

Negative and Positive Anisotropic Thermal Expansion in 2D Fullerene Networks

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We find a design principle for tailoring thermal expansion properties in nearly spherical molecular networks. Using 2D fullerene networks as a representative system, we realize positive thermal expansion along intermolecular [2 + 2] cycloaddition bonds and negative thermal expansion along intermolecular C-C single bonds by varying the structural frameworks of molecules. The microscopic mechanism originates from a combination of the framework's geometric flexibility and its transverse vibrational characteristics. Based on this insight, we find molecular networks beyond C_{60} with tunable thermal expansion. These findings shed light on the fundamental mechanisms governing thermal expansion in molecular networks towards rational materials design.

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Thermal expansion is a fundamental property of materials that indicates increases in length, area, or volume upon heating, which is important in applications such as construction [1], seismographs [2], and aerospace design [3,4]. Positive thermal expansion occurs as a result of an anharmonic potential energy surface, where interatomic distance increases with increasing temperature [5,6]. Counterintuitively, some materials exhibit negative thermal expansion, where increasing temperature leads to a contraction along certain crystallographic directions [7–15]. Such behaviors are attributed to flexible crystalline networks [16,17], rigid unit modes [18–21], and transverse displacements of bridging atoms [22,23] or membranes [24,25]. However, a general design principle for developing materials with negative thermal expansion is still lacking.

Recent synthesis of monolayer C_{60} networks [26] provides new avenues for designing materials with tunable thermal expansion. These networks exhibit diverse crystalline frameworks [26–34] with nearly spherical, stable units [35,36] beyond rigid unit modes, as well as various intermolecular bridge bonds [37] with tunable transverse displacements. Compared to thermal expansion in C_{60} molecules and solids [38–41], the thermal behavior of C_{60} monolayers has yet to be understood. In 2D form, the

rotational degree of freedom of C_{60} leads to different types of intermolecular bonds in varied crystalline networks [Fig. 1(a)]. In this context, it would be insightful to study

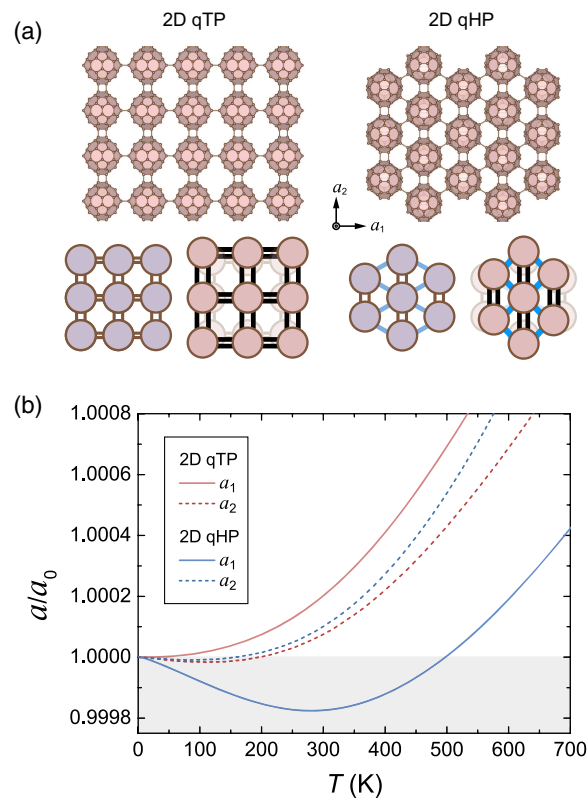


FIG. 1. (a) Crystal structures and (b) thermal expansion of monolayer qTP and qHP C_{60} networks. The schematics in (a) show the structural changes with increased temperature.

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whether thermal expansion in molecular networks can be controlled by intermolecular bridge bonds.

