Ambient-Stable Polymeric Nitrogen Achieved through Multi-Stage Computational Design

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The four-decade quest for synthesizing ambient-stable polymeric nitrogen, a promising high-energy-density material, remains an unsolved challenge in materials science. We develop a multi-stage computational strategy employing density functional tight-binding-based rapid screening combined with density functional theory refinement and global structure searching, effectively bridging computational efficiency with quantum accuracy. This integrated approach identifies four novel polymeric nitrogen phases ($Fddd$, $P3221$, $I\bar{4}m2$, and $P6522$) that are thermodynamically stable at ambient pressure. Remarkably, the helical $P6522$ configuration demonstrates exceptional thermal resilience up to 1500 K, representing a predicted polymeric nitrogen structure that maintains stability under both atmospheric pressure and high-temperature extremes. Our methodology establishes a paradigm-shifting framework for the accelerated discovery of metastable energetic materials, resolving critical bottlenecks in theoretical predictions while providing experimentally actionable targets for polymeric nitrogen synthesis.

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1. Introduction. The exploration of polymeric nitrogen began in the 1990s, and as the research progressed, scientists gradually recognized their potential as high-energy-density materials (HEDMs) because of the energy difference between the N−N single bond and N≡N triple bond. Consequently, the design and synthesis of polymeric nitrogen under various conditions have emerged as a critical field of solid-state physics and materials science. In 1985, McMahan and LeSar predicted[1] that nitrogen atoms would be connected by a single covalent bond to form a solid polymer, that is, polymerized nitrogen, under ultra-high pressure and high-temperature conditions. This prediction was confirmed in 2004 with the successful synthesis of cubic gauche nitrogen (cg-N),[2] the first single-bonded nitrogen polymer network. The successful synthesis of cg-N has stimulated extensive theoretical exploration of various other phases of polymeric nitrogen, including the layered $Pba2$ phase,[3] cage-like diamondoid nitrogen,[4] and so on. Up to now, in addition to cg-N, four other polymeric nitrogen phases have been experimentally observed: LP-N,[5] HLP-N,[6] BP-N,[7,8] and PLP-N.[9] These phases cover a wide pressure-temperature range of 110–244 GPa and 2000–4000 K, but none have yet been successfully quenched to ambient conditions, which limits their application as HEDMs.

Many efforts have been made to identify polymeric nitrogen that remains stable at lower pressures. For example, Zhang *et al.* reported the successful synthesis of cyclo-N_5^- in the $(N_5)_6(H_3O)_3(NH_4)_4Cl$ salt,[10] which is stable below 117 °C. However, it is generally difficult to obtain stable polynitrogen clusters or their ions through conventional chemical methods. In contrast, introducing heteroatoms during synthesis to form a nitrogen-rich system for further stabilizing polynitrogen units has been proven to be a successful strategy. Currently, the introduced heteroatoms can be mainly categorized into metallic and nonmetallic types. The introduction of heteroatoms significantly reduces the pressure required for stability.[11–14] So far, some metal nitrogen-rich compounds have been successfully quenched at ambient pressure.[15] However, the introduction of heteroatoms results in a reduction of energy density, making all-nitrogen polymeric structures still the ideal and most promising candidates for HEDMs.[16] At ambient pressure, a high-efficiency synthesis of cg-N has been achieved by thermally treating KN_3 powders.[17–19] However, the yield of cg-N obtained by this method remains very low,[20] highlighting the continued need to explore methods for achieving stable all-nitrogen polymeric structures under low-pressure conditions.

To overcome the current challenges between achieving low-pressure stability and maintaining high energy density, our study proposes an effective strategy: combining the density functional tight-binding (DFTB) method[21] with the CALYPSO software package[22,23] (CALYPSO/DFTB approach) to perform potential energy surface searches. This approach aims to identify metastable structures that exhibit sufficient stability under ambient conditions and that can release significant amounts of energy upon decomposition to the ground state [see Fig. S1 in the Supplementary Materials (SM)]. The CALYPSO software package has been highly successful in predicting the crystal structures of nitrogen-containing compounds under extreme temper-

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ature and pressure conditions.[24–27] As an approximate density functional theory (DFT)-based technique, the DFTB method significantly improves computational efficiency while maintaining high accuracy, achieving speeds 100–1000 times faster than traditional DFT.[28,29] By using DFTB in combination with CALYPSO's structural search capabilities, we can efficiently and accurately explore a broader phase space to identify potential nitrogen polymer structures, with the goal of discovering all-nitrogen polymer structures stable under ambient conditions. This method provides a promising approach for the design of polymeric nitrogen materials with improved stability and energy density, combining computational efficiency with near-DFT-level accuracy.

