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# Armchair shaped polymeric nitrogen N<sub>8</sub> chains confined in h-BN matrix at ambient conditions: stability and vibration analysis†

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A new hybrid material comprising of armchair shaped polymeric nitrogen chains (N<sub>8</sub>) encapsulated in h-BN matrix is proposed and studied through *ab initio* calculations. Interestingly, the theoretical results demonstrate that N<sub>8</sub> chains, confined in h-BN matrix, are effectively stabilized at ambient pressure and room temperature. Moreover, N<sub>8</sub> chains can dissociate and release energy at a much milder temperature of 600 K. The confined polymer N<sub>8</sub> unit needs to absorb 0.68 eV energy to span the decomposition energy barrier before decomposing. Further research shows that the charge transfer between N<sub>8</sub> chain and h-BN layer is the stabilizing mechanism of this new hybrid material. And the low dissociation temperature is due to a much smaller amount of charge transfer compared to other confined systems in previous reports. The IR and Raman vibrational analyses suggest that host–guest interactions in the hybrid material influence the vibration modes of both the confined N<sub>8</sub> chain and h-BN layer.

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## 1 Introduction

Polymeric nitrogen, a typical high-energy-density material (HEDM), is a potential candidate in several applications such as explosives, propellants and energy storage.<sup>1–3</sup> Due to the large energy difference between the single bond and the triple bond, a large amount of energy is released during the transformation of nitrogen phase from single-bonded state to molecular state.<sup>4,5</sup> More importantly, nitrogen gas, the decomposition product of polymeric nitrogen, is environmentally friendly.<sup>5,6</sup> Over the years, remarkable progress has been made towards the design and synthesis of polymeric nitrogen.<sup>7–10</sup> In theoretical calculations, many novel forms of polymeric nitrogen have been proposed under high pressure, including purely single-bonded structures,<sup>1,6,9,11–14</sup> chain structures containing alternating single and double bonds,<sup>15</sup> and the molecular solids.<sup>8,16</sup> In experiments, the single-bonded network form of polymeric nitrogen (cg-N) was synthesized at 110 GPa and 2000 K for the first time. In 2014, a layered polymeric nitrogen (LP-N) has also been obtained under much harsher conditions (150 GPa, 3000 K) using laser-heated diamond anvil cells.<sup>5</sup> Lately, a hexagonal layered polymeric nitrogen phase (HLP-N) was prepared near

250 GPa by compressing and laser heating pure nitrogen.<sup>7</sup> Unfortunately, these obtained polymeric nitrogen are unstable at ambient conditions. Thus, an effective strategy is needed to stabilize polymeric nitrogen at ambient pressure and room temperature.

Recently, a new hybrid material comprising of polymeric nitrogen chains (N<sub>8</sub>) with armchair shape encapsulated in the confined space has gathered significant interest. Theoretical studies indicate that N<sub>8</sub> chains could be effectively stabilized at ambient conditions by being confined in 1-D space of nanotubes or 2-D space of a graphene matrix.<sup>17–21</sup> Further analysis shows that the charge transfer from the host materials to N<sub>8</sub> chains is the major reason for the stability of guest material.<sup>17,19</sup> In experiment, N<sub>8</sub><sup>−</sup> molecular anion is stabilized at ambient conditions on the positively charged sidewalls of multi-walled carbon nanotubes (MWNTs).<sup>22</sup> Several theoretical researches have revealed that nano-confinement is an effective strategy for stabilizing polymeric nitrogen at ambient conditions.<sup>17,19–21</sup> The MD studies indicate that the strong host–guest interaction in these hybrid structures results in a dissociation temperature of N<sub>8</sub> chains higher than 1400 K, and over 5000 K.<sup>17,19</sup> This is the drawback that limits their applications. Thus, it is urgent to explore an ideal host material for both stabilizing N<sub>8</sub> chain at ambient conditions and allowing its energy releasing under controllable conditions.

Boron nitride (BN) matrix, analogous to graphene matrix, is commonly used in pollutant adsorption, catalysis and especially in protective capsules for holding materials under extreme conditions due to its superb heat resistance, low density, admirable temperature stability, chemical durability and

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oxidizing properties.<sup>23–27</sup> However, BN matrix has not been investigated as a host material to confine polymeric nitrogen chains.