Here we show that intermolecular bonds govern thermal expansion behaviors in fullerene networks. Interfullerene $[2 + 2]$ cycloaddition bonds yield positive thermal expansion, whereas thermal contraction is found along single bonds. We identify the microscopic mechanism by analyzing the geometric flexibility of these bridge bonds. Remarkably, we find that the low-frequency transverse vibrations along the single bonds favor thermal contraction, in contrast to the transverse vibrations associated with the $[2 + 2]$ cycloaddition bonds. Based on this understanding, we rationally design molecular networks beyond C_{60} with tailored thermal expansion.

Thermal expansion is simulated under the quasiharmonic approximation [42,43] with volume-dependent phonons computed from density functional perturbation theory [44,45] using VASP [46,47]. The Gibbs free energy is obtained by finding the unique minimum value of the Helmholtz free energy [48–50] with varied lattice constants a and b at a strain step of 0.2% [28,51].

Figure 1(a) shows the crystal structures of two distinct networks of C_{60} monolayers, namely, the quasitetragonal phase (qTP) and quasihexagonal phase (qHP). For the qTP, each carbon cage is connected by vertical and horizontal $[2 + 2]$ cycloaddition bonds along the a_1 and a_2 directions, respectively. Such bonds are expected to expand rigidly along their axis upon heating. In the qHP, only the buckyballs along a_2 are linked by the $[2 + 2]$ cycloaddition bonds, while C-C single bonds link the neighboring cages along a_1 . Figure 1(b) shows the thermal expansion of the two phases. While the qTP along both directions has positive thermal expansion, negative thermal expansion along a_1 is found for the qHP up to 500 K, in contrast to the positive thermal expansion along a_2 (here we neglect the tiny negative thermal expansion along a_2 which might come from the soft vibrational modes of the isolated molecule with ellipsoidal deformation that keeps the surface area constant [40,41]).

To understand the thermal expansion behaviors, we study the geometric flexibility of the two phases. Figure 2 shows the variations of structural parameters for qTP and qHP monolayer networks at varied strains along a_1 and a_2 . These structural parameters measure the geometric flexibility of both intermolecular bonds ($L_{1,2}$) and individual molecules ($W_{1,2}$) along a_1 and a_2 , as shown in Figs. 2(a) and 2(c) for the qTP and qHP, respectively.

For the qTP, both the intermolecular bond L_1 and the molecular width W_1 expand rigidly upon uniaxial strains along a_1 . However, ΔL_1 and ΔW_1 remain nearly unchanged for strains along the other direction a_2 , as shown by the color map in Fig. 2(b). The same conclusion also holds for L_2 and W_2 .

For the qHP, the intermolecular $[2 + 2]$ cycloaddition bonds L_2 and molecular width W_2 also expand rigidly for

parallel strains along a_2 , while resisting deformations for perpendicular strains along a_1 , as shown in Fig. 2(d), exhibiting behaviors similar to the $[2 + 2]$ cycloaddition bonds in the qTP. However, the intermolecular single bonds L_1 and molecular width W_1 in the qHP respond differently to the strains. As shown by the ΔL_1 color map in Fig. 2(d), the L_1 in the qHP C_{60} becomes shorter with increased strain along a_2 . This notable contraction along L_1 with increasing a_2 indicates that the single bonds deform more readily, with compression specifically along a_1 being favorable for positive strains along a_2 . This hingelike motion is expected in the single bonds as they are less resistant to perpendicular strains. On the other hand, the W_1 in qHP C_{60} expands upon strains along a_2 . Therefore, we can attribute negative thermal expansion in the qHP to the geometric flexibility of the intermolecular single bonds instead of the molecules themselves.