2. CALYPSO/DFTB Approach. To provide an intuitive understanding of the CALYPSO/DFTB approach, we present a flowchart of the crystal structure prediction process in Fig. 1. Detailed information regarding the calculations is provided in the SM. Pressure can significantly alter the potential energy surface, promoting the formation of additional metastable structures, a strategy for discovering new phases across various systems.[30,31] This not only broadens the scope of the search but also facilitates the identification of more potential candidate structures. The use of the particle swarm optimization (PSO) algorithm within the CALYPSO framework played a key role in efficiently identifying high-energy metastable states. Several novel nitrogen structures were identified, producing a range of candidate crystal structures. In this study, we extended the search to pressures ranging from 0 to 300 GPa, with a step size of 50 GPa. The maximum number of nitrogen atoms per unit cell was limited to 40. For each pressure point, we performed structure optimizations and phonon frequency calculations at the Γ point for 10000 candidate structures using the DFTB approach, allowing us to filter out any unstable configurations. Subsequently, we calculated their Γ-point phonon frequencies at 0 GPa using the DFTB approach and discarded the unstable configurations at 0 GPa. Finally, to assess the stability of these structures, we used DFT to calculate their thermal and mechanical properties, identifying polymeric nitrogen structures that are stable at ambient temperature. Furthermore, we calculated the electronic properties and energy density of the identified stable structure.

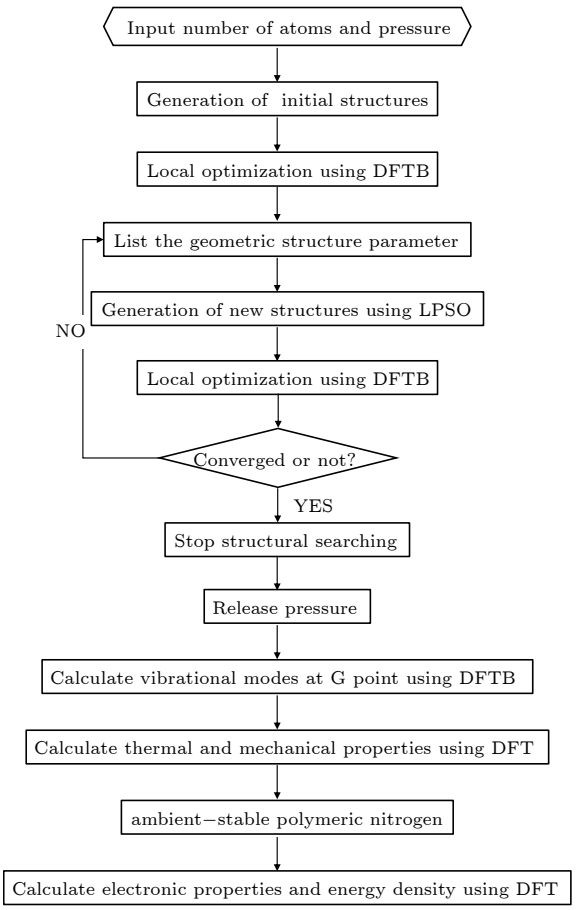

Fig. 1. Illustration of the flowchart of the multi-stage computational design of polymeric nitrogen.

3. Thermal and Mechanical Properties. Through the above structural search, we obtained many metastable structures. To enable safe storage and utilization, metastable structures must exhibit sufficient stability under ambient conditions to prevent spontaneous decomposition. At each pressure point, we optimized the candidate structures and computed their phonon frequencies at the Γ point. We identified 124 structures with no imaginary frequencies at the Γ point across the 0–300 GPa range. After releasing the pressure, we found that 32 of these structures remained stable (i.e., no imaginary frequencies at the Γ point).

