1 Introduction

Two-dimensional (2D) materials play an important role in the development of nanotechnology and nanoelectronics.1–4 However, a tunable band gap is essential for 2D materials to be applied in electronic devices. There have been numerous methods used to tailor the band gap, such as cutting into nanoribbons, rolling into nanotubes, doping with atoms, chemical functionalization, stacking layer structures and applying strain or external electric field. These methods can be classified into two types depending on whether they preserve the integrity of the sheet structure.5,6 The carrier mobility and the on/off ratio are hugely reduced if the sheet structure is destroyed, due to the introduction of scattering centers. Previous studies have proved that 2D stacking structures maintain the fantastic properties of the parent 2D material, such as high carrier mobility, and thus provide an optimal way of tuning the electronic properties of 2D materials.7–9 Additionally, to successfully modulate the electronic properties of 2D layered structures without destroying the integrity, the use of external strain and an electric field are the two most effective approaches.10–17 Up to now, numerous studies on layered stacking structures, including homo- and hetero-stacking structures have been reported, such as bilayer graphene,14,18–20 bilayer h-BN,21,22 graphene/h-BN,9,23,24 bilayer MoS2,25,26 graphene/MX2,27,28 bilayer phosphorene,29–31 graphene/phosphorene,32 and so forth.33–35

Graphyne (Gyne), a novel allotrope of carbon, has attracted great interest due to its superior and more diverse properties compared to graphene.36–38 It was proposed by Baughman et al. in 1987,39 and after more than two decades, γ-graphdiyne and β-graphdiyne were successfully synthesized in 2010 and 2017, respectively.40,41 A variety of Gynes with different percentages of C≡C linkages have been widely investigated to predict the stability, mechanical, electronic and optical properties, and their potential applications.42–45 Recently, inspired by the rich chemical and physical properties...
of layered graphene, Gyne layered structures have been studied, revealing new results and unique characteristics. For example, Shin et al. used quantum Monte Carlo simulations to study AB- and Ab-stacking bilayer z-Gyne and found that both of the stacking modes occur with about the same probability at room temperature.\textsuperscript{33} The study reports that the band gap of bilayer z-Gyne can be opened up to 120 meV under the influence of an external electric field, and compressive strain can be used to further enlarge the gap up to 160 meV.\textsuperscript{5,26,46} Moreover, uniaxial compressive strain applied to monolayer and bilayer 6,6,12-Gyne induces n- and p-type self-doping effects, while application of tensile strain results in a transition from a gapless to a finite gap system.\textsuperscript{47} Apart from that, it has also been reported that the band gap of bilayer and trilayer graphdiyne gradually decreases upon an increase in the external vertical electric field.\textsuperscript{48} All of these studies show the possibility of tuning the electronic structure of stacking structures using external strain and an electric field.

Very recently, some investigations based on density functional theory (DFT) have been carried out on the graphene-like BN (BNyne) structure, which is an analogue of Gyne, just as h-BN is of graphene. Therefore, Gyne and BNyne have similar crystal structures with a lattice constant difference of only 2%, which could enable them to act as a substrate for one other. The stability of the BNyne structure has been proven by phonon dispersion and molecular dynamics, and its electronic structure with a wide band gap is entirely different compared to that of Gyne.\textsuperscript{49,50} In particular, the capacitive behaviour of bilayer Gyne and its boron nitride derivatives have been investigated by Bhattacharya et al. They also found that substitutional boron-nitrogen doping can tune the band gap of the system, which provides a useful and flexible method for building nanoscale electronic and optoelectronic devices.\textsuperscript{51}

Inspired by the studies on bilayer graphene, bilayer h-BN and graphene/h-BN, in this study, we first systematically investigate the stability of different stacking sequences of Gyne/Gyne, BNyne/BNyne and Gyne/BNyne bilayers and their relevant electronic structures, and then the band gap engineering via external strain and a vertical electric field in the most stable stacking structures studied. Additionally, the physical mechanisms of the band gap variation are also illustrated in terms of the band degeneracy and band edge arrangement.

## 2 Computational details

All of the calculations on the Gyne/Gyne, BNyne/BNyne and Gyne/BNyne bilayers were performed using DFT in conjunction with the plane-wave total energy calculation method as implemented in the CASTEP package.\textsuperscript{52,53} The Vanderbilt ultra-soft pseudo-potential was used to describe the core electrons.\textsuperscript{54} The exchange–correlation potential of the interacting electrons was modeled using the Perdew–Burke–Emzerhof (PBE) version of the generalized gradient approximation (GGA).\textsuperscript{55,56} The DFT-D approach with the Ortman–Bechstedt–Schmidt (OBS) van der Waals (vdW) correction was included to acquire accurate results for the bilayer structures.\textsuperscript{57} As a benchmark, the DFT-D of the OBS calculations gave a good interlayer distance of $c = 3.325$ Å and a binding energy per carbon atom of $E_b = -29$ meV per atom for bilayer graphene, which is in full agreement with previous experimental measurements ($c = 3.350$ Å and $E_b = -26$ meV per atom).\textsuperscript{58}