The overall behavior demonstrates general features for different types of intermolecular bonds. The $[2 + 2]$ cycloaddition bonds expand rigidly when strain is applied parallel to their direction while resisting deformations against perpendicular strains. Therefore, qTP C_{60} networks exhibit nearly isotropic positive thermal expansion. On the other hand, the single bonds allow for hingelike compression when applying perpendicular strains. Unlike the qTP, the flexible single bonds in the qHP contract like hinges along a_1 when the rigid $[2 + 2]$ cycloaddition bonds along a_2 expand upon heating. Our findings demonstrate a distinctive interplay between flexibility-driven lattice contraction via C-C single bonds and rigidity-induced structural expansion through $[2 + 2]$ cycloaddition bonds. This drives a strong anisotropic thermal response in qHP C_{60} , as summarized by the schematics in Fig. 1(a).

To further explore the microscopic mechanism of negative and positive anisotropic thermal expansion in qHP fullerene networks, we examine their vibrational modes. At 300 K, only phonons below 0.6 (4.3) THz have an occupation number above 10 (1) according to the Bose-Einstein distribution. Thus, we focus on low-frequency phonons hereafter. Figure 3 shows the phonon dispersion curves and the corresponding mode Grüneisen parameters γ . The phonon dispersion along $Y - \Gamma$ corresponds to the vibrations associated with the intermolecular $[2 + 2]$ cycloaddition bonds along a_2 . The mode Grüneisen parameters of these vibrations are either positive or near zero, leading to thermal expansion. In contrast, the transverse displacements associated with the intermolecular single bonds have large negative γ along $\Gamma - X$. There are two transverse phonon branches with the largest negative γ : an out-of-plane acoustic (ZA) mode with the coherent movement of all molecules along z , and an out-of-plane optical (ZO) mode with alternating displacements between neighboring molecules, as illustrated by the schematics in Fig. 3. Both modes with large negative γ favor lattice contraction. In comparison, the longitudinal acoustic (LA) mode has