To evaluate the stability of these 32 structures, we performed more accurate phonon frequency calculations using the supercell method with the finite displacement approach[28] and the Phonopy code.[29] Figure 2 presents the calculated phonon dispersions, which confirm that there are no imaginary frequencies throughout the entire Brillouin zone at 0 GPa, indicating that the $Fddd$, $P3_221$, $I\bar{4}m2$, and $P6_522$ phases are dynamically stable at ambient pressure. Therefore, we selected four polymeric nitrogen structures that are stable at 0 GPa.

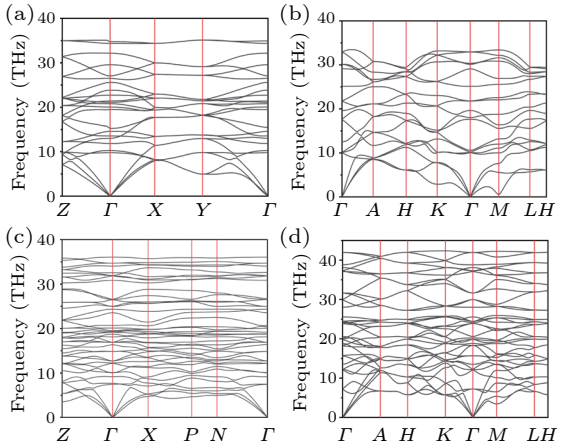

Fig. 2. Phonon spectrum of predicted polymeric nitrogen at 0 GPa. (a) $Fddd$ phase. (b) $P3_221$ phase. (c) $I\bar{4}m2$ phase. (d) $P6_522$ phase.

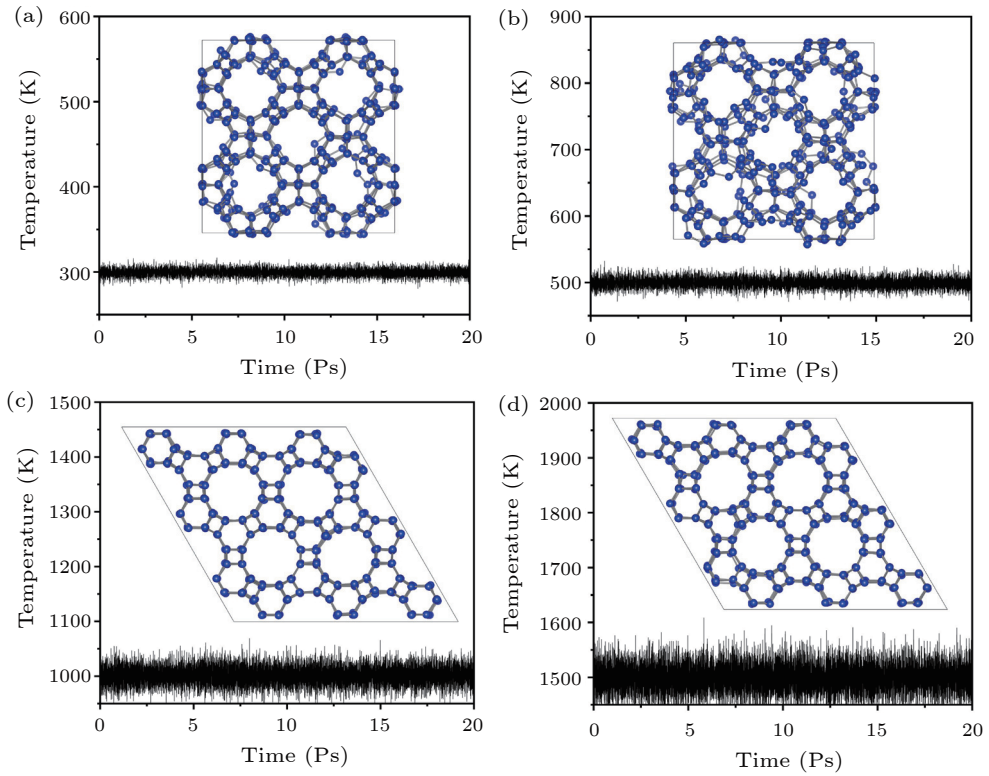

Fig. 3. Temperature as a function of time for the predicted polymeric nitrogen at 0 GPa in our AIMD simulations. (a) and (b) The $I\bar{4}m2$ phase at 300 K and 500 K. (c) and (d) The $P6_522$ phase at 1000 K and 1500 K. Insets show the snapshots of structures at the end of 20 ps simulations.