Furthermore, our benchmark computations on AA-bilayer h-BN, the atomic arrangement of bulk h-BN, using this DFT-D method predicted an interlayer distance of 3.358 Å, which is in good agreement with the theoretical and experimental data (3.33–3.37 Å).\textsuperscript{23,59} A plane-wave basis set with a cutoff energy of 680 eV was set and for the Brillouin zone integration, a fine $9 \times 9 \times 1$ grid was sampled for structure optimization and the properties calculations. The positions of the atoms were fully relaxed until the energy satisfied a convergence tolerance of $1 \times 10^{-6}$ eV per atom and the force reached a convergence tolerance of 0.01 eV Å$^{-1}$. A vacuum of 30 Å along the z-direction was added to avoid any interaction between the periodical stacking structures during geometry optimization.

Uniaxial strain (labeled as $\varepsilon_{xx}$ for the $x$ direction and $\varepsilon_{yy}$ for the $y$ direction) and biaxial strain (labeled as $\varepsilon_{xy}$ in a symmetric manner) were applied to the bilayers, respectively, to investigate their variation in energy band gap ($E_g$). The biaxial strain can be calculated using $\varepsilon_{xy} = \Delta a/a_0 \times 100\%$, in which $\Delta a$ represents the change in the lattice parameter, and $a_0$ denotes the origin lattice parameter. Under biaxial strain, the hexagonal symmetry was retained because the same deformation magnitude is applied in both the $x$ and $y$ directions. The value of the uniaxial strain can be defined as $\varepsilon_{xx(\text{y})} = \Delta u(u_0 \times 100\%$, where $u_0$ and $\Delta u + u_0$ are the undeformed lattice length and deformed lattice length in the $x$ or $y$ direction, respectively. As a consequence, the hexagonal symmetry was disturbed under the influence of uniaxial strain and the corresponding first Brillouin zone is illustrated in Fig. 1(f). An external electric field was applied along the z-axis from $-0.6$ to $+0.6$ V Å$^{-1}$ to study the effect on the electronic properties of the bilayers.

Five different types of bilayer stacking, namely, AA, AB1, AB2, AB3 and AB4 were considered. Therefore, 5 stacking modes of the Gyne/Gyne bilayers, 10 stacking modes of the BNyne/BNyne bilayers and 6 stacking modes of the Gyne/BNyne bilayers were derived and are illustrated in Fig. 1, 2 and 3, respectively. The stacking modes could transform into one another by horizontally sliding into a corresponding displacement in the $x$ direction (AB3 and AB4) or in the $y$ direction (AB1 and AB2). The stacking modes AA’, AB1’, AB2’, AB3’ and AB4’ were obtained by changing the atomic arrangement of one of the BNyne layers, that is to say, using N atoms to replace the original B atoms and B atoms to replace the original N atoms.

To evaluate the energetic stability of the bilayer structures with different stacking modes, the formation energy was calculated using:

$$E_{\text{form}} = (E_{\text{bi}} - E_{\text{mono1}} - E_{\text{mono2}})/n,$$

where $E_{\text{mono1}}, E_{\text{mono2}}$ and $E_{\text{bi}}$ are the total energies of pristine monolayer 1, monolayer 2 and the bilayer structures, respectively, and $n$ represents the number of atoms in the cell.
Moreover, we also calculated the binding energy to evaluate the influence of the vdW force:

\[ E_b = \frac{E_{bi}}{C_0} E_{\text{mono1+mono2}}/S, \]  

where \( E_{\text{mono1+mono2}} \) is the sum of the total energies of the independent monolayer 1 and monolayer 2 fixed in the same lattice with bilayers and \( S \) denotes the contact area.

In addition, in order to understand the charge transfer mechanism between the two monolayers, the charge density difference, \( \Delta \rho \), can be calculated using:

\[ \Delta \rho = \rho_{bi} - \rho_{\text{mono1}} - \rho_{\text{mono2}}, \]

where \( \rho_{bi} \), \( \rho_{\text{mono1}} \) and \( \rho_{\text{mono2}} \) are the charge densities of the bilayer structure and monolayers, respectively. Furthermore, the plane-averaged electron density difference of the bilayers along the \( z \) direction can be defined as:

\[ \Delta \rho_z = \int \rho_{bi}dx\,dy = \int \rho_{\text{mono1}}dx\,dy = \int \rho_{\text{mono2}}dx\,dy. \]

Therefore, positive values indicate charge accumulation and negative values indicate charge depletion at a given position.

