Ab Initio Calculations on the Vibrational Behavior of Ladder Type Oligo(*p*-phenylenes)

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Summary: Ab initio calculations of the Raman spectra of ladder type oligo (*p*-phenylenes) (LOPP) were done in order to study the influence of the side chains attached on the methine bridge and the aromatic rings. We found that the aromatic CC stretching modes and the interring CC stretching modes are significantly influenced. Due to the attachment of an aromatic side chain on the methin bridge, an additional strong mode appears in the interring CC stretching region. Side chains on the aromatic rings cause a splitting of the aromatic CC stretching mode.

Introduction

Ladder type poly(*p*-phenylene)s (LPPP),[1, 2] and their oligomers, ladder type oligo(*p*-phenylene)s (LOPP)[3] are a class of conjugated materials with high potential for light emitting device applications.[4] The side chains attached to the conjugated backbone render them soluble in common organic solvents and allow the preparation of thin films for the use as active layers in light emitting devices by a spin-coating process.

In order to get a better understanding of the photophysics of these polymers, what is essential for a further improvement of their application in optoelectronics a more detailed characterisation is necessary. For these items Raman spectroscopy is known to be a powerful tool that allows one to study the structural and electronic properties of conjugated oligomers and polymers.

Although the Raman behavior of LPPP was reported in the past,[5-7] the spectra are not well understood so far. Kertesz et al.[5] calculated the vibrational spectrum of LPPP, but without taking the side chains into consideration. Therefore, the experimentally observed Raman spectrum of LPPP shows significant differences compared to the calculations. A strong splitting of the aromatic CC stretching modes and further strong modes located in the region of the interring CC stretching vibrations were reported by this group. Later on, C. Godon[7] reported on calculations due to the splitting of the

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aromatic modes, caused by the side chain R_6 (according to Figure 1, left). But, up to now, a simulation of the splitting of the aromatic CC stretching modes is still missing, as well as an explanation for the existence of further strong interring CC stretching modes, as observed in the experiment.[6, 8]

In order to clarify these open questions the present calculations focus on the influence of the side chains. Experimental investigations on the Raman behavior of LPPP and 5LOPP[8] show us a valuable matching of both spectra. This allows us, to focus our calculations on 5LOPP. The results will further help us to explain the spectrum of LPPP as well.[9]

Method and systematic of calculations

The calculations were performed with the quantum chemical software package Gaussian 98.[10] According to the large model molecules with more than 120 atoms, all the calculations here were done with a fast method based on restricted Hartree Fock (HF) theory and a split valence basis set (RHF 3-21G). The obtained frequencies were corrected by the factor 0.9, due to well known overestimation of the vibrational frequencies in HF theory. In order to evaluate and confirm the significance of the RHF 3-21G level we compared HF calculations on small oligomers without side chains with density functional calculations and a basis set including two sets of higher angular momentum polarising functions, the split valence 4-31G(d,p). Only small differences were observed.[9] Figure 1 shows the chemical structures of the experimentally investigated 5LOPP and the 5LOPP(m) model compound used for the calculations.

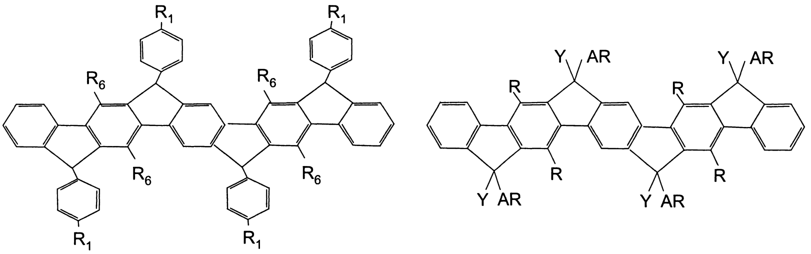

Figure 1. Chemical structures of 5LOPP (left) with R_6: C_6H_{13}; R_1: $C(CH_3)_3$, and 5LOPP(m) (right) occasionally with R = CH_3; AR = phenyl + CH_3, Y = H used for the calculation of the Raman frequencies.