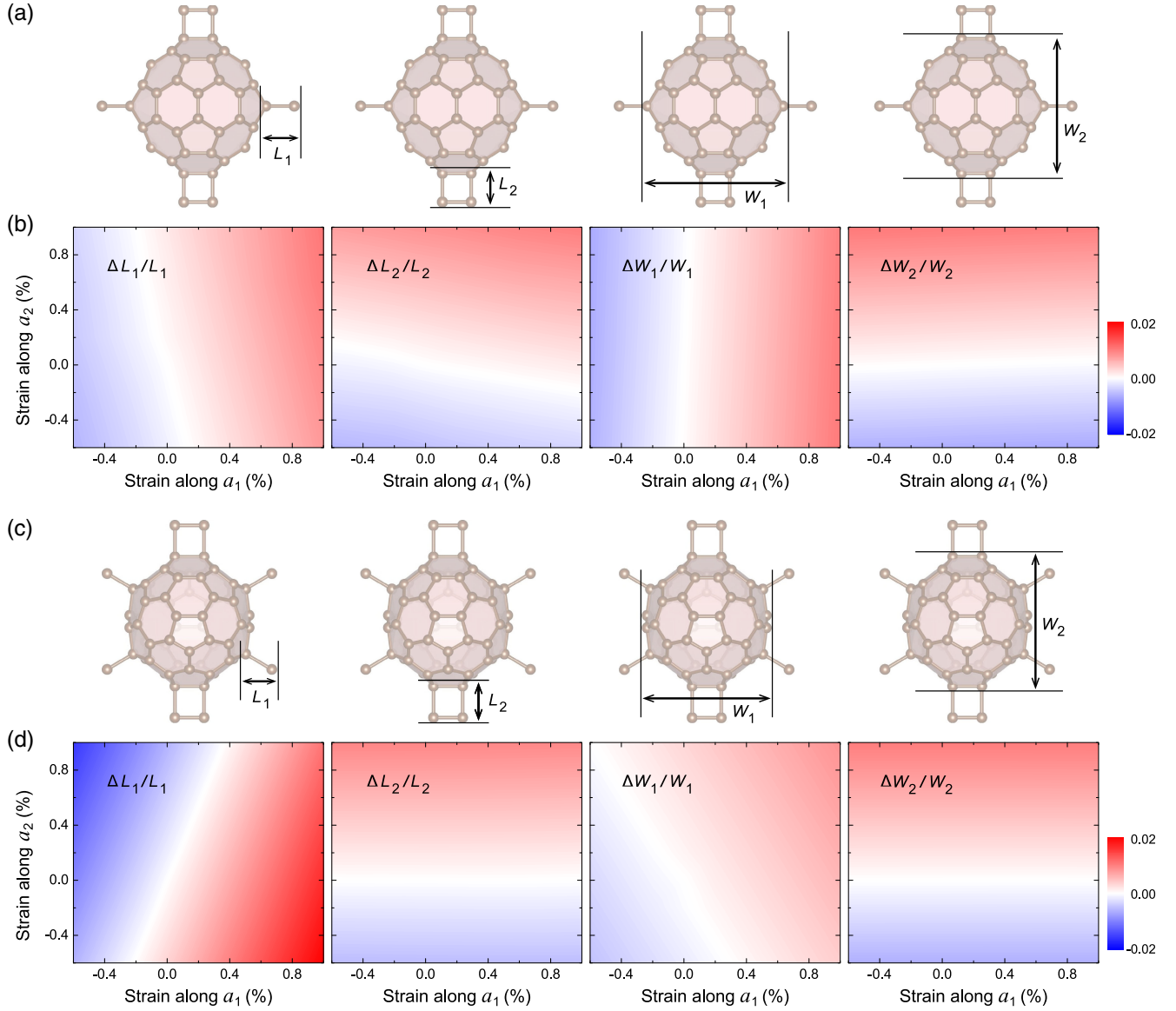


FIG. 2. (a) Structural parameters of monolayer qTP fullerene networks and (b) their variations under strains. (c) Structural parameters of monolayer qHP fullerene networks and (d) their variations under strains.

positive γ , which contributes to lattice expansion instead but less strongly ($\gamma < 1.5$) than the ZA and ZO modes ($|\gamma| > 2.5$). The overall picture confirms that transverse displacements of the single bonds yield thermal contraction, while the $[2+2]$ cycloaddition bond oscillations contribute to expansion behaviors.

The rigidity of the $[2+2]$ cycloaddition bonds, as well as the flexibility of the C-C single bonds, provide a universal design principle to tailor thermal expansion behaviors. The $[2+2]$ cycloaddition bonds between molecular cages impose structural, elastic, and vibrational constraints that only allow positive thermal expansion. Contrastingly, the flexible single bonds bridging the molecules allow for lattice contraction when perpendicular strains are applied, and the vibrational modes associated

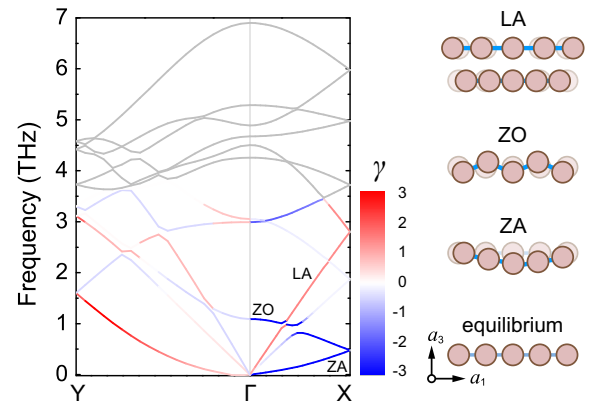


FIG. 3. Low-frequency phonons, mode Grüneisen parameters, and vibrational modes along $\Gamma-X$.

with these single bonds yield strong transverse displacements that favor thermal contraction. The flexibility of the single bonds is therefore the main driving factor in negative thermal expansion. Similar thermal behaviors in fullerene-based networks have also been found in previous molecular dynamics simulations [52]. Intuitively, we can either realize positive thermal expansion through intermolecular [2 + 2] cycloaddition bonds to resist lattice contraction, or utilize less rigid intermolecular single bonds to yield negative thermal expansion.

