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1. Introduction

Clusters are aggregates of atoms or molecules which start to exhibit the structural and bonding characteristics of bulk materials in certain size ranges. Boron clusters as a special case with prototypical electron deficiency exhibit great diversity in size-dependent structural motifs and bonding patterns, which are much different from those of their carbon counterparts.^{1–3} Persistent joint photoelectron spectroscopy (PES) and first-principles theory investigations in the past two decades by Wang and coworkers^{4–12} show that size-selected boron clusters $B_n^{-/0}$ in an unexpectedly wide size range (n = 3-42, 48) possess planar or quasi-planar ($B_3^--B_{38}^-$, B_{41}^- , and B_{42}^-), seashell-like ($C_2 B_{28}^{-/0}$ and $C_s B_{29}^-$), cage-like ($D_{2d} B_{40}^{-/0}$ and $C_3/C_2 B_{39}^-$), or bilayer ($D_{2h} B_{48}^-$) structures featuring $\sigma + \pi$ double delocalization bonding patterns. The experimentally observed cage-like $B_{40}^{-/0}/B_{39}^-$ have been extended to the B_n^q

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A bottom-up approach from medium-sized bilayer boron nanoclusters to bilayer borophene nanomaterials⁺

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Inspired by the experimentally observed bilayer $B_{48}^{-/0}$ and theoretically predicted bilayer $B_{50}-B_{72}$ and based on extensive density functional theory calculations, we report herein a series of novel mediumsized bilayer boron nanoclusters $C_1 B_{84}$ (I), $C_{2v} B_{86}$ (II), $C_1 B_{88}$ (III), $C_1 B_{90}$ (IV), $C_1 B_{92}$ (V), $C_1 B_{94}$ (VI), $C_{2v} B_{96}$ (VII), and $C_1 B_{98}$ (VIII) which are the most stable isomers of the systems reported to date effectively stabilized by optimum numbers of interlayer $B-B \sigma$ bonds between the inward-buckled atoms on top and bottom layers. Detailed bonding analyses indicate that these bilayer species follow the universal bonding pattern of $\sigma + \pi$ double delocalization, rendering three-dimensional aromaticity in the systems. More interestingly, the AA-stacked bilayer structural motif in B_{96} (VII) with a B_{72} bilayer hexagonal prism at the center can be extended to form bilayer $C_2 B_{128}$ (IX), $D_{2h} B_{214}$ (X), $C_{2v} B_{260}$ (XI), $D_{2h} B_{372}$ (XII), and D_2 B_{828} (XIII) which contain one or multiple conjoined B_{72} bilayer hexagonal prisms sharing interwoven zigzag boron triple chains between them. Such bilayer species or their close-lying AB isomers can be viewed as embryos of the newly reported most stable freestanding $BL-\alpha^+$ bilayer borophenes and quasi-freestanding bilayer borophenes on Ag(111) which are composed of interwoven zig-zag boron triple chains shared by conjoined BL B_{72} hexagonal prisms, presenting a bottom-up approach from medium-sized bilayer boron nanoclusters to two-dimensional bilayer borophene nanomaterials.

> borospherene family $(n = 36-42, q = n-40)^{10,11,13-16}$ at the firstprinciples theory level and are all composed of twelve interwoven boron double chains with six hexagonal or heptagonal faces. In the quasi-planar boron cluster series, the dual π -aromatic $C_{6\nu}$ $B_{36}^{17,18}$ with a B_6 hexagonal hole at the center surrounded by three co-centric boron rings as the boron analog of coronene D_{6h} C₂₄H₁₂ was firstly used as a building block to form the two-dimensional (2D) monolayer (ML) α-sheet,¹⁹ dubbed borophene. Various supported 2D ML borophenes including α -sheets on the Ag(111) substrate have been synthesized later in MBE experiments.^{20,21} The bilayer (BL) structural motif firstly observed in $B_{48}^{-/0}$ ^{12,22} has been extended recently to a series of novel BL boron clusters by our group at the density functional theory (DFT) level in the size range between B₅₀ and B₇₂ including C₁ B₅₀, C_{2h} B₅₂, C₂ B₅₄, C₁ B_{56} , $C_{2\nu}$ B_{58} , C_{2h} B_{60} , C_1 B_{62} , C_2 B_{64} , D_2 B_{66} , D_2 B_{68} , C_1 B_{70} , and $C_i B_{72}^{23-25}$ which are all the global minima (GMs) of the systems effectively stabilized by interlayer B–B σ-bonds between inward-buckled boron atoms on the top and bottom layers. These BL species follow the universal bonding pattern of $\sigma + \pi$ double delocalization, making them three-dimensionally (3D) aromatic in nature. Using the experimentally observed dually π -aromatic $C_{6\nu}$ B₃₆ as building blocks and based on

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extensive global searches augmented with DFT calculations, Li and Zhang's groups^{26,27} recently reported the most stable semiconducting freestanding 2D BL- α^+ borophenes in a vacuum and quasi-freestanding BL- α^+ borophenes on Ag(111) in both close-lying AA and AB modes which proved to be obviously more stable than both their ML counterparts^{20,21,28} and the previously proposed BL- α borophene.²⁹ More importantly, such BL- α^+ borophenes²⁶ composed of interwoven zigzag boron triple chains (BTCs) shared by conjoined BL B₇₂ hexagonal prisms proved to well reproduce the experimentally measured STM images and Moire patterns of the supported BL borophenes on Ag(111),²⁹ evidencing their existence in experiments.