In this work, a multilayer h-BN matrix is proposed as a host material to confine the polymeric N<sub>8</sub> chains, forming a new hybrid material (N<sub>8</sub>@h-BN matrix). The research focuses on three goals: investigating the stability of confined polymeric N<sub>8</sub> chains; obtaining a further understanding of its stability mechanism; exploring the influence of systematic interactions on the vibration optic modes of host and guest materials.

## 2 Model and computational method

Two comparative calculations are performed to confirm the optimal structure and arrangement of confined N<sub>8</sub> chain inside h-BN matrix. Firstly, we performed the geometry optimization for both the zigzag and armchair N<sub>8</sub>@h-BN crystal structures (see Fig. S1†). The results show that the zigzag N<sub>8</sub> chain relaxed into the twisty armchair N<sub>8</sub> chain, indicating that the confined zigzag N<sub>8</sub> chain is unstable. For comparison, the energy (−268.87 eV) of armchair N<sub>8</sub>@h-BN structure is smaller than that (−268.82 eV) of twisty armchair N<sub>8</sub>@h-BN structure, which means that the confined armchair N<sub>8</sub> chain is energetic stability. Secondly, in order to obtain the optimal arrangement of N<sub>8</sub>@h-BN structure, the 1 × 2 × 2 supercell structure of h-BN matrix with the different molecular orientation of N<sub>8</sub> is constructed. The DFT total energy calculation shows that the hybrid N<sub>8</sub>@h-BN structure with the laying N<sub>8</sub> molecule in the *oc* direction is the optimal structure (Fig. S2†). As shown in Fig. 1, a triclinic periodic unit model is built for the theoretical study with lattice constants of *oa*, *ob* and *oc* being 8.72, 8.68 and 7.6 Å, respectively. The angles *aob*, *aoc* and *boc* are 105°, 90° and 90°, respectively. The h-BN matrix and armchair-shape N<sub>8</sub> chain are parallel to each other on the *obc* plane and N<sub>8</sub> chain extends along the *oc* direction. The lattice mismatch is 0.0435 (see ESI†) and it allowed to keep the system size at computationally affordable level. The length of alternating single and double bonds of N<sub>8</sub> chain are 1.30 and 1.29 Å, respectively, which is in agreement with the reported values of 1.34 Å and 1.29 Å.<sup>19</sup> The initial distance of h-BN matrix and N<sub>8</sub> chain is about 3.5 Å.

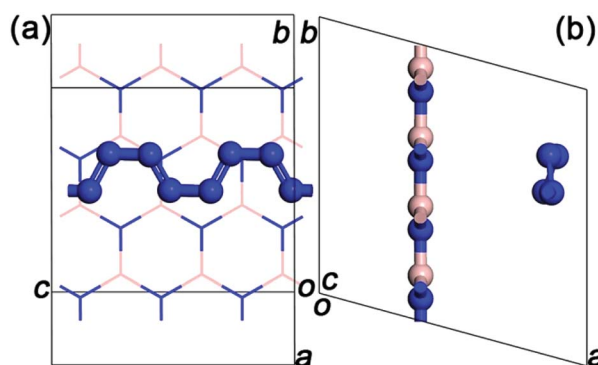


Fig. 1 (a) Unit cell of N<sub>8</sub>@h-BN crystal structure. (b) View in the oab plane.

Calculations of the geometry relaxation and the electronic properties are performed within the unit cell model. Molecular dynamic (MD) simulations are performed within the 2 × 1 × 1 supercell model. The Vienna *ab initio* simulation package (VASP), which is based on the density functional theory (DFT), is applied in the calculation.<sup>28,29</sup> The exchange–correlation interaction is described by the generalized gradient approximation (GGA).<sup>30</sup> The plane-wave energy cutoff is taken as 520 eV. For Brillouin zone integrations, 5 × 5 × 5, 9 × 9 × 9 and 1 × 1 × 1 Monkhorst Pack grid are used for the structural relaxation, electronic properties and MD simulation, respectively. The convergence criterion of force and energy are 0.05 eV per atom and 10<sup>−6</sup> eV, respectively. For the MD simulation, the total simulation time is 10 ps, and the time step is  $\Delta t = 1 \times 10^{-3}$  ps. The temperature of simulated system is controlled by the Nose thermostat. We performed the MD simulation at constant number of molecules *N*, constant volume *V* and constant temperature *T*, representing a canonical or NVT-ensemble.

