

Supporting Information

Low-Temperature Heat Capacity Anomalies in Ordered and Disordered Phases of Normal and Deuterated Thiophene

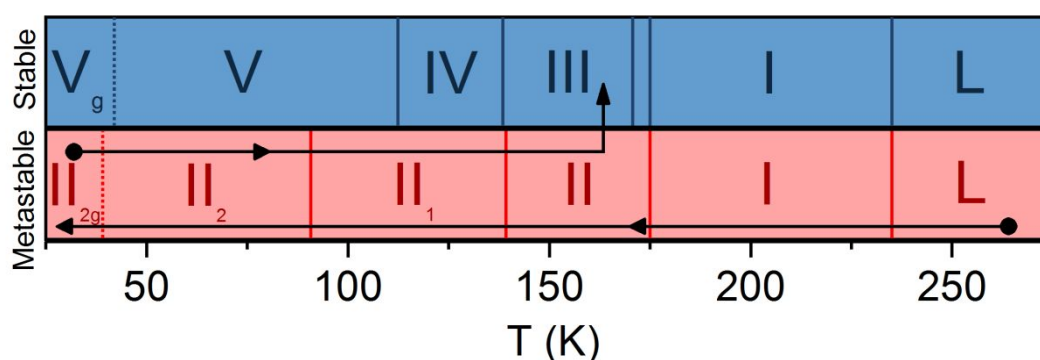
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Scheme 1. Stable and metastable phase transitions of normal and deuterated thiophene. Metastable sequence (red) on cooling: $L \rightarrow I \rightarrow II \rightarrow II_1 \rightarrow II_2 \rightarrow II_g$. On heating: $II_g \rightarrow II_2 \rightarrow II_1 \rightarrow II \rightarrow I \rightarrow L$. Annealing phase II at ca. 160 K results in the formation of the stable phase III, and consequently to the Stable sequence (blue). Phase V_g is the glass

state of the disordered phase V for normal thiophene, while deuterated thiophene only displays an ordered phase V.

ab initio molecular dynamics simulations based on density functional theory

We performed density functional theory (DFT) calculations based on the PBEsol functional¹ with the VASP software². Long-ranged dispersion interactions in the system were captured with Grimme's DFT-D3 method³. Wave functions were represented in a plane-wave basis truncated at 650 eV and a Monkhorst-Pack k-point grid of 4x6x4 was employed for integrations within the Brillouin zone. Geometry relaxations were performed for optimizing the lattice vectors of bulk C₄D₄S (ordered phase V) at zero temperature. To estimate the harmonic density of vibrational states, $g(\omega)$, we employed the small-displacement method⁴ and a 2x2x2 supercell containing 576 atoms. To estimate $g(\omega)$ by fully taking into account the anharmonicity of the system, we calculated the Fourier transform of the velocity-velocity autocorrelation function⁵ obtained from a long *ab initio* molecular dynamics (AIMD) run (~100 ps) performed at a fixed temperature of 100 K and the equilibrium volume. The supercell employed in the AIMD simulations contained 576 atoms.

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