Locating the most stable structures of medium-sized boron clusters beyond B₈₀ has been proved to be a challenging task in chemistry and materials science. The first fullerene-like boron cluster I_h B₈₀ theoretically proposed in 2007 was later proved to be much less stable than its amorphous core-shell C_1 B₈₀ counterparts obtained via extensive global minimum (GM) searches at the DFT level.³⁰⁻³⁴ Similarly, extensive CALYPSO searches showed that an incomplete core-shell C_1 B₈₄ was much more favored in thermodynamics over its previously reported quasi-planar, core-shell, cage-like, and tubular counterparts.³⁵⁻⁴⁰ Icosahedral-B₁₂ stuffing appeared to effectively improve the stabilities of fullerene-like B_{84} - B_{116} , with a core-shell C_s B₁₁₂, recently predicted to be the most stable core-shell boron cluster in the size range with an icosahedral B_{12} core at the center.^{41,42} However, there have been no BL boron species proposed or reported to date in this size range in the literature, with medium-sized BL B_n nanoclusters containing one or multiple conjoined B72 BL hexagonal prisms at the center as BL stacks of the experimentally observed quasi-planar $C_{6\nu}$ B₃₆ remaining unknown in both experiments and theory.

Based on extensive global searches and manual structural constructions augmented with DFT calculations, we report in this work a series of medium-sized 3D aromatic BL boron clusters B_{84} - B_{98} (I-VIII) which appear to be the most stable isomers of the systems reported to date, with effective interlayer B-B σ bonds formed as "nails" to bind the top and bottom layers together. The BL structural motif in B_{96} (VII) with a B₇₂ BL hexagonal prism at the center can be employed to construct the AA-stacked bilayer B_{128} (IX), B_{214} (X), B_{260} (XI), B_{372} (XII), and B_{828} (XIII) which can be viewed as embryos or fragments of the recently reported most stable semiconducting freestanding $BL-\alpha^+$ bilayer borophenes and quasi-freestanding bilayer borophenes on Ag(111) consisting of conjoined B₇₂ BL hexagonal prisms in either AA or AB mode, indicating a viable bottom-up approach from medium-sized bilayer boron nanoclusters to 2D bilayer borophene nanomaterials.

2. Theoretical procedure

Global searches on B_{84} , B_{86} , B_{88} , B_{90} , B_{92} , B_{94} , B_{96} , and B_{98} were performed using both the TGMin2 program⁴³ and

Minima Hopping algorithms,⁴⁴ in conjunction with extensive manual structural constructions based on the previously predicted BL B48-B72. 12,23-25 Low-lying isomers were firstly re-optimized at the PBE0/6-31G(d) level, with vibrational frequencies being checked to ensure that all isomers obtained were true minima of the systems. The relative energies were further refined for the first two lowest-lying isomers at both PBE0/6-311+G(d)^{45,46} and TPSSh/6-311+G(d).⁴⁷ Detailed chemical bonding analyses were performed using the adaptive natural density partitioning (AdNDP) approach.⁴⁸⁻⁵⁰ Iso-chemical shielding surfaces (ICSSs)^{51,52} of the concerned species were generated employing the Multiwfn 3.7 code⁵³ and visualized using the visual molecular dynamics (VMD) software.⁵⁴ The IR and Raman spectra of the high-symmetry $C_{2\nu}$ B₈₆ (II) and $C_{2\nu}$ B₉₆ (VII) were simulated at PBE0/6-31G(d) and their UV-vis absorption spectra were calculated using the time-dependent density functional method (TD-DFT-PBE0).^{55,56} All the above calculations were performed using the Gaussian09 package.57 Nucleus-independent chemical shifts (NICS)^{58,59} were calculated at the geometrical centers of the concerned BL systems. Born-Oppenheimer molecular dynamics (BOMD) simulations were performed on B₈₆ (II) and B₉₆ (VII) at 1000 K and 700 K for 30 ps, respectively, using the software suite CP2K⁶⁰ with the GTH-PBE pseudopotential and DZVP-MOLOPT-SR-GTH basis set for boron. The cohesive energies per atom of the BL clusters and 2D BL borophenes in Fig. 5 were calculated using the Vienna *ab initio* simulation package (VASP)^{61,62} within the framework of the projector-augmented wave (PAW) pseudopotential method^{63,64} and PBE generalized gradient approximation (GGA),⁶⁵ with their band structures and projected densities of states (PDOS) obtained at the more reliable Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional level.⁶⁶

