Abstract of diploma thesis

«Intra- and intermolecular vibrational structure of organic semiconducting crystals»

Semiconducting crystals of π-conjugated oligomers are perspective materials for organic optoelectronics combining high luminescent properties and effective charge transport. The charge carrier mobilities in such crystals depends on thermal molecular vibrations and high-frequency intramolecular vibrations. The influence of these vibrations on the charge carrier transfer is still commonly understood and requires studies. Raman spectroscopy is a powerful technic to control vibrations in such π-conjugate systems.

In this paper, low- and high-frequency Raman spectra of two series of conjugated oligomers were measured and analyzed: thiophene-phenylene conjugated oligomers with the same core and different terminal substituents (TPCOs) and fluorinated tetracyanoquinodimethane (Fn-TCNQ) with different amounts of fluorine on the phenyl ring. Such modifications strongly affect the structure and rigidity of the molecule and the crystal lattice and consequently, vibrational spectra.

The influence of the molecular structure on high-frequency Raman spectra was studied. It was shown that this method allows observe experimentally the distribution of the electron density in a molecule as a function of substituents. The distribution of the electron density changes the equilibrium geometry of the molecule and increases the energy of several high-frequency vibrations (frequency shifts up to 20 cm^{-1} in TPCOs) compared to the unsubstituted molecule. The influence of the mass of substituents on high-frequency Raman spectra was also revealed. Heavy substituents fix carbon atoms, hence changing the rigidity of the molecule and strongly affecting the vibrational frequency (shift exceeds 60 cm^{-1} in F_n-TCNQ).

The influence of the molecule and crystal structure on low-frequency Raman spectra was studied depending on the substituents and temperature. It was found that in crystals with low mobilities the vibrational frequencies, supposedly limiting the charge transport, are 2-4 times lower than in crystals with high mobilities. It is shown that the low-frequency lattice vibrations mostly have a mixed nature, that is, they do not separate into intramolecular and intermolecular vibrations, and also strongly depend on to temperature. The vibrational frequencies linearly decrease with increasing temperature (from -190 ^{0}C to +100 ^{0}C several frequencies shift up to 20 cm^{-1} in TPCOs and F_n-TCNQ), which is a consequence of strong intermolecular interactions.

This research can shed light on determination of a role of thermal molecular and high-frequency intramolecular vibrations in charge carriers transport.

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