### 3 Results and discussion

#### 3.1 Bilayers of Gyne/Gyne, BNyne/BNyne and Gyne/BNyne

Fig. 1 shows the optimized bilayer crystal structures of Gyne/Gyne with different stacking sequences, and there was no meaningful buckling observed for all of the Gyne layers after full relaxation. The optimized lattice constant of the Gyne/Gyne bilayers are 6.87 Å, which is 0.03 Å smaller than the data obtained from the local density approximation with the vdW density functional (vdW-DF2).51 But, the independence of the lattice constants in terms of the stacking sequences is consistent with the results in the literature. Furthermore, as listed in Table 1, the trend in the overall interlayer distances AA > AB1 > AB4 is...
consistent with the findings of Bhattacharya,\(^\text{51}\) which could prove the accuracy of our calculations. The difference is that in virtue of the calculation of the formation energy, the most stable configuration with a value of \(E_\text{f} = -40.79\) meV per atom is AB1-Gyne/Gyne in our calculation results, while in ref. 51, AB4-Gyne/Gyne shows the most favorable energy (about \(-23.79\) meV per atom).

However, our calculated formation energy of AB4-Gyne/Gyne is \(-39.38\) meV per atom, which carries an energy penalty of about 1.41 meV per atom compared with that of AB1-Gyne/Gyne.

The optimized geometries of the BNyne/BNyne and Gyne/BNyne bilayers are presented in Fig. 2 and 3, respectively. Similar to the Gyne/Gyne bilayers, the BNyne/BNyne and Gyne/BNyne bilayers also have no obvious wrinkling after geometry optimization. The calculated lattice constants of the BNyne/BNyne and Gyne/BNyne bilayers were 6.93 and 7.01 Å, which are in agreement with Bhattacharya’s results of 6.95 and 7.00 Å.\(^\text{51}\) Also, the lattice constants were not affected by the stacking sequences.

The interlayer distance, adhesive energy and binding energy for all the Gyne/Gyne, BNyne/BNyne and Gyne/BNyne configurations are listed in Tables 1, 2 and 3, respectively. The vertical theoretical equilibrium distances of all the studied bilayers are in the range of 3.296 to 3.554 Å, which are much larger than the sum of the covalent atomic radii (0.75 Å for the C atoms, 0.85 Å for the B atoms and 0.71 Å for the N atoms, respectively), indicating that the two monolayers are beyond the bonding range with only weak interactions, such as electrostatic interactions and vdW interactions.

Moreover, the interlayer binding energies of all the stacking models were found to have a small energy interval of 14.59 to 19.08 meV Å\(^{-2}\), very close to the typical weak vdW bonding of around 20 meV Å\(^{-2}\) calculated by DFT calculations in layered compounds.\(^\text{60,61}\) This further confirms that the Gyne/Gyne, BNyne/BNyne and Gyne/BNyne bilayers are bonded by weak vdW forces.

Note that the negative formation energies, seen respectively in Tables 1, 2 and 3, reveal that all the bilayers are more stable than their intrinsic monolayers. This result is in agreement with the results of other layered systems.\(^\text{6,62,63}\) Additionally, the formation energies of the Gyne/Gyne, BNyne/BNyne homobilayers and Gyne/BNyne heterobilayers were in the range of \(-40.79\) to \(-35.46\), \(-32.79\) to \(-24.88\) and \(-57.58\) to \(-54.42\) meV per atom, respectively, which have the same order of magnitude as the values for other vdW crystals, such as bilayer graphene,\(^\text{64}\) graphene/h-BN,\(^\text{65}\) graphene/silicene,\(^\text{66}\) and g-C\(_2\)N/XSe\(_2\).\(^\text{63}\) Furthermore, the energy differences between the most unstable and most stable stacking configurations were 5.33, 7.91 and 3.16 meV per atom for Gyne/Gyne, BNyne/BNyne and Gyne/BNyne, respectively. The differences are much smaller than the room temperature energy, so all the configurations are highly likely to co-exist.

With our convention referred to in eqn (1), the more negative the formation energy is, the more stable the stacking structure is. Therefore, we conclude that the most stable configuration is the Gyne/BNyne heterobilayer structure, followed by the Gyne/Gyne homobilayers and finally the BNyne/BNyne homobilayers. Additionally, the most stable structures in the different systems were AB1-Gyne/Gyne, AA’-BNyne/BNyne and AB2-Gyne/BNyne, respectively.