3. Results and discussion

3.1. Structures and stabilities

We started from B₈₄, which is one of the most concerned neutral boron clusters extensively studied in the literature. Yang et al.³⁸ reported in 2010 an amorphous core-shell C_1 B₈₄ with a partially encapsulated icosahedral B12 core which appeared to be much more stable than its previously reported "inner" I_h (B₁₂@B₁₂@B₆₀), ^{36,37} "outer" I_h (B₁₂@B₆₀@B₁₂), two-, three-, and four-ring tubular isomers,³⁵ and D_{2h} cage-like counterparts. Kumar et al.³⁹ proposed in 2015 a quasi-planar $C_{2\nu} \alpha$ -B₈₄ with four evenly distributed hexagonal holes which was found to be more favored in energy over its previously reported core-shell C_1 isomer. More recently, based on global searches using the particle swarm optimization algorithm implemented in the CALYPSO package, Ma et al.40 proposed in 2018 an amorphous core-shell C_1 B₈₄ as the putative global minimum of B₈₄ which appeared to be more stable than quasiplanar $C_{2\nu}$ α -B₈₄. Surprisingly and encouragingly, extensive TGmin and Minima Hopping global searches starting from manually constructed BL B84 "seeds" based on the previously originated BL B48-B72 12,22-24 performed in this work indicate

that the bilayer $C_1 B_{84}$ (I) (¹A) with two staggered B_6 hexagonal holes on the top and bottom layers is much more stable in thermodynamics than its previously reported isomers in other structural motifs. With five effective interlayer B-B σ-bonds formed between inward-bulked boron atoms on the top and bottom layers around the B_6 hexagonal holes, B_{84} (I) lies 2.92 eV, 3.40 eV, 3.78 eV, and 4.44 eV lower in energy than the previously reported core-shell C1 B84,40 core-shell C1 B84,38 quasiplanar ML $C_{2\nu}$ B₈₄,³⁹ and tubular $C_{2\nu}$ B₈₄³⁹ at the PBE0/6-311+G(d) level, respectively (Fig. 1 and Fig. S1a⁺). We also notice that the twelve lowest-lying isomers of B₈₄ within 2.58 eV with or without B₆ hexagonal holes all possess BL structures, with the second lowest-lying BL C_1 B₈₄ with two eclipsed hexagonal holes lying only 0.15 eV and 0.15 eV higher than B₈₄ (I) at PBE0/6-311+G(d) and TPSSh/6-311+G(d), respectively. B_{84} (I) is the first medium-sized boron cluster reported to date which contains a B₃₆ BL hexagonal prism (BLHP) at the center (Fig. 1) with two staggered B₆ hexagonal holes on the top and bottom layers.^{14,23–25} The formations of five interlayer B–B σ bonds between the top and bottom layers and two staggered

 ${\rm B}_6$ hexagonal holes on the top and bottom layers effectively help to stabilize the system.

Adding two B atoms to fill in the two staggered B_6 hexagonal holes on the top and bottom layers of B_{84} (I) generates high-symmetry BL $C_{2\nu}$ B_{86} (II) (¹A₁) which well inherits the five interlayer B–B σ -bonds from its parent cluster (Fig. 1 and Fig. S1b†). B_{86} (II) is 0.66 eV and 0.66 eV more stable than the second lowest-lying BL isomer C_1 B_{86} with two staggered B_6 hexagonal holes at PBE0/6-311+G(d) and TPSSh/6-311+G(d), respectively (Fig. S1b†). It contains a B_{38} BLHP at the center, without B_6 hexagonal holes on either the top or the bottom layer. The remaining eleven low-lying BL isomers obtained within 1.71 eV all contain one or two hexagonal holes on the top or bottom layers (Fig. S1b†).

With two more boron atoms being added to the right bottom corner of B_{86} (II), BL C_1 B_{88} (III) is produced which contains a B_{38} BLHP at the center lying only 0.01 eV and 0.01 eV higher than the second lowest-lying BL isomer with one hexagonal hole on the top at PBE0/6-311+G(d) and TPSSh/6-311+G(d), respectively (Fig. 1 and Fig. S1c†). The first two BL isomers



Fig. 1 Top and side views of the optimized BL $C_1 B_{84}$ (I), $C_{2\nu} B_{86}$ (II), $C_1 B_{90}$ (IV), $C_1 B_{92}$ (V), $C_1 B_{94}$ (V), $C_{2\nu} B_{96}$ (VII), $C_1 B_{98}$ (VIII), $C_2 B_{128}$ (IX), $D_{2h} B_{214}$ (X), $C_{2\nu} B_{260}$ (XI), and $D_{2h} B_{372}$ (XII), with the inward-buckled B atoms interconnected by interlayer B–B σ bonds colored in blue, B_{36} or B_{38} BL hexagonal prisms at the center of I–VIII highlighted in black dotted circles, B_{72} BL hexagonal prisms at the center of VII and IX–XII surrounded in purple dotted circles, and the hexagonal holes on the bottom layers highlighted in green dotted circles.