Theoretical results

The calculated spectrum of the hydrogen saturated ladder oligomer (5LOPP without side chains, Figure 2a) is dominated by a few significant vibrations located at the oligomer backbone. The mode at 1599 cm^{-1} is an aromatic CC stretching, at 1540 cm^{-1} an aromatic CC stretching normal to the methine bridge, at 1289 cm^{-1} an interring CC stretching, and at 1238 cm^{-1} a mixing of interring CC stretching with CH bending. The broad peak between 900 cm^{-1} and 1000 cm^{-1} is the overtone of the silicon substrate the film was drop casted on.

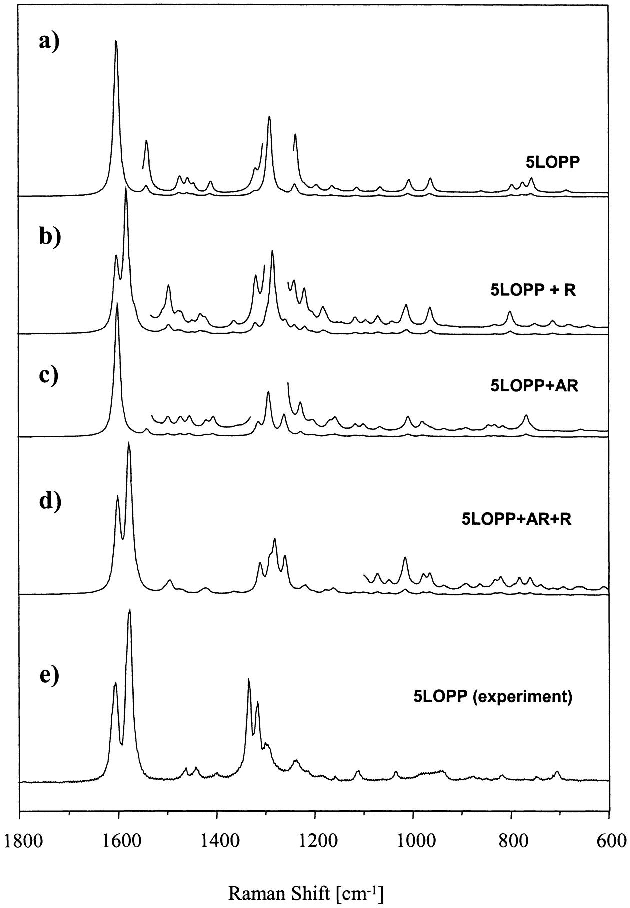

Figure 2. Raman spectra calculated in RHF 3-21G without side chains (a) and with side chains (b – d) due to Figure 1 - right. e): experimentally recorded Raman spectrum of 5LOPP (due to Figure 1 - left).

As one can clearly see from Figure 2b and Figure 2d, the influence of the side chain R yields to a double peak in the aromatic CC stretching region, as also observed in the experiment. The experimentally investigated oligomer has a hexyl (C_6H_{13}) group as a side chain on this position, but even CH_3 alone as used for the calculations, gives them their characteristic appearancy.

The AR side chains cause a strong new mode at 1260 cm^{-1} in 5LOPP + AR. With the help of normal coordinate analysis[9] we identified it as an intermix of a CH bending vibration at the methine bridge with the strong interring CC stretching mode and a further quite silent interring mode. This behavior of the interring modes give us an explanation for the existence of a further strong mode as experimentally observed in 5LOPP and LPPP. The additional influence of another substituent ($Y = C_4H_9$) has been investigated yielding to a further changed modes structure in the interring region, in good agreement to experimental results.[8]

Conclusion

Two significant features of the experimentally recorded Raman spectra of LPPP and 5LOPP can be explained on bases of these calculations. The interring modes are strongly effected by the side chain AR located at the methine bridge. This side chains are due to an additional strong interring mode. The splitting of the aromatic CC stretching modes is caused by the side chain R and is due to the altered energetic situations on neighbored aromatic rings.

Acknowledgements

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