The electronic band structures (BS) along the high symmetry points for the Gyne/Gyne bilayers as well as the Gyne monolayer are plotted in Fig. 4. The Gyne monolayer shows a finite direct band gap of 0.450 eV, in good agreement with other calculation results.\(^\text{67-69}\) A more accurate BS of Gyne based on HSE06 is plotted in Fig. S1(a) (ESI†), which shows the same direct-gap characteristics, but the calculated band gaps are enlarged to 0.875 eV. Due to weak vdW influences, the interlayer atomic interactions were found to have a minimal impact on one another, and thus, the electronic band diagrams of the Gyne/BNyne bilayers were very similar to that of the monolayer Gyne. All the BS of the Gyne/Gyne bilayers show direct band gap semiconductor properties, and both the conduction band minimum (CBM) and valence band maximum (VBM) are located at the \(M\) point in the Brillouin zone, which is the same as Bhattacharya’s results.\(^\text{51}\) However, doubly degenerate states induced by the split of the bands of the monolayer emerged in the bilayer Gyne/Gyne due to the interlayer atomic interactions and vdW force, which was proved from the calculation of the interlayer distances and binding energies above. In particular, the band

### Table 1

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<tr>
<th>Stacking order</th>
<th>(d) (Å)</th>
<th>(E_\text{form}) (meV per atom)</th>
<th>(E_b) (meV Å(^{-2}))</th>
<th>(E_g) (eV)</th>
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<td>17.15</td>
<td>0.226</td>
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### Table 2

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<th>(d) (Å)</th>
<th>(E_\text{form}) (meV per atom)</th>
<th>(E_b) (meV Å(^{-2}))</th>
<th>(E_g) (eV)</th>
</tr>
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</tr>
<tr>
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<tr>
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<td>-30.00</td>
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<td>-29.75</td>
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gap values were observed to be very distinct for the different stacking sequences. As listed in Table 1, a narrower band gap of 0.094 eV was observed in the AA stacking than in all the AB stacking structures, which is in accordance with the reported results of Gyne/Gyne stacking sequences, that AA-Gyne/Gyne shows the smallest band gap of 0.120 eV, which is 26 meV larger than in our results. This is because the BS of the vdW layer structures is sensitive to the lattice symmetry, which can be broken by different interlayer interactions or different alternate stacking sequences. The destruction of the symmetry can be understood by the straightforward analysis of the partial density of states (PDOS) of AA- and AB1-Gyne/Gyne.

In the case of AA-Gyne/Gyne, the uniformity of the 2p state of the C atoms is preserved. Thus, the PDOS distributions of the six sp-hybridized C atoms in Fig. 5(a) are the same as one another, and the PDOS of the sp$^2$-hybridized C atoms are also the same, as shown in Fig. 5(b). However, for AB1-Gyne/Gyne, due to the asymmetry in the chemical environment, as shown in the inserted illustration, the uniformity of the 2p state of the C atoms in the Gyne layer is broken. As depicted in Fig. 5(c), there is a significant difference in the PDOS distribution, so that the six PDOS diagrams can be obviously categorized into four types of curves. To be more specific, the PDOS of the sp-5 C atoms corresponds to that of the sp-1 C atoms, and the PDOS of the sp-6 C atoms is consistent with that of the sp-2 C atoms. The PDOS of the sp$^2$-hybridized C atoms possess similar characteristics. Therefore, the break in the uniformity of the 2p state of the C atoms in Gyne induces a different PDOS distribution for the AB stacking structures, which demonstrates the interlayer coupling effect between the two layers and the break in symmetry with respect to the c-axis.

To better understand the nature of the bonding mechanism and explore the charge transfer between the layers more intuitively, the charge density difference, as well as the calculated plane-averaged electron density difference in the z-direction of the Gyne/Gyne bilayers were investigated and the results are shown in Fig. 6. Relative to the isolated monolayers, the positive blue region indicates the electron accumulation, while the negative yellow region denotes the electron depletion. There was no obvious electron transfer observed between the two layers, and the charge accumulation was found to occur in the vdW gap near the Gyne layers. A significant charge depletion was observed in the vdW gap for the AA, AB2 and AB3 stacking models, while for the AB1 and AB4 stacking modes, there was an obvious charge accumulation in the middle of the vdW gap.

The BS of the BNyne monolayer based on the PBE and HSE06 functionals are plotted in Fig. S1(b) (ESI†), respectively. They show the same characteristics, but the bandgap based on HSE06 is 1.282 eV larger than that based on PBE. Fig. 7 and Fig. S2 (ESI†) illustrate the BS of the BNyne/BNyne bilayers. Unlike the Gyne/Gyne bilayers, all the BNyne/BNyne bilayers show wide direct semiconductor character and both the VBM and CBM are located along $\Gamma$ to M. The wide band gap properties of the BN systems compared to those of the C systems with the same structures arise from the ionic character of the...
B–N bonds. The total electron density plots of Gyne/Gyne and BNyne/BNyne presented in Fig. 8 give an insight into the distribution of the electronic charge in the C–C and B–N bonds, respectively. In the Gyne/Gyne systems depicted in Fig. 8(a), the bonds have significant covalent character due to the sharing of charge between neighboring C atoms. Charge accumulation is higher in the Csp–Csp bond, which indicates stronger –C≡C– bonds. On the contrary, as shown in Fig. 8(b), the electron density cloud is lumpy, as the charge density is more localized around the N atom. We can see that, the B–N bond arises from the fact that the nitrogen lone pair directly interacts with the empty p orbital of the boron. The charge transfer occurs mainly from B to N atoms, and a net charge accumulation is observed around the N atoms, and charge depletion is observed around the B atoms. Clearly, the N atoms in BNyne/BNyne are ionic in nature, although the charge density contours around the nitrogen are not completely circular, but they show the ionic bonding due to its high electronegativity, which attracts the electron cloud of the boron atoms. Hence, the B–N bonds show ionic characteristics. The covalency of the C–C bonds and the partial ionicity of the B–N bonds were also demonstrated in ref. 51. Thereupon, the accumulation of electrons around the N atoms was observed to shift the Fermi level towards the CB, and the depletion of electrons around the B atoms caused a shift in the VB, which resulted in a wide band gap. The PDOS diagrams of the AB10- and AA0-BNyne/BNyne bilayers in Fig. 7 show the identical result that the top of the valence band is mainly contributed to by N atoms and that B atoms only slightly contribute, while the bottom of the conduction band is almost dominated by B atoms. This result is accordance with the PDOS of reported AB4-BNyne/BNyne structures. 51