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are practically iso-energetic species which may coexist in experiments. B₈₈ (**III**) with five effective interlayer B–B σ -bonds proves to be much more stable (by 6.77 eV) than the high-symmetry quasi-planar ML $C_{3\nu} \alpha$ -B₈₈ with three hexagonal holes at PBE0/6-311+G(d) (Fig. S1c†). The other twelve low-lying isomers within 1.51 eV all have BL structures with a B₃₆ or B₃₈ BLHP at the center.

The most stable BL C_1 B₉₀ (**IV**) can be obtained by adding a B_6 hexagonal window to $C_1 B_{84}$ (4) (Fig. 1 and Fig. S1b[†]) on the upper end, similar to the situation in BL $C_2 B_{54}^{23}$ which was constructed from D_{2h} B₄₈ by forming an additional B₆ hexagonal window on the upper side. B_{90} (IV) with a B_{36} BLHP at the center and two staggered B₆ hexagonal holes on the top and bottom layers possesses six interlayer B-B σ-bonds to effectively stabilize the system (Fig. S1d[†]). Followed by thirteen BL lowest-lying isomers within 1.62 eV, C_1 B₉₀ (IV) is only 0.03 eV, 0.05 eV, and 0.20 eV more stable than the second, third, and fourth lowest-lying isomers in different stacking modes at PBE0/6-311+G(d), respectively (Fig. S1d[†]). Remarkably, our BL B_{90} (IV) with six interlayer B-B σ bonds lies much lower than the previously reported three-ring tubular (TRT) $C_1 B_{90}$,³⁵ quasi-planar C1 B90, and core-shell C1 B90 obtained in this work by 5.46 eV, 7.60 eV, and 8.44 eV at PBE0/6-311+G(d), respectively.

The most energetically favored BL C_1 B₉₂ (**V**) originates from B₉₀ (**IV**) by adding two B atoms to the system to form a B₅ pentagonal window at the right bottom corner, with six interlayer B–B σ bonds between the top and bottom layers and two staggered hexagonal holes on the structural surface (Fig. S1e†). It is followed by eleven lowest-lying BL species in different stacking modes within 1.56 eV, with the second lowest-lying isomer being only 0.2 eV and 0.1 eV higher than B₉₂ (**V**) at PBE0/6-311+G(d) and TPSSh/6-311+G(d), respectively (Fig. S1e†).

Ten low-lying BL isomers within 1.79 eV are obtained for B_{94} at PBE0/6-31G(d) (Fig. S1f†). The most stable BL C_1 B_{94} (VI) with six interlayer B–B σ bonds can be obtained by adding a B_4 rhombus over the B_6 hexagonal window on the upper end of B_{90} (2) (Fig. 1 and Fig. S1f†), with the two staggered B_6 hexagonal holes being well retained on the cage surface. The first two lowest-lying BL isomers lying within 0.04 eV at PBE0/6-311+G(d) can be viewed as iso-energetic isomers (Fig. S1f†).

The AA-stacked $C_{2\nu}$ B₉₆ (VII) is another high-symmetry BL species mainly concerned in this work. It is the first B_n cluster big enough to contain a complete B₇₂ BLHP at the center effectively stabilized by seven interlayer B–B σ bonds between the top and bottom layers (of which six serving as the edges of the B₃₆ inner BLHP and one going across the geometrical center in the vertical direction), with the interlayer bonding intensity³² of u = 1/5.29. Such an off-centered $C_{2\nu}$ bilayer structure appears to be much more stable (by 7.78 eV) than the AAstacked C_1 B₉₆ (10) isomer with two hexagonal holes at the center which possesses four interlayer B–B bonds at PBE0/6-31G(d) (Fig. S1g†). The eight low-lying isomers of B₉₆ within 2.38 eV all possess BL structures with seven interlayer B–B σ bonds between the inward-buckled atoms on the top and bottom layers. Remarkably, B₉₆ (VII) is much more stable than the previously reported severely distorted core–shell I_h B₉₆,⁴² quasi-planar C_1 B₉₆, core–shell C_1 B₉₆, cage-like C_1 B₉₆, and triple-ring tubular C_1 B₉₆³⁵ by 7.40, 8.55, 9.77, 10.70, and 11.44 eV at PBE0/6-31G(d), respectively (Fig. S1g†).

