Giant thermal expansion of a two-dimensional supramolecular network triggered by alkyl chain motion

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Thermal expansion, the response in shape, area or volume of a solid with heat, is usually large in molecular materials compared to their inorganic counterparts. Resulting from the intrinsic molecule flexibility, conformational changes or variable intermolecular interactions, the exact interplay between these mechanisms is however poorly understood down to the molecular level. Here, we investigate the structural variations of a two-dimensional supramolecular network on Au(111) consisting of shape persistent polyphenylene molecules equipped with peripheral dodecyl chains. By comparing high-resolution scanning probe microscopy and molecular dynamics simulations obtained at 5 and 300, we determine the thermal expansion coefficient of the assembly of 980 ś 110 Œ 10−6−1, twice larger than other molecular systems hitherto reported in the literature, and two orders of magnitude larger than conventional materials. This giant positive expansion originates from the increased mobility of the dodecyl chains with temperature that determine the intermolecular interactions and the network spacing.
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