The discovery that C-C single and [2 + 2] cycloaddition bonds contribute distinctively to thermal behavior provides a predictive tool for the rational design of thermally responsive materials with nearly spherical building blocks such as icosahedral B₁₂ units [53–55], fullerene cages [56,57], and all-metal clusters [58] (for thermal expansion of 2D icosahedral B₁₂ networks, see Fig. 5 in the End Matter). As a proof-of-principle study, we extend this design principle to monolayer qHP C₂₄ networks, where the C₂₄ molecules are linked through similar single bonds along a_1 but three intermolecular bonds between six carbon atoms along a_2 [59]. The crystal structure of qHP C₂₄ is shown in Fig. 4(a). Unlike the nearly planar single bonds in qHP C₆₀, the single bonds in C₂₄ monolayers have a buckled structure owing to a larger molecular curvature and asymmetric intermolecular bonding positions. This, in combination with the smaller molecular size, leads to a

higher density of interfullerene bonds and larger elastic constants than qHP C₆₀ [59]. It is therefore expected that the single bonds in C₂₄ are more rigid than those in qHP C₆₀, leading to stronger resistance to perpendicular deformations. Figure 4(b) shows smaller negative thermal expansion in C₂₄ compared to C₆₀ along a_1 as expected. Additionally, the positive thermal expansion along a_2 in C₂₄ is also larger than that in C₆₀. This is unsurprising since the three intermolecular bonds along a_2 in C₂₄ are much more rigid than the [2 + 2] cycloaddition bonds in monolayer qHP C₆₀ networks.

The recent experimental realization of monolayer fullerene networks [26] offers a timely opportunity to directly test our predictions, which influence numerous fullerene-based applications such as device integration in photo-detectors [60] and catalytic activity in photocatalysis [27,29,30,61]. The temperature-dependent structural properties can be measured using high-resolution capacitance dilatometers [38] and synchrotron x-ray diffraction [39]. The low-frequency phonon modes can be detected by Raman and infrared spectroscopy [41], enabling verification of the predicted transverse vibrational mechanisms. From an application perspective, molecular networks with tunable thermal expansion present compelling possibilities. Materials with designed negative or near-zero thermal expansion are in high demand in flexible electronics [2], aerospace composites [3], and precision instrumentation [62], where thermal mismatch must be minimized. Our results indicate that such properties can be achieved not through complex multiphase composites, but through intrinsic molecular architecture. Previous experimental data on thermal expansion in molecular networks [7,10,12,16,17,63–66] including polymeric fullerene [38,67] confirm the fact that thermal expansion in molecular crystals can be controlled by bonding motifs and crystalline geometries, and similar mechanisms have been observed experimentally such as flexibility-driven “hinge-like” motion in crystalline networks [7,10,16,17] and transverse displacements of bridging atoms [22,23] or membranes [24,25]. This, again, supports the broader generalizability of our proposed mechanism.

In summary, we establish a general method for engineering thermal expansion in cage-like molecular networks through different intermolecular bonds. Using fullerene as a representative system, we show that intermolecular [2 + 2] cycloaddition bonds result in positive thermal expansion, whereas C-C single bonds lead to negative thermal expansion. By varying the structural frameworks of fullerene molecules, we can design a nearly square lattice with positive thermal expansion through [2 + 2] cycloaddition bonds along both in-plane directions. Similarly, we can also realize negative and positive anisotropic thermal expansion in a nearly triangular lattice through single bonds along one direction and [2 + 2] cycloaddition bonds along the other direction. The origin is related to both