Adding two more B atoms to $C_{2\nu}$ B₉₆ (VII) produces BL C_1 B₉₈ (VIII) which is the first boron BL boron cluster containing three hexagonal holes on the top and bottom layers. It is 0.07 eV and 0.10 eV more stable than the second close-lying BL isomer C_1 B₉₈ at PBE0/6-311+G(d) and TPSSh/6-311+G(d), respectively (Fig. S1h[†]), followed by seven BL isomers within 1.95 eV. More interestingly, B₉₈ (VIII) lies 4.46 eV and 6.59 eV lower than the previously reported distorted core–shell C_1 B₉₈⁴² and quasi-planar $C_s \alpha$ -B₉₈³⁸ at PBE0/6-311+G(d), respectively, demonstrating again the huge advantage of the bilayer structures over other structural motifs in this size range.

The AA-stacked bilayer structural motif in $C_{2\nu}$ B₉₆ (VII) with an off-centered B_{72} BLHP is firstly extended to C_2 B_{128} (IX) which contains a C2 B72 BLHP unit at the center with two hexagonal holes on the top and bottom layers. B_{128} (IX) turns out to be the first BL boron cluster with ten effective interlayer B-B σ bonds evenly distributed between the top and bottom layers within the central B72 BLHP as an AA-stack of two quasi-planar $C_{6\nu}$ B₃₆.¹⁷ Lying within 0.17 eV with its nine BL counterparts, B_{128} (IX) appears to be much more stable (by 1.99 eV) than the previously reported core-shell C_{2h} B₁₂₈⁴² (Fig. S1i†). With the interlayer bonding intensity of u = 1/3.7, B_{128} (IX) has exactly the same number of interlayer B-B σ bonds as that in each B₇₂ BLHP unit in both the most stable freestanding $BL-\alpha^+$ borophenes and quasi-freestanding BL- α^+ borophenes on Ag(111) in AA and AB modes which are composed of interwoven zigzag boron triple chains shared by conjoined B72 BLHPs with the optimum interlayer bonding intensity of u = 1/4.^{26,27} Such a bilayer structural "gene" can be readily "cloned" to the AAstacked BL D_{2h} B₂₁₄ (**X**), $C_{2\nu}$ B₂₆₀ (**XI**), D_{2h} B₃₇₂ (**XII**), and D_2 B₈₂₈ (XIII) which possess two, three, seven, and nineteen conjoined B₇₂ BLHPs at the center with nineteen, twenty-four, and thirty, and eighty interlayer B-B σ bonds, respectively (Fig. 1 and Fig. S2[†]). The BL structural motif can be extended to infinity in two dimensions to form two-dimensional bilayer borophenes. BL B₁₂₈ (IX), B₂₁₄ (X), B₂₆₀ (XI), B₃₇₂ (XII), and B₈₂₈ (XIII) and their close-lying AB-stacked configurational isomers with one or multiple conjoined B72 BLHPs can thus be viewed as embryos or fragments of both the most stable freestanding BL- α^+ borophenes in a vacuum and quasi-freestanding BL- α^+ borophenes on the Ag(111) substrate in either AA or AB mode confirmed by experiments, unveiling a bottom-up approach from medium-sized bilayer boron nanoclusters to two-dimensional bilayer borophene nanomaterials.

To evaluate the relative stabilities of the $B_{84}-B_{98}$ series, we calculated their cohesive energies per atom $E_{\rm coh} = (E_n - nE_{\rm B})/n$, second-order energy differences $\Delta^2 E = (E_{2(n-1)} + E_{2(n+1)}) - 2E_{2n}$ and HOMO–LUMO energy gaps $\Delta E_{\rm gap} = E_{\rm LUMO} - E_{\rm HOMO}$ in different structural motifs at PBE0/6-311+G(d) as shown in Fig. 2 and Table 1. As clearly shown in Fig. 2a, compared with their previously reported core–shell, planar, tubular, and cage-like isomers, the BL species possess universally the highest



Fig. 2 (a) Cohesive energies per atom of the $B_{84}-B_{98}$ clusters in different structural motifs at the PBE0/6-311+G(d) level: bilayer (red circles), core-shell (black squares), planar (green triangles), tubular (blue inverted triangles), and cage-like (pink rhombuses). (b) Variations of HOMO-LUMO energy gaps (ΔE_{gap}) and (c) second-order energy differences ($\Delta^2 E$) with cluster size in bilayer $B_{84}-B_{98}$ species.