## 3 Results and discussion

The stability analysis of confined polymeric N<sub>8</sub> chain is performed by the MD simulation. Seven temperatures (100–700 K) are considered for the simulation of NVT-ensemble. In Fig. 2(a), we extract the last 2 ps from the 10 ps. The bond lengths of single and double bonds in N<sub>8</sub> chain are recorded as the MD time at different temperatures. As the MD time progresses, lengths of single and double bonds are found to oscillate irregularly in the range of 1.29–1.39 Å and 1.21–1.30 Å, respectively. Meanwhile, the average length of single and double bonds as a function of simulated temperatures is shown in Fig. 2(b). To visualize our analysis, four MD simulated N<sub>8</sub>@h-BN matrix structures are presented in Fig. 3. As the temperature increases, the average length of single bond increases linearly with a slope of  $2.39 \times 10^{-5}$ , whereas a decreasing trend is observed for the double bond with a slope of  $-8.03 \times 10^{-7}$ . For comparison, length of single bond length exhibits a much larger varying rate. The increasing and decreasing tendency of single and double bonds suggest that the N<sub>8</sub> chain gradually loses its uniform chain properties with the increased temperature, but also keeps its chain configuration up to 500 K (Fig. 3(a) and (b)). At a temperature of 600 K, one bond length (1.125 Å) is obtained, indicating that the chain structure begins to decompose and transforms to the N<sub>2</sub> molecular phase (see Fig. 3(c)). A much larger decompose rate is evident at a temperature of 700 K (see Fig. 3(d)). These results suggest that the confined N<sub>8</sub> chain inside h-BN matrix is stable at ambient conditions and maintains its configuration up to 500 K. The decomposition temperature is 600 K, which is lower than that of N<sub>8</sub> chain being confined inside the 1-D BN nanotube (1400 K)<sup>19</sup> and much lower than that of N<sub>8</sub> chain being confined inside 1-D carbon nanotube (5000 K).<sup>17</sup> Thus, the h-BN matrix can be an excellent confinement material for polymeric N<sub>8</sub> chain, due to the mild and controllable energy releasing temperature of N<sub>8</sub> chain as well as the high stability of host molecule.

Furthermore, the decomposition energy and the corresponding energy barrier are calculated to further confirm the