Interestingly, the band gaps of the ten BNyne/BNyne configurations could be categorized into two groups. As listed in Table 2, combined with the images shown in Fig. 7 and Fig. S2 (ESI†), group I includes AA, AB1′, AB2′, AB3 and AB4′-stacked configurations with a band gap of less than 4 eV, while group II consists of AA′, AB1, AB2, AB3′ and AB4-stacked configurations with band gaps larger than 4 eV. This can be explained by the different chemical environments, which lead to different distortions of the bands and different band gap values. Taking the AB1′ mode in group I and AA′ mode in group II as a contrasting example to describe the chemical environment, as shown in Fig. 2, there are more B atoms in the bottom layer that can act
on the same B atoms in the top layer of AB1', while in the AA' structures, the B atoms in the bottom layer take effect on the contrasting N atoms in the top layer. In group I, a large overlap in the $p$ electron wave functions between the same atoms in the top and bottom BNyne layers leads to a strong interlayer $p$-$p$ interaction and thus a larger energy splitting occurs for the CBM, as shown in Fig. 7(a) and Fig. S2(a) (ESI†). However, in group II, the coupling between the B and N atoms shifts the energy levels of the N and B atoms upward and downward, respectively, because the energy levels of the orbitals of the B atoms are larger than those of the N atoms, according to the difference in the electronegativity. As a consequence, the $E_g$ values of group I are smaller than those of group II.

Next, we focused on the bilayers of the Gyne/BNyne hybrid structures. The BS are illustrated in Fig. 9 and Fig. S3 (ESI†). Their $E_g$ values, from 0.454 to 0.508 eV, are closer to but larger than that of the Gyne monolayer (about 0.450 eV), which indicates that the insertion of a BNyne layer induced a slightly larger band gap. Obviously, the Gyne/BNyne bilayers have an almost identical BS around the Fermi energy to monolayer Gyne, as shown in Fig. 9(a and b). Taking the thorough insight into the PDOS, as shown in Fig. 9(b), it can be seen that both the VBM and CBM of the AB2-Gyne/BNyne bilayer reside in the Gyne layer. However, the weak interaction between the B (or N) atoms and C atoms shifts the CBM upward (or VBM downward), thus the Gyne/BNyne bilayers have a larger band gap than the Gyne monolayer. In order to further confirm the band contribution, a more accurate BS, as well as corresponding PDOS of AB2-Gyne/BNyne based on HSE06 was determined and the results are shown in Fig. S4 (ESI†). The data were found to be consistent with the results obtained at the PBE level.

### 3.2 Tunable bandgaps via strain

Strain-induced band gap modulation has been commonly used in 2D systems, so it is of fundamental and practical interest to study the effect of strain on the electronic structures of bilayers. The fracture strain values of Gyne under uniaxial strain were 17.7% along the $x$ direction and 11.2% along the $y$ direction. The fracture strain value of BNyne was 14% under uniaxial strain, but 10% under biaxial strain. Thus, a tensile strain was applied up to a limit of 10%, while only a small compressive strain ranging from $-2\%$ to 0 was applied to preserve the planar structure of the single layers. So strains were applied in the range of $-2\%$ to 10\% with an increment of 1\% to the energetically preferred stacking configurations of AB1-Gyne/Gyne, AA'-BNyne/BNyne and AB2-Gyne/BNyne structures.

In order to further confirm the suitability of the strain range, the strain energy was calculated. The strain energy can be defined as $E_s = (E_{\text{tot}} - E_0)/n$, where $E_{\text{tot}}$ and $E_0$ are the total energy of the strained system and the strain-free system, respectively, and $n$ is the number of atoms in the cell. Fig. 10(a), (b) and (c) show $E_s$ as a function of the strain for the AB1-Gyne/Gyne, AA'-BNyne/BNyne and AB2-Gyne/BNyne structures, respectively. The $E_s$ values were observed to monotonously increase upon an increase in the strain applied, which indicates that the deformation is

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![Fig. 9](image_url) Calculated BS of the (a) Gyne monolayer and (b) AB2-Gyne/BNyne bilayer. (c) Wave functions of the VBM and CBM in AB2-Gyne/BNyne. The iso-surface value is $0.04 \text{ e \AA}^{-3}$.