For a predicted compound, establishing its thermal stability is the prerequisite for practical applications. Hence, we calculated the *ab initio* molecular dynamics (AIMD) of these structures under finite temperature conditions. AIMD simulations were performed using larger supercells, with canonical (NVT) ensemble over 20 ps at a 1 fs time step. The simulations covered a temperature range from 300 K to 2000 K at 0 GPa. Figure 3 shows the temperature evolution over time for the $I\bar{4}m2$ and $P6_522$ phases at their respective temperatures. Top and side views of snapshots of the predicted polymeric nitrogen crystal structures at equilibrium after 20 ps of AIMD simulations are also presented. The structural frameworks of the $I\bar{4}m2$ and $P6_522$ phases are retained after the molecular dynamics simulations at 300 K, suggesting structural stability at ambient temperature. In contrast, the $Fddd$ and $P3_221$ phases exhibit instability, as evidenced by their structural degradation at 300 K during the AIMD simulations (see Fig. S2 of SM). Notably, the equilibrium position and structural integrity of the $P6_522$ phase are preserved up to 1500 K [Fig. 3(d)], confirming its excellent thermal stability.

We also investigated the mechanical stability of the predicted structures. Elastic constants provide the necessary information to estimate the mechanical properties of materials. The elastic constants C_{ij}, bulk modulus B, shear modulus G, Young's modulus E, and Poisson's ratio ν have been calculated and presented in Table S1 of SM. The elastic constants of these predicted polymeric nitrogen satisfy the Born–Huang stability criterion,[32] proving these structures are mechanically stable under ambient conditions.

4. Crystal Structures. The atomic configurations of the four polymeric nitrogen structures confirmed to be stable at 0 GPa are illustrated in Fig. 4, with their corresponding lattice parameters and atomic positions provided in SM Table S2. These structures are presented here for the first time. Enthalpy difference curves (relative to the ε–N structure) for the various structures are presented in Fig. S3 of SM. Figure 4(a) shows the $Fddd$ phase of polymeric nitrogen, where all nitrogen atoms are three-fold coordinated, exhibit bond lengths of 1.38 Å and 1.54 Å, and feature pore sizes of approximately 2.6 Å × 3.5 Å. Figure 4(b) is the $P3_221$ phase, characterized by nitrogen atoms adopting a combination of two- and three-fold coordination, showing bond lengths of 1.38 Å and 1.44 Å, respectively. Figure 4(c) is the $I\bar{4}m2$ phase, where each nitrogen atom is bonded to three different nitrogen atoms with bond lengths of 1.361 Å, 1.407 Å, and 1.509 Å, respectively and forms a free pore diameter of 4.1 Å. The electronic analysis reveals that the nitrogen atoms in this phase are in sp^2 hybridization and that this structure is a semiconductor with a band gap of 1.31 eV (Fig. S4a of SM). Figure 4(d) is the $P6_522$ phase, where each nitrogen atom forms three single N–N bonds with its neighbors, displaying bond lengths of 1.306 Å, 1.376 Å, and 1.457 Å, respectively. Further, the crystal structure of the $P6_522$ phase is illustrated in Figs. 4(e) and 4(f), where the building blocks consist of six-membered and twelve-membered spiral rings, respectively. The six-membered ring, shown