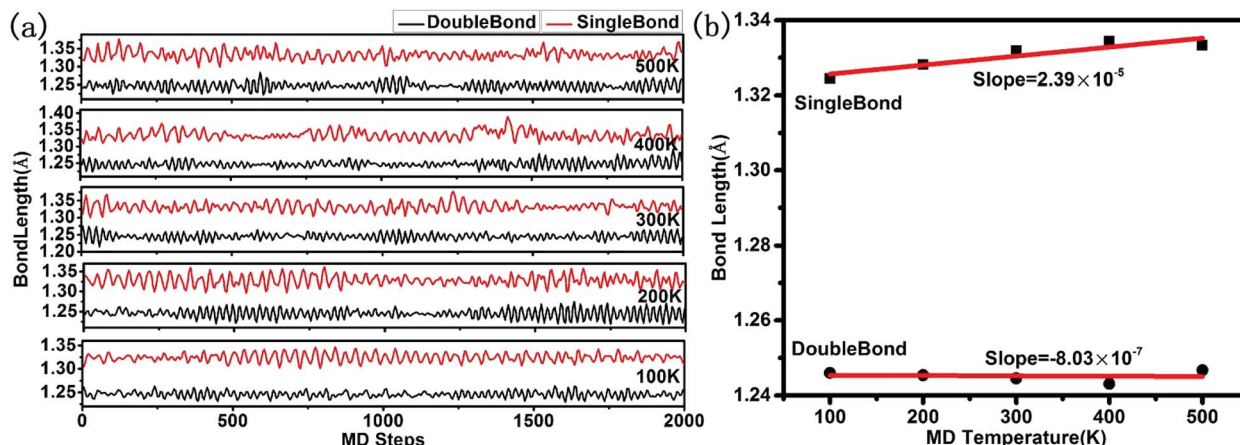


Fig. 2 (a) The evolution of single and double bond length of  $N_8$  chain with the MD time at different temperatures. (b) The average of single and double bond length as the function of the simulated temperatures.

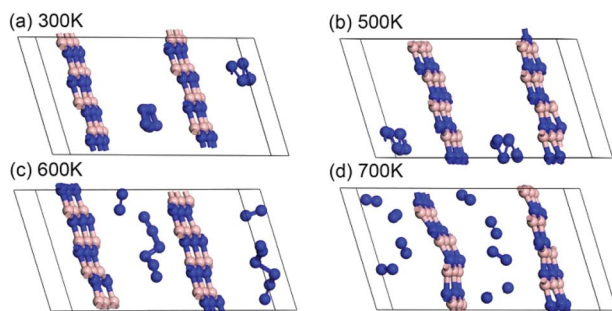


Fig. 3 Snapshots of  $N_8$ @h-BN matrix structure at 300 K (a), 500 K (b), 600 K (c) and 700 K (d).

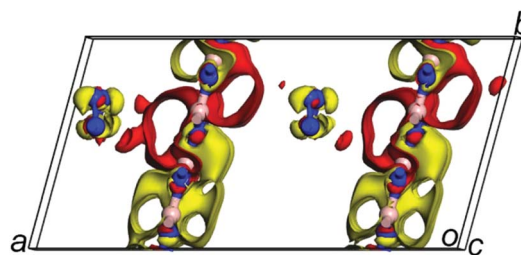


Fig. 5 The electron density difference of  $N_8$ @h-BN matrix at ambient conditions. Red and yellow colours represent effective positive and negative charges, respectively.

stability of encapsulated  $N_8$  chain in h-BN matrix. We extract the confined  $N_8$  chain,  $N_2 + N_6$  and  $4N_2$  structures and performed the DFT total energy calculation. As shown in Fig. 4, the left  $N_8$  chain with the energy of  $-57.96$  eV is the full relaxed structure; while the right one with the energy of  $-57.28$  eV is the structure before decomposing in MD simulation. The energies of intermediate structure ( $N_2 + N_6$  in MD simulation) and the

decomposed structure ( $4N_2$  after the relaxation) are  $-60.65$  eV and  $-65.13$  eV, respectively. The decomposition energy barrier ( $0.68$  eV) is just the energy difference ( $\Delta E = 57.96 - 57.28$ ) of two  $N_8$  structures; while the decompose energy of one  $N_8$  unit ( $7.17$  eV) is the energy difference ( $\Delta E = 65.13 - 57.96$ ) of two relaxed structures. Thus, the confined polymer  $N_8$  unit needs to absorb  $0.68$  eV energy to span the decomposition energy barrier before

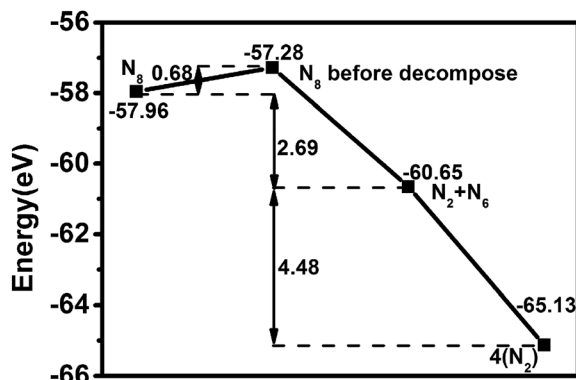


Fig. 4 Energy of  $N_8$  with full relaxed, the  $N_8$  before decompose in MD simulation,  $N_2 + N_6$  in MD simulation,  $4N_2$  with full relaxed.

