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## MS34-P02

### An isosymmetric supercritical-like transition in an organic semiconductor

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We show that a high mobility thiophene-based organic semiconductor, **BHH-BTBT**, has an exceptionally large negative non-linear thermal expansion ( $-216 < \alpha_2 < -333 \text{ MK}^{-1}$ ) between 95 and 295K along the crystallographic *b*-axis, being compensated by an even larger positive expansion in the perpendicular direction ( $287 < \alpha_1 < 634 \text{ MK}^{-1}$ ) [1]. The temperature evolution of the angle between neighbouring thiophene moieties and the optical band gap show a clear transition around 210 K but no space group change is detected, *i.e.* the transition is isosymmetric. A complete theoretical characterization of **BHH-BTBT** using *ab initio* molecular dynamics shows that below  $\sim 200 \text{ K}$  two different domains exist of which one is dominant but which dynamically coexist around and above 210 K. This transition is reminiscent to the ‘diffuse’ or ‘crossover’ phase transition analyzed theoretically by Christy [2] that leads to solid-state supercritical behaviour. The origin of the extreme negative and positive thermal expansion is related to a steric hindrance between adjacent tilted thiophene units and strongly enhanced by attractive S $\cdots$ S and S $\cdots$ C interactions within the highly anharmonic dynamic mixed-domain phase.

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