-threading polythiophene with a polyrotaxane-like 3D architecture (PSTB, see Figure 1), for which an intrawire hole mobility of 0.9 $cm^2\ V^{-1}\ s^{-1}$ has been measured.[2] Here, we aim to evaluate the extent of π-conjugation along polythiophene backbones sheathed within defect-free "insulating" layers. A comparison between the experimental Raman spectra of the self-threading oligomers (*i.e.* 2STB-5STB) and the corresponding PSTB polymer indicates that: (i) the ratio of relative intensities of the two most intense Raman bands ($I_{1375/1445}$) increases with the elongation of the size chain but does not saturate up to the pentamer, and (ii) π-conjugation spreads over 17–18 thiophene units in the polymer. Whether the effective conjugation length of the polymer is better described by using the long *oligomer* extrapolation *approach*[3] or periodic DFT calculations of the polymer is discussed in detailed by exploiting the very recent potentialities of state-of-the-art quantum chemical simulations of vibrational properties for crystalline solids.[4]



Compound	$I_{1375/1445}$
2STB	0.22
3STB	0.53
4STB	0.60
5STB	0.62
PSTB	0.77

Figure 1. a) Chemical structure of the insulated polythiophene PSTB, b) the ratio of relative intensities of the two most intense Raman bands ($I_{1375/1445}$) and c) experimental Raman spectra for oligomers 2STB-5STB and polymer PSTB.

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