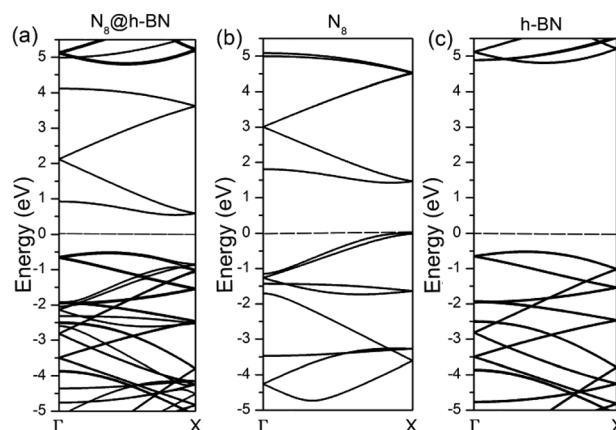


Fig. 6 Band structures of  $N_8$ @h-BN system (a), isolated  $N_8$  chain (b) and isolated h-BN layer (c).





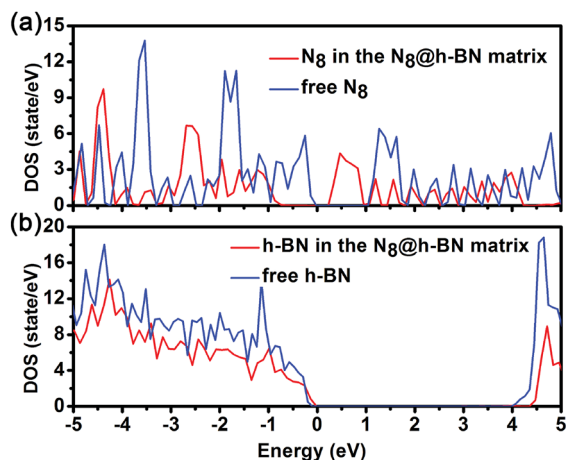


Fig. 7 Density of states for free h-BN layer and h-BN layer in the  $N_8$ @h-BN system (a) and density of states for the free  $N_8$  chain and  $N_8$  chain in the  $N_8$ @h-BN system (b).

decomposing, which confirms its dynamical stability at ambient conditions. After spanning the energy barrier, one polymer  $N_8$  unit releases 7.17 eV when it decomposed into  $4N_2$  molecules.

For the second goal: obtaining a further understanding of stable mechanism. As previous reports, the charge transfer between the guest and the host materials is responsible for the stability of guest material.<sup>17</sup> Thus, the stability and much lower decomposition temperature of confined  $N_8$  chain inside h-BN matrix should be induced by the different charge transfer. The electronic density difference of  $N_8$ @h-BN matrix, which is the total electronic density minus the electronic density of isolated h-BN matrix and  $N_8$  chain, is shown in Fig. 5. Increased negative charges can be seen around the  $N_8$  chain indicating the capture of electrons; while increased positive charges near the h-BN matrix suggests losing of electrons. Charge transfer mainly occurs between the  $N_8$  chain and the nitrogen atoms in h-BN matrix, due to the polar B–N bonds since most of electrons are located near nitrogen atoms. Bader charge transfer analysis shows that each nitrogen atom of  $N_8$  chain captures  $0.004e$  from

the h-BN layer, which is smaller than the  $N_8$ @CNTs<sup>17</sup> ( $0.05e$  per atom) and  $N_8$ @BNNTs<sup>19</sup> ( $0.04e$  per atom) systems. Thus, it can be concluded that the charge transfer between host and guest molecule tends to stabilize the confined  $N_8$  chain. More importantly, the stability of confined guest material is sensitive to the quantity of electrons transfer. This indicates that the more or less quantities of electrons transferring are corresponds to the more or little stable guest molecular respectively. Compared to  $N_8$ @CNTs<sup>17</sup> and  $N_8$ @BNNTs<sup>19</sup> systems, the  $N_8$ @h-BN matrix transfers fewer number of electrons, which not only stabilizes the confined  $N_8$  chain at ambient conditions, but also favors its application due to the much lower decomposition temperature.