![Fig. 10](image_url) The strain energy ($E_s$) as a function of the strain for the (a) AB1-Gyne/Gyne, (b) AA'-BNyne/BNyne and (c) AB2-Gyne/BNyne structures, respectively.
elastic and that the systems can return to their original geometry structures once the strain is removed, which further demonstrates that the strain range of −2 to 10% could not induce breakage of the structures.

The band gap variations as a function of strain are summarized in Fig. 11. Like the Gyne monolayer, the AB1-Gyne/Gyne bilayer is sensitive to external strain and shows a similar trend in the band gap variation. Under biaxial strain $\varepsilon_{xx}$, the band gap increased upon an increase in the tensile strain but decreased under compressive strain. By contrast, under uniaxial strain ($\varepsilon_{xx}$ and $\varepsilon_{yy}$), the band gap was observed to always decrease regardless of tension or compression. The BS of AB1-Gyne/Gyne under a biaxial strain of $\varepsilon_{xx} = 2\%$, $-1\%$, $1\%$ and $2\%$ are shown in Fig. S5 (ESI†). The same as unstrained AB1-Gyne/Gyne, both the CBM and VBM remained at the $M$ point under biaxial strain and thus the direct gap feature was preserved. As for the BS under $\varepsilon_{xx}$ strain, as shown in Fig. S6 and Table S1 (ESI†), the CBM was always observed at the $M$ point regardless of the strain type, while the VBM shifted to the $M'$ point when compressive strain was applied. Therefore, AB1-Gyne/Gyne exhibits an indirect band gap under compressive strain in the x-direction. Under $\varepsilon_{yy}$ strain, a persistent direct band gap was observed, but the position of the VBM, as well as the CBM, changed between the $M$ point and $M'$ point, as shown in Fig. S7 (ESI†). Specifically, under compressive strain, both the VBM and CBM were located at the $M'$ point, and at the $M$ point under tensile strain conditions.

In order to reveal the underlying mechanism in the band gap variation in the strained Gyne/Gyne bilayer, the orbital energy fluctuations in the HOMO and LUMO at the $M$ and $M'$ points were further investigated. As shown in Fig. 12, the gap variation upon strain arose from the orbital energy shift in $M_C$, $M_V$, $M'_C$ and $M'_V$. Fig. 12(a) shows the corresponding orbital energy shift in the Gyne/Gyne bilayer under biaxial strain $\varepsilon_{xy}$. An obvious decrease in both the $M_C$ and $M_V$ values was observed upon an increase in the tensile strain. However, the decreasing trend of the $M_V$ value was steeper than that of the $M_C$ value, so a relatively larger band gap was obtained under tensile strain, and a narrower band gap appeared under compressive strain. Meanwhile, under uniaxial strain, as shown in Fig. 12(b and c), the band gap value was found to be dependent on the relative position of the orbital energy levels at the $M$ and $M'$ points. Under $\varepsilon_{xx}$ tensile strain, there was a slower decrease in the orbital energy of $M_V$ than that of $M'_V$, and the orbital energy of $M_C$ was lower than that of $M'_C$. Thus, Gyne/Gyne has a smaller direct gap at the $M$-point. When a compressive strain of $\varepsilon_{yy}$ was applied, the $M'_V$ value increased rapidly compared to $M_V$, which contributed to the VBM in the BS of the Gyne/Gyne bilayer, while the CBM of the Gyne/Gyne bilayer is contributed to by the orbital of $M_C$, because the orbital energy of $M_C$ is slightly smaller than that of $M'_C$. Consequently, a relatively small indirect band gap was obtained in the compressive Gyne/Gyne bilayer. Simultaneously, as shown in Fig. 12(c), it was found that the orbital energy variations in $\varepsilon_{yy}$ were generally similar to those of $\varepsilon_{xy}$ so the same analysis could be conducted under a strain of $\varepsilon_{xy}$.

Fig. 13(a), (b) and (c) illustrate the BS of the AA′-BNyne/BNyne bilayer under a strain $\varepsilon_{xy} = -2\%$, 0 and 10%, respectively. Both the VBM and CBM were found to have a similar location to that in the unstrained structure and were located along $\Gamma$ to $M$. As plotted in Fig. 11(b), the band gap tunability of the AA′-BNyne/BNyne bilayer clearly showed the opposite character to that of AB1-Gyne/Gyne under $\varepsilon_{xy}$, that is, an increase feature was exhibited for compressive strain, but a decreasing trend was observed when subjected to tensile strain. To explain this opposite trend, the electron density distribution and the Mulliken charge at $\varepsilon_{xy} = -2\%$, 0 and 10% are shown in Fig. 13(d), (e) and (f), respectively. It can be obviously observed that fewer electrons accumulate around the N atoms for $\varepsilon_{xy} = 10\%$. 