Table 1 Calculated minimum vibrational frequencies v_{min} (cm⁻¹), HOMO-LUMO energy gaps ΔE_{gap} (eV), cohesive energy per atom E_{coh} (eV per atom), NICS (ppm) values at the geometry centers, and numbers of effective interlayer B-B σ bonds N_{B-B} for the bilayer B₈₄-B₉₈ series (I-VIII)

B _n	$\left(\mathrm{cm}^{-1} \right)^{a}$	${\Delta E_{ m gap}\over m (eV)}^b$	$E_{\rm coh}^{\ b}$ (eV per atom)	NICS ^b (ppm)	N _{B-B}
$C_1 B_{84}$	126.30	1.74	-5.565	-13.03	5
$C_{2\nu} B_{86}$	84.66	1.57	-5.566	-24.29	5
$C_1 B_{88}$	73.45	1.27	-5.558	-23.98	5
$C_1 B_{90}$	115.36	1.47	-5.570	-18.05	6
$C_1 B_{92}$	108.57	1.20	-5.565	-9.74	6
$C_1 B_{94}$	117.55	1.41	-5.581	-8.58	6
$C_{2\nu} B_{96}$	90.87	1.73	-5.596	-50.21	7
$C_1 B_{98}$	94.11	1.38	-5.597	-49.31	7

^{*a*} At the PBE0/6-31G(d) level. ^{*b*} At the PBE0/6-311+G(d) level.

 $E_{\rm coh}$ values in the whole size range between B₈₄ and B₉₈, with $E_{\rm coh}$ increasing from -5.565 eV per atom in BL C_1 B₈₄ (I) to -5.597 eV per atom in C_1 B₉₈ (VIII) (Table 1). Fig. 2b and c collectively reveal that both the HOMO-LUMO energy gaps $\Delta E_{\rm gap}$ and second-order energy differences $\Delta^2 E$ of B₈₄-B₉₈ show the same variation trends, with C_1 B₈₄ (I), C_1 B₉₀ (IV), and $C_{2\nu}$ B₉₆ (VII) as three local maxima with $\Delta E_{\rm gap} = 1.74$, 1.47, and 1.73 eV and $\Delta^2 E = 0.089$, 0.056, and 0.047, respectively, and C_1 B₈₈ (III) and C_1 B₉₂ (V) as two local minima lying in between (Table 1), generally in line with the $E_{\rm coh} \sim n$ curve in Fig. 2a. BL C_1 B₈₄ (I), C_1 B₉₀ (IV), and $C_{2\nu}$ B₉₆ (VII) may thus be tentatively viewed as "magic number" boron clusters in the size range between B₈₄ and B₉₈.

The BL B_{84} – B_{98} species discussed above also turn out to be highly dynamically stable during extensive BOMD simulations, as demonstrated in the cases of high-symmetry $C_{2\nu}$ B_{86} (II) and $C_{2\nu}$ B_{96} (VII) in Fig. S4† which have the small average root-mean-square-deviations of RMSD = 0.15 and 0.12 Å and maximum bond length deviations of MAXD = 0.79 and 0.66 Å at 1000 K and 700 K, respectively, similar to the situations in the previously reported BL B_{48} – B_{72} $^{12,23-25}$ series. No lower-lying isomers were observed during MD simulations in 30 ps.

3.2. Bonding pattern and 3D aromaticity analyses

To better interpret the high stability of these BL structures, we performed detailed AdNDP bonding analyses on $C_{2\nu}$ B₉₆ (**VII**) and C_2 B₁₂₈ (**IX**) as shown in Fig. 3 and $C_{2\nu}$ B₈₆ (**II**) as shown in Fig. S3.† As clearly indicated in Fig. 3a, the off-centered $C_{2\nu}$ B₉₆ (**VII**) possesses 117 σ bonds in the first row with the occu-



Fig. 3 AdNDP bonding patterns of (a) $C_{2\nu} B_{96}$ (VII) and (b) $C_2 B_{128}$ (IX).

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pation numbers between ON = 1.65 and 1.96|e|, including 7 2c-2e interlayer B-B σ-bonds between fourteen inward-buckled B atoms on the top and bottom layers, 44 2c-2e B-B σ-bonds on the periphery, 56 3c-2e in-plane σ -bonds, and 10 4c-2e inplane σ -bonds on the top and bottom layers. The remaining 27 pairs of electrons form the π -bonding system over the bilayer surface in the second and third rows, including 12 5c-2e π -bonds at the six corners, 4 9c-2e π -bonds on the top layer, 4 8c-2e π -bonds on the bottom layer, 1 8c-2e π -bonds on the upper end, and 6 18c-2e π bonds with ON = 1.83|*e*| around the two hexagonal holes on the top and bottom layers, with an overall symmetry of $C_{2\nu}$. Remarkably, the 3 18c–2e π bonds on the top layer and 3 18c–2e π bonds on the bottom layer over the hexagonal holes follow the 4n + 2 aromatic rule (n = 1) and render local π aromaticities in the system, similar to the situation in dually π -aromatic ML $C_{6\nu}$ B₃₆¹⁷ which has two cocentric π systems over the hexagonal hole at the center.