To deeply understand the interaction between h-BN layer and  $N_8$  chain, the band structure and density of states (DOS) of  $N_8$ @h-BN system are calculated, as shown in Fig. 6 and 7, respectively. The band structure and DOS of isolated  $N_8$  chain and h-BN matrix are also calculated for comparative analysis. It is evident that the band structure of  $N_8$ @h-BN matrix is nearly the simple superposition of the individual band structures of isolated  $N_8$  chain and h-BN matrix. The conduction band of  $N_8$  chain in the system exhibits a downward shift compared to that isolated case, which is consistent with the fact that the charge transfer occurs from h-BN matrix to  $N_8$  chain. Moreover, this charge transfer also induces a decrease of band gap of  $N_8$ @h-BN matrix. As shown in Fig. 7, the DOS curves of isolated h-BN matrix and  $N_8$  chain are similar to that of  $N_8$ @h-BN matrix, while the energy of DOS peaks of  $N_8$  chain exhibits a downshift compared to the isolated  $N_8$  chain, which is also consistent with above analysis that the charge transfer occurs from h-BN matrix to  $N_8$  chain. Thus, the band structure and DOS analysis further corroborate the electronic density difference analysis suggesting that the charge transfer is the mainly responsible for the stability of confined  $N_8$  chain inside h-BN matrix.

For the third goal: exploring the influence of the systemic interaction on the vibration optic modes of host and guest materials. Calculated IR and Raman spectrum of isolated h-BN, isolated  $N_8$  chain and  $N_8$ @h-BN matrix are shown in Fig. 8(a) and (b), respectively. Vibration modes are shown in Fig. 9 and

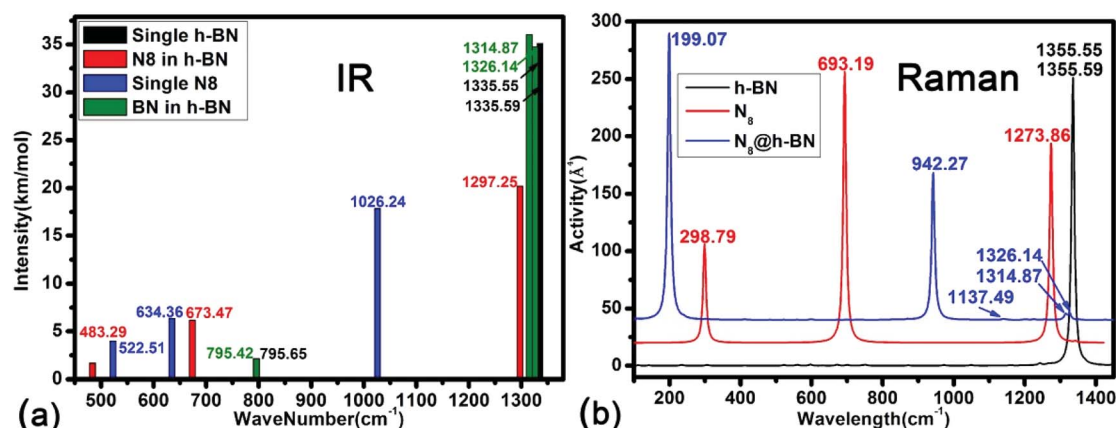


Fig. 8 Calculated IR and Raman spectrum of isolated h-BN, isolated  $N_8$  chain and  $N_8$ @h-BN matrix are presented in (a) and (b).