![Fig. 11](image1.png)

**Fig. 11** Variation in the band gap of the (a) AB1-Gyne/Gyne, (b) AA′-BNyne/BNyne and (c) AB2-Gyne/BNyne structures as a function of the strain under $\varepsilon_{xy}$, $\varepsilon_{xx}$ and $\varepsilon_{yy}$, respectively.

![Fig. 12](image2.png)

**Fig. 12** Orbital energies of the HOMO and LUMO levels at the $M$ and $M'$ points of the Gyne/Gyne bilayer under $\varepsilon_{xy}$, $\varepsilon_{xx}$ and $\varepsilon_{yy}$ strain, respectively. The vacuum energy level was taken as a zero reference in the calculation of the orbital energy.
The Mulliken charge analysis further confirmed that fewer electrons transfer from the B to N atoms under a strain of $\varepsilon_{yy} = 10\%$. The reduction in the electron transfer implied weaker ionic character of the B–N bond. BN compounds have fairly large band gaps due to the ionic character of the B–N bond. Therefore, the decrease in the ionic nature between the B and N atoms induced a decrease in the $E_G$ value upon an increase in the tensile strain.

In the case of AA$^0$-BNyne/BNyne under a uniaxial strain of $e_{xx}$ and $e_{yy}$, the band gap trends were observed to be similar to that of AB1-Gyne/Gyne and always decreased regardless of whether under tension or compression. However, a noticeable indirect BS character emerged, as shown in Fig. S8 and Table S2 (ESI†). For a strain of $e_{xx}$, the VBM was located along G to M and the CBM was between G and K under compression, however, the VBM was between $\Gamma$ and K and the CBM was located along $\Gamma$ to $M'$ under tension. On the contrary, as for the strain of $e_{yy}$, the VBM and CBM were in the opposite positions.

For the AB2-Gyne/BNyne bilayer, the gap variation as a function of the strain was investigated and the results are shown in Fig. 11(c). The results showed similar trend to that of AB1-Gyne/Gyne. The band gap also decreased under uniaxial tensile strain but increased upon the application of biaxial tensile strain. Furthermore, a direct band gap feature was observed under all types of strains, and the locations of the VBM and CBM changed between the M and $M'$ points, as shown in Fig. S9 and Table S3 (ESI†).

### 3.3 Tunable bandgaps via the application of an external electric field

It has been proven that applying a gate voltage is an effective method to control the properties of layers, which also shows enormous potential application in the field of nanoelectronic devices and optoelectronic devices.\textsuperscript{14,32,62,74} The electronic responses of the AB1-Gyne/Gyne, AA$^0$-BNyne/BNyne and AB2-Gyne/BNyne bilayers were measured under a vertical electric field.

The band gap variations of AB1-Gyne/Gyne as a function of the electric field ranging from $-0.6$ to $0.6$ V Å$^{-1}$ are plotted in Fig. 14(a), and were found to be symmetric under both positive and negative electric fields. The band gaps were reduced linearly under an electric field of $<0.3$ V Å$^{-1}$, but a non-monotonic change was observed when the electric field was larger than $0.3$ V Å$^{-1}$ due to the movement of the band gap position, which changed from the $M$ point to the $\Gamma$–$M$ path, as shown in Fig. 14(a). In order to explain the decreasing trend of the band gap under the influence of the electric field, molecule orbital models were constructed and are shown in Fig. 15. When there was no external electric field applied, the split of the lowest unoccupied orbitals (LUMO) and the highest occupied orbitals (HOMO) led to a reduction in the band gaps of the bilayers compared with the monolayer. However, when a vertical electric field was applied from the bottom layer to the top layer, the energy level of the top layer rose. So, there was a reduction in the energy difference between the CBM of the bottom layer and the VBM of the top layer. Besides this, the split in the HOMO and LUMO of the monolayer also enlarged, which can be observed in the BS in Fig. 14(a).

Fig. 14(b) shows the band gap variation as a function of the electric field, as well as the partial BS of AA$^0$-BNyne/BNyne. The band gap variation generally resembled those of the Gyne/Gyne bilayer, but a dramatic drop occurred when the field strength reached $0.6$ V Å$^{-1}$. According to the BS in Fig. 14(b), the CBM under $0.6$ V Å$^{-1}$ moved to the $\Gamma$ point. Furthermore, it was
proved that this huge band gap reduction could be interpreted by the fact that a strong electric field yields a dielectric breakdown and then charge tunnelling occurs. Intriguingly, due to the existence of a tunneling barrier between the layers in the vdW nanostructure, the semiconductor-to-metal transition did not occur under dielectric breakdown.