The slightly distorted C_2 B₁₂₈ (IX) exhibits a similar bonding pattern (Fig. 3b). It contains the first row 10 2c-2e interlayer B-B σ-bonds, 45 2c-2e B-B σ-bonds on the peripherv, and 88 3c-2e in-plane σ -bonds and 4 4c-2e in-plane σ bonds on the top and bottom layers. The corresponding π system in the second and third rows includes 12 5c-2e π -bonds at the six corners, 8 8c-2e π -bonds on the left and right, 4 9c-2e π -bonds on the upper and down ends, and 6 $28c-2e \pi$ bonds with ON = 1.81-1.92|e| on the top and bottom layers around two B₆ hexagonal holes. Similar to the situation in B_{96} (VII), the 3 28c-2e π bonds on the top layer and 3 28c-2e π bonds on the bottom layer follow the 4n + 2 aromatic rule (n = 1) and render local π aromaticities in B₁₂₈ (IX) on both the top and bottom layers. As shown in Fig. S3,† a similar bonding pattern exists in $C_{2\nu}$ B₈₆ (II) which also exhibits local π aromaticities over the two central B-filled B₇ hexagons on both the top and bottom layers. The delocalized π -aromatic bonding patterns in these BL nanoclusters are in line with the π -bonding models of both the AA- and ABstacked aromatic freestanding BL- α^+ borophenes which possess one delocalized 12c-2e π bond over each B₆ hexagonal hole in 2D periodicity.²⁶

The $\sigma + \pi$ double delocalization bonding patterns unveiled above render 3D aromaticity in the BL medium-sized boron clusters concerned in this work, as evidenced by their calculated negative NICS values of NICS = -50.21 to -8.58 ppm at the geometrical centers (Table 1). The iso-chemical shielding surfaces (ICSSs) based on the calculated NICS-ZZ components^{51,52} of (b) $C_{2\nu}$ B₈₆ (II), (c) $C_{2\nu}$ B₉₆ (VII), and (d) C_2 B_{128} (IX) are collectively shown in Fig. 4, in comparison with those of the experimentally known 3D aromatic D_{2h} B₄₈.¹² As clearly indicated in Fig. 4, the chemical shielding areas with negative NICS-ZZ values cover the whole space inside the BL cages and areas within about 1.0 Å above the cage surface in the vertical direction, while the chemical de-shielding areas with positive NICS-ZZ values are mainly distributed in belt-like areas on the waist of the BL cages in the horizontal direction, well indicating that these medium-sized BL boron clusters are 3D aromatic in nature.



Fig. 4 Calculated iso-chemical shielding surfaces (ICSSs) of (b) $C_{2\nu} B_{86}$ (II), (c) $C_{2\nu} B_{96}$ (VII), and (d) $C_2 B_{128}$ (IX) compared with that of (a) $D_{2h} B_{48}$, with the corresponding NICS-ZZ components being indicated. Yellow regions stand for chemical shielding areas, while green areas represent chemical de-shielding areas.

3.3. Simulated IR, Raman, and UV-Vis spectra

We computationally simulate the IR, Raman, and UV-Vis spectra of $C_{2\nu}$ B₈₆ (II) and $C_{2\nu}$ B₉₆ (VII) at the PBE0/6-31G(d) level to facilitate their future spectral characterization. As shown in Fig. S5,[†] B_{86} (II) exhibits four major IR active peaks at 984 (b₂), 1160 (b₂), 1185 (b₂), and 1286 (b₂) cm⁻¹, while B₉₆ (VII) exhibits three strong IR peaks at 925 (b_2) , 997 (b_2) , and 1455 (a_1), respectively. The major Raman active peaks of B_{86} (II) appear at 231 (a_1), 306 (a_1), 395 (a_1), 708 (a_1), 1142 (a_1), 1168 (a_1), and 1287 (a_1) cm⁻¹, while B_{96} (VII) shows three strong Raman peaks at 328 (a_1) , 1176 (a_1) , and 1233 (a_1) cm⁻¹, respectively. The low wavenumber vibrational peaks at 272.2 $(a_1) \text{ cm}^{-1}$ in B_{86} (II) and 249.3 $(a_1) \text{ cm}^{-1}$ in B_{96} (VII) represent typical radial breathing modes (RBMs) of the two BL cages. The simulated UV-Vis spectrum of $C_{2\nu}$ B₈₆ (II) exhibits strong absorption peaks at 384 (¹B₁), 385 (¹A₁), 471 (¹B₁), and 582 $({}^{1}B_{1})$ nm, while $C_{2\nu}$ B₉₆ (VII) shows major UV-vis absorptions at 360 (¹A₁), 439 (¹B₂), 617 (¹B₂), and 692 (¹A₁) nm, respectively.