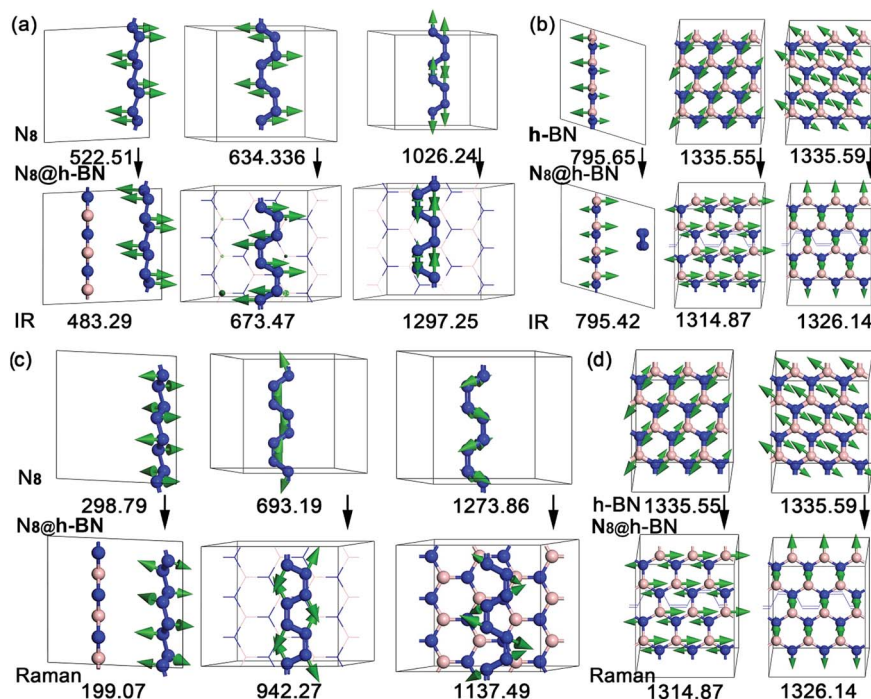


Fig. 9 Vibration modes of IR and Raman spectrums of isolated h-BN, isolated  $N_8$  chain and  $N_8@h\text{-BN}$  matrix.

the corresponding vibration mode assignments are listed in Table 1. From the IR spectrum shown in Fig. 8(a), it is evident that  $N_8$  chain and h-BN matrix exhibit three vibration models. For the  $N_8$  chain, the host-guest interaction induces a blue shift and two red shift vibrations, which correspond to the blue shift of  $N_2-N_2-N_2$  bending vibration ( $522.51\text{ cm}^{-1} \rightarrow 483.29\text{ cm}^{-1}$ ), the red shift of  $N_2-N_2-N_2$  bending vibration ( $634.36\text{ cm}^{-1} \rightarrow 673.47\text{ cm}^{-1}$ ) and N-N stretch vibration ( $1026\text{ cm}^{-1} \rightarrow 1297.25\text{ cm}^{-1}$ ), respectively (see Fig. 9(a)). For the h-BN matrix, the host-guest interaction induces a blue shift of three vibration modes, which correspond to the B-N-B bending vibration ( $795.65\text{ cm}^{-1} \rightarrow 795.42\text{ cm}^{-1}$ ), the B-N stretch vibrations of ( $1335.55\text{ cm}^{-1} \rightarrow 1314.87\text{ cm}^{-1}$ ) and ( $1335.59\text{ cm}^{-1} \rightarrow 1326.14\text{ cm}^{-1}$ ) (see Fig. 9(b)). For the Raman spectrum shown in Fig. 8(b), it can be seen that the  $N_8$  chain and h-BN exhibit three and two vibration modes, respectively. As induced by the host-guest interaction, two blue shifts ( $298.79\text{ cm}^{-1} \rightarrow 199.07\text{ cm}^{-1}$ ), ( $1273.86\text{ cm}^{-1} \rightarrow 1137.49\text{ cm}^{-1}$ ) and one red shift ( $693.19\text{ cm}^{-1} \rightarrow 942.27\text{ cm}^{-1}$ ) are observed for the N-N-N bending vibrations of  $N_8$  chain (see Fig. 9(c)). Since the B-N-B bending and B-N stretch vibrations can be detected by both the IR and Raman spectrum, the same blue shift of B-N-B bending vibration ( $1335.55\text{ cm}^{-1} \rightarrow 1314.8\text{ cm}^{-1}$ ) and B-N stretch vibration ( $1335.59\text{ cm}^{-1} \rightarrow 1326.14\text{ cm}^{-1}$ ) are evident in the IR spectrum (see Fig. 9(d)). For the  $N_8$  chain, the vibrations ( $522.51\text{ cm}^{-1} \rightarrow 483.29\text{ cm}^{-1}$ ,  $298.79\text{ cm}^{-1} \rightarrow 199.07\text{ cm}^{-1}$ ,  $1273.86\text{ cm}^{-1} \rightarrow 1137.49\text{ cm}^{-1}$ ), which are mainly perpendicular to the h-BN layer plane, exhibit a blue shift due to the confinement effect that suppresses these vibrations. The vibrations ( $634.36\text{ cm}^{-1} \rightarrow 673.47\text{ cm}^{-1}$ ,  $1026\text{ cm}^{-1} \rightarrow 1297.25\text{ cm}^{-1}$ ,  $693.19\text{ cm}^{-1} \rightarrow 942.27\text{ cm}^{-1}$ ) which are mainly parallel to the h-BN layer plane,