However, for the AB2-Gyne/BNyne heterobilayer, the band gap decreased upon an increase in the positive electric field, but remained almost constant at an increase in the negative electric field, as shown in Fig. 16(a). The detailed BS diagrams under different external electric fields are plotted in Fig. S10 (ESI†). To understand the electric field-tunable evolution of the band gap, the band offset diagrams were also calculated and are shown in Fig. 16. Due to a different work function, the electrons of the BNyne layer transferred to the Gyne layer once they stacked together until both layers possessed the same Fermi level. Thus, the band offset diagram with no electric field was obtained, as shown in Fig. 16(b). Since the positive electric field was applied from the Gyne layer to the BNyne layer, the electrons of the BNyne layer further transferred to the Gyne layer, which induced the VBM of the BNyne layer to shift upward and the CBM of the Gyne layer to shift downward to approach the quasi-Fermi level ($E_f$). As a result, the CBM and VBM of the band diagram are contributed to by Gyne and BNyne, respectively, which was also proved using the Gyne/BNyne PDOS under $E = +0.6$ V Å$^{-1}$, as depicted in Fig. 16(e). Consequently, a decrease in the band gap was observed under a positive electric field. On the contrary, when it comes to negative bias, due to the fact that electrons transferred from the Gyne layer to the BNyne layer, the CBM of Gyne and the VBM of BNyne shifted away from the quasi-Fermi level, as illustrated in Fig. 16(d and f), which resulted in an almost invariable band gap.

In particularly, both the external electric field and strain can not only be used to effectively tune the band gap effectively, but also their modulating results of these two methods are

![Fig. 14](image-url) The band gap variation as a function of the electric field and the corresponding BS under 0, 0.2, 0.5 and 0.6 V Å$^{-1}$, respectively, for (a) AB1-Gyne/Gyne and (b) AA*-BNyne/BNyne.
sometimes comparable. For example, for the Gyne/Gyne bilayer, as shown in Fig. 14(a), the band gap decreased from 0.4 to 0.116 eV when the electric field strength was 0.6 V Å⁻¹, while the band gap also reduced to 0.112 eV (see Fig. 11(a)) when uniaxial strain εyy = 9% was applied. As for the case of the BNyne/BNyne bilayer, the band gap was about 3.620 eV under an electric field strength of 0.5 V Å⁻¹, and a similar band gap of 3.584 eV was found under εyy = 9%. However, for the heterobilayer Gyne/BNyne, the band gap modulation of the external electric field was pretty limited, in that the band gap only reduced to 0.444 eV under a higher electric field of E = +0.5 V Å⁻¹. A similar band gap could be obtained under a very small strain of about 1% (see Fig. 11(c)). These comparable results based on different modulation methods make graphene-based materials more flexible and convenient for use in practical device applications.

4 Conclusions

In conclusion, the electronic properties of Gyne/Gyne, BNyne/BNyne and Gyne/BNyne were systematically investigated using first-principles calculations. These layered structures were found to be coupled by vdW forces. All the bilayers were found to be more stable than their corresponding monolayers and the stability of the three types of stacking systems was found to be in the order of Gyne/BNyne > Gyne/Gyne > B Nyne/BNyne. The electronic structures were modulated by the stacking sequences, external strain and a vertical electric field. (1) The band gap was found to be sensitive to the stacking sequences due to the varying degrees of symmetry destruction caused by the weak coupling effect between the bottom and top layers. For the different stacking sequences, the band gap of the Gyne/Gyne bilayers was in the range of 0.094–0.418 eV and a wide band gap of 3.488–4.164 eV was observed in the B Nyne/BNyne system. For the Gyne/BNyne system, the BS are similar to the Gyne monolayer, but slightly larger band gaps were observed at around 0.454–0.508 eV. (2) The band gap modulation by strain shows that different modulation results were obtained by the changing strain direction. For Gyne/Gyne, the band gap was observed to increase upon an increase in the biaxial tensile strain, whereas it decreased upon an increase in the biaxial compressive strain and uniaxial strain. However, an opposite trend was observed for B Nyne/BNyne where the band gap decreased under biaxial tension strain, but increased under biaxial compressive strain. It was found to have a curve similar in appearance to that of Gyne/Gyne under uniaxial strain. As for the Gyne/BNyne bilayer, the variation as a function of the strain appeared to have almost the same trend as that of Gyne/Gyne, while a larger modulation range was observed. (3) As for the electronic structures modulated by vertical external electric field, for the homo-bilayers (Gyne/Gyne and B Nyne/BNyne), the band gap was reduced by the electric field, and almost the same trend was observed under either a positive and negative electric field. However, in the case of the hetero-bilayer Gyne/BNyne structure, the band gap maintained a constant value under a negative electric field and decreased under a positive electric field, which can be explained by the moving of the band edge under an electric field. All of these interesting features provide a new perspective for the application of vdW layered materials in nanoelectronics and optoelectronic devices.

Conflicts of interest

There are no conflicts to declare.

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