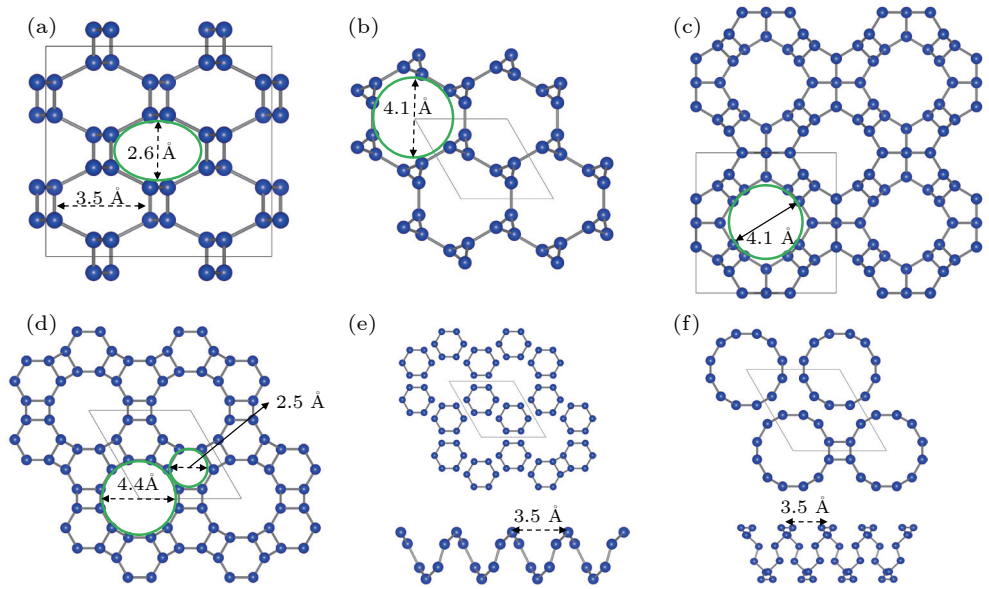

Fig. 4. Crystal structures of predicted 3D polymeric nitrogen. (a) *Fddd* phase. (b) $P3_221$ phase. (c) $I\bar{4}m2$ phase. (d) $P6_522$ phase. Crystal structure of the $P6_522$ phase with (e) six-element and (f) twelve-element spiral rings as building blocks. The upper sections of (e) and (f) are top views, and the lower sections are side views.

in Fig. 4(e), consists of six rings with a diameter of approximately 2.5 Å, while the twelve-membered ring shown in Fig. 4(f) has a diameter of approximately 4.4 Å. Electronic property analysis indicates that the nitrogen atoms in the $P6_522$ phase are also in sp^2 hybridization, with lone pair lobes (p_z) located on both sides of the triangular plane, and that this structure is a semiconductor with a band gap of 3.15 eV (Fig. S4b of SM). The calculated N–N distances of these 3D polymeric nitrogen structures range from 1.31 Å to 1.55 Å, similar to the N–N distance in cg-N (1.41 Å).

We calculated the mass density and energy density of these four three-dimensional polymeric nitrogen structures and compared them with cg-N in Table 1. The results show that these newly discovered polymeric nitrogen phases exhibit similar nitrogen content and excellent energy density comparable to cg-N. However, the pressure and temperature required for their stable existence are lower than those needed for cg-N, making them promising candidates for HEDMs.

Table 1. The mass density and energy density of the *Fddd*, $P3_221$, $I\bar{4}m2$, and $P6_522$ phases at 0 GPa, respectively.

	Fddd	$P3_221$	$I\bar{4}m2$	$P6_522$	cg-N
Mass density (g/cm^3)	3.101	2.902	2.814	2.899	3.388
Energy density (kJ/g)	11.77	12.02	11.32	10.99	10.36

5. Discussion. In this study, we utilized the PSO algorithm implemented in CALYPSO, combined with the DFTB method from the DFTB+ software package, to investigate two novel polymeric nitrogen structures. These structures exhibit high energy densities (11.32 kJ/g and 10.99 kJ/g relative to α-N_2 gas) and are stable under ambient conditions, making them promising candidates for practical applications as HEDMs. Our approach demonstrates that it is possible to rapidly access metastable states of polymeric nitrogen, including their geometric structures and vibrational modes at the Γ point, while maintaining the qualitative accuracy of the DFT-level method. By combining the computational efficiency of DFTB with the structural search capabilities of CALYPSO, we provide an effective strategy for designing and exploring new high-energy-density polymeric nitrogen materials. This method not only broadens the scope of metastable structure discovery but also offers a novel pathway for the exploration of high-energy materials.

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