exhibit a red shift due to the much smaller confinement effect along this direction. All the vibrations of filled h-BN layer are blue shift compared with the single h-BN layer due to the host-guest interaction. The exhibited blue shift of vibration modes indicates a decreased vibration energy of h-BN layer, which is consistent with our electronic analysis that indicated a loss of electrons for the h-BN layer. Thus, the weak host-guest

Table 1 Vibration modes of IR and Raman spectra along with their assignments

		Symmetry	Assignment	$N_8$	$N_8@h\text{-BN}$
IR	—	—	$N_2-N_2-N_2$ bend	522.51	483.29
	—	—	$N_2-N_2-N_2$ bend	634.36	673.47
	—	—	N-N stretch	1026.24	1297.25
		Symmetry	Assignment	h-BN	$N_8@h\text{-BN}$
IR	$A_{2u}$	$A_{2u}$	B-N-B bend	795.65	795.42
	$E_{2g}$	$E_{2g}$	B-N-B bend	1335.55	1314.87
	$E_{1u}$	$E_{1u}$	B-N stretch	1335.59	1326.14
		Symmetry	Assignment	$N_8$	$N_8@h\text{-BN}$
Raman	—	—	N-N-N bend	298.79	199.07
	—	—	N-N-N bend	693.19	942.27
	—	—	N-N-N bend	1273.86	1137.49
		Symmetry	Assignment	h-BN	$N_8@h\text{-BN}$
Raman	$E_{2g}$	$E_{2g}$	B-N-B bend	1335.55	1314.87
	$E_{1u}$	$E_{1u}$	B-N stretch	1335.59	1326.14



interaction also induces a red or blue shift of both the confined N<sub>8</sub> chain and h-BN matrix by the IR and Raman vibration analyses. This vibration analysis as well as the modes assignment can be used to guide the further studies in experiment.

## 4 Conclusions

In summary, we proposed a new hybrid structure, comprising of polymeric nitrogen chains (N<sub>8</sub>) confined in a multilayer h-BN matrix and investigated its properties using *ab initio* DFT calculations. MD simulation results show that the polymeric nitrogen chains confined in h-BN matrix can be effectively stable at ambient conditions. A low decomposition temperature of 600 K for N<sub>8</sub> chain is obtained, indicating that the h-BN matrix is an ideal confinement template for polymeric nitrogen N<sub>8</sub> chain. The dissociation barrier is 0.68 eV when polymer N<sub>8</sub> decomposed, which further confirms its kinetical stability at ambient conditions. The analyses of electronic density difference, band structure and DOS indicate that the charge transfer between host material and N<sub>8</sub> chain is the major responsibility for the stabilizing mechanism. Further analysis reveals that the charge transfer between N<sub>8</sub> chain and h-BN layer is much smaller than that of the previous works. Compared to the N<sub>8</sub>@CNTs and N<sub>8</sub>@BNNTs systems, the N<sub>8</sub>@h-BN system has a smaller charge transfer due to the weaker host-guest interaction, which leads to a milder decomposition temperature. Finally, the weak host-guest interaction induces a red or blue shift of both the confined N<sub>8</sub> chain and h-BN matrix by the IR and Raman vibration analyses. These results provide an effective strategy for capturing and storing nitrogen-based HEDMs at ambient conditions and facilitating a more controlled energy release mechanism.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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