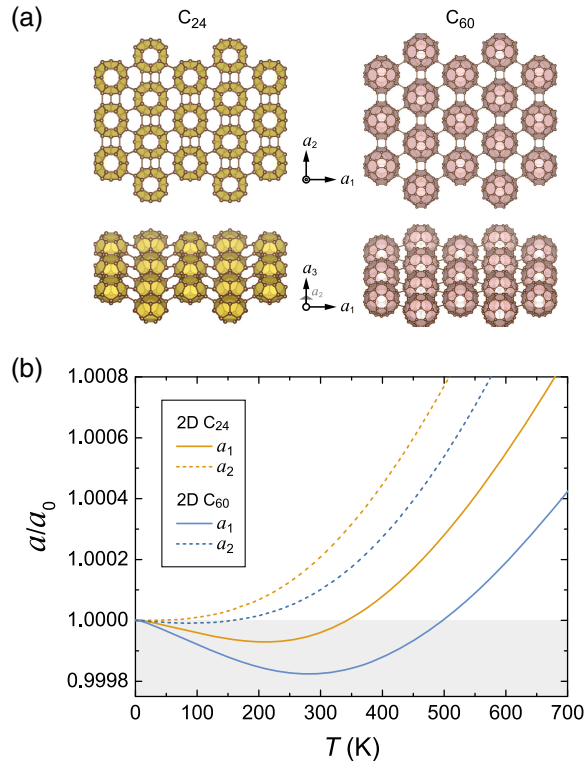


FIG. 4. (a) Crystal structures and (b) thermal expansion of 2D qHP monolayer C₂₄ and C₆₀ networks.

the geometric flexibility of different intermolecular bonds and their corresponding transverse vibrations. By identifying and uncovering this microscopic mechanism, we can further design molecular networks with tailored thermal expansion.

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Data availability—The data that support the findings of this article are openly available [70], embargo periods may apply.

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End Matter

Thermal expansion of 2D icosahedral B_{12} networks— To demonstrate the wide applicability of our design principle beyond carbon-based materials, we provide another example based on the icosahedral B_{12} units in

Fig. 5(a), as these clusters form the most stable allotropes of boron including the α and β phases [71]. We explicitly compute thermal expansion of monolayer qHP B_{12} networks and find the same trend in Fig. 5(b).

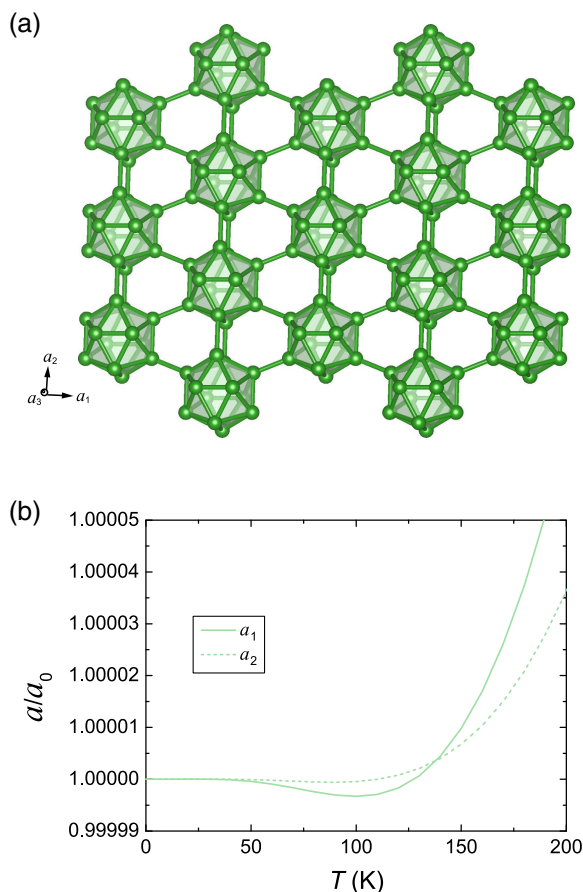


FIG. 5. (a) Slightly rotated top view of the crystal structures (to show the double intercluster bonds) and (b) thermal expansion of monolayer icosahedral B_{12} networks.