Unidirectional coherent energy transport via conjugated oligo(p-phenylene) chains

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Abstract: We used relaxation-assisted two-dimensional spectroscopy (RA 2DIR) to interrogate the energy transport within oligo(p-phenylene) chains and discovered a way to funnel high-frequency vibrational quanta rapidly (8.6 km/s) and unidirectionally over large distances. The study opens avenues for developing materials with controllable energy transport properties, and devices photonic or electrical properties.

Short summary of goals, methods, and findings:

A ballistic transport regime is required to have high efficiency and directionality of energy transport in molecular chains. Oligomeric backbones offer an attractive medium for fast transport, as the covalent interactions within chains are among the strongest chemical interactions, capable of supporting very high ballistic transport speed and efficiency. We used dual-frequency relaxation-assisted two-dimensional infrared (RA 2DIR) spectroscopy to interrogate the energy transport in compounds featuring oligo(p-phenylene) chains of various length (1-3), forming a molecular wire terminated with carboxylic acid and nitro end groups. We discovered a very efficient transport initiation (~60% by energy) and efficient through-chain transport with a speed reaching 86 Å/ps.

We computed chain bands for a oligo(p-phenylene) chains and identified the bands contributing to the energy transport initiated by C=O and NO_2 stretching modes by computing relaxation pathways for them. Multiple chain bands were found to contribute to the transport, supporting wide range of transport speeds.

The advantage that oligo(p-phenylene) chains have over other previously studied chains (e.g. alkanes) is the presence of conjugation. The conjugation provides strong site-to-site coupling within the chain and strong end-group to chain coupling, thus displaying bands that have the ability to support high speeds. This leads to an exciting prospect in developing devices involving both electron and energy transports. Modification of the chain properties could also control the transport speed and efficiency as the extent of electronic conjugation is found to play a key role in the transport speed and efficiency. For example, one could dope the chain to form a quinoid structure which displays a greater extent of conjugation. Such chains may display even greater speed and transport efficiency, opening avenues to the development of devices such as molecular junctions, to macroscopic devices with the ability to control them with external stimuli.

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