3.4. The bottom-up approach from bilayer boron nanoclusters and bilayer borophenes

To further rationalize the bottom-up approach from BL boron nanoclusters to BL borophenes, we compare the calculated cohesive energies per atom $E_{\rm coh}$ of all the reported BL B_n clusters at PBE in the size range between B48 and B830 with the corresponding values of the most stable freestanding ML α -sheet,¹⁹ close-lying AA- and AB-stacked BL- α^+ borophenes,²⁶ the thermodynamically most stable α and and β -rhombohedral boron allotropes³ at the same theoretical level. As clearly shown in Fig. 5, the cohesive energies per atom of BL B_n clusters increase almost monotonously with cluster size, from $E_{\rm coh}$ = -5.820 eV in D_{2h} B₄₈ with one B₃₈ BLHP at the center to $E_{\rm coh} = -5.984, -6.051, -6.064,$ and -6.116 eV per atom in C_2 B₁₂₈ (IX), $C_{2\nu}$ B₂₆₀ (XI), D_{2h} B₃₇₂ (XII), and D_2 B₈₂₈ (XIII) with one, three, seven, and nineteen conjoined B72 BLHPs, respectively. Among the large BL boron clusters, B_{260} (XI) with $E_{coh} = -6.051$ eV per atom has almost the same cohesive energy as that of the most stable ML α -sheet



Fig. 5 Variation of the cohesive energies per atom of bilayer $B_{48}-B_{830}$ clusters (I–XIII) (red) at the PBE level, compared with the corresponding values of the most stable ML α -sheet (blue), AA-stacked (black) and AB-stacked (purple) freestanding BL- α^+ borophenes, and 3D α -(green) and β -rhombohedral (orange) boron allotropes at the PBE level.

 $(E_{\rm coh} = -6.055 \text{ eV per atom})$, while both bilayer B₃₇₂ (**XII**) and B₈₂₈ (**XIII**) which have exceeded the ML α -sheet in cohesive energies lie between the ML α -sheet and the close-lying AA-stacked ($E_{\rm coh} = -6.234 \text{ eV per atom}$) and AB-stacked ($E_{\rm coh} = -6.237 \text{ eV per atom}$) BL- α^+ borophenes, indicating a continuing increasing trend of BL B_n clusters in stabilities with increasing cluster sizes to approach the up-limit of BL- α^+ bilayer borophenes. As anticipated, both bilayer boron nanoclusters and 2D bilayer borophenes are obviously less stable than 3D α - and β -rhombohedral bulk boron allotropes with $E_{\rm coh} = -6.573$ and -6.533 eV per atom, respectively.

The calculated projected density of states (PDOS) of the (a) C_1 B₈₄ (I), (b) $C_{2\nu}$ B₈₆ (II), and (c) $C_{2\nu}$ B₉₆ (VII) BL clusters are compared with that of (d) the most stable freestanding AAstacked $BL-\alpha^+$ borophene²⁵ in Fig. 6 at the HSE06 level to show their relationship with electronic properties. The overall PDOS feature of these BL clusters resembles that of the BL- α^+ borophene closely, with their HOMO-LUMO energy gaps (ΔE_{gap} = 0.929-1.042) falling within the vicinity of the indirect band gap (0.952 eV) of the AA-stacked BL- α^+ borophene near the Fermi level and the total DOSs primarily contributed by B 2p_z orbitals as a result of the interlayer B-B σ bonds originated mainly from p_z-p_z overlapping. The valence bands of the 2D BL- α^+ borophenes correspond to the occupied delocalized π orbitals of the conjoined B72 BLHPs, while their conducting bands mainly originate from the unoccupied delocalized π systems of the conjoined B72 BLHPs composed of B 2p2 contributions.

4. Conclusions

In summary, extensive DFT calculations performed in this work indicate that BL B_{84} – B_{98} (I–VIII) are the most stable isomers of the systems reported to date in comparison with their previously reported isomers in other structural motifs. The high stability of these BL species mainly originates from their effective interlayer B–B σ -bonds and universal $\sigma + \pi$ double delocalization bonding pattern. The BL structural



Fig. 6 Calculated projected densities of states (PDOS) of (a) $C_1 B_{84}$ (I), (b) $C_{2\nu} B_{86}$ (II), (c) $C_{2\nu} B_{96}$ (VII), and (d) A–A stacked BL- α^+ borophene at the HSE06 level, with the HOMO–LUMO energy gaps of the BL clusters and the band gap of AA-stacked BL- α^+ borophene indicated in eV.

motif in $C_{2\nu}$ B₉₆ (VII) can be readily extended to BL B₁₂₈ (IX), B₂₁₄ (X), B₂₆₀ (XI), and B₃₇₂ (XII) with one or multiple conjoined B₇₂ BLHPs at the center which are the embryos of the most stable semiconducting freestanding BL- α^+ borophenes and quasi-freestanding BL- α^+ borophenes on Ag(111) consisting of infinite conjoined B₇₂ BLHPs. The bottom-up approach achieved in this work presents a rational structural growth pattern from medium-sized BL boron nanoclusters to BL- α^+ borophenes which are semiconducting in nature due to the formation of optimum interlayer B–B σ -bonding interactions. How such a 2D bilayer bottom-up approach transfers to 3D bottom-up mechanisms based on icosahedral-B₁₂ cages to form bulk boron allotropes remains an open question to answer in boron chemistry.

Conflicts of interest

There are no conflicts to declare.

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