MS13 Structural Characterization of Functional Materials

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Negative thermal expansion and organic semiconductors
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Abstract
Negative thermal expansion is usually considered to be an extremely rare phenomenon, but this is mainly due to the fact that structure determinations as a function of temperature are not done systematically, and whenever structural data are available at different temperatures negative thermal expansion is not always recognized as such. We show here that approximately 35% of the organic structures in the Cambridge Structural Database for which structural data at different temperatures exist display negative thermal expansion along at least one of the orthogonal axes. About one hundred structures have been identified which could present negative volumetric expansion.
We give a detailed description of colossal uniaxial negative thermal expansion in a dense organic benzothieno-benzothiophene compound which shows high mobility values of up to 0.17 $cm^2V^{-1}s^{-1}$ under an inert atmosphere, but also in air. We show that the uniaxial negative thermal expansion persists beyond a supercritical-like first-order phase transition. The origin of the extreme negative and positive thermal expansion is due to a steric hindrance between adjacent tilted thiophene units and strongly enhanced by attractive S-S and S-C interactions within the highly anharmonic mixed-domain phase. This material could trigger the tailoring of optoelectronic devices highly sensitive to strain and temperature.