B$_{12}$F$_n^{0/-}$ ($n = 1–6$) series: when do boron double chain nanoribbons become global minima?\(^\dagger\)

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We present an extensive density-functional and wave function theory study of partially fluorinated B$_{12}$F$_n^{0/-}$ ($n = 1–6$) series, which show that the global minima of B$_{12}$F$_n^{0/-}$ ($n = 2–6$) are characterized to encompass a central boron double chain (BDC) nanoribbon and form stable B$_2$F$_2$ groups at the corresponding BDC corner when $n = 3$, but the B$_{12}$F$_0^{0/-}$ system maintains the structural feature of the well-known quasi-planar C$_{60}$ B$_{12}$. When we put the spotlight on B$_{12}$F$_n^{0/-}$ species, our single-point CCSD(T) results unveil that albeit with the 3D icosahedral isomers not being their global minima, C$_2$ B$_{12}$F$_6$ (6.1, 1A) and C$_1$ B$_{12}$F$_6^{−}$ (12.1, 2A) as typical low-lying isomers of 0.60 and 1.95 eV more stable than their 2D planar counterparts D$_{3h}$ B$_{12}$F$_6$ (6.7, 1A) and C$_{2v}$ B$_{12}$F$_6^{−}$ (12.7, 2A), respectively, alike to B$_{12}$H$_6^{0/-}$ species in our previous work. Detailed bonding analyses suggest that B$_{12}$F$_n^{0/-}$ ($n = 2–5$) possess ribbon aromaticity with $\pi$ plus $\pi$ double conjugation along the BDC nanoribbon on account of their total number of $\sigma$ and $\pi$ delocalized electrons conforming the common electron configuration ($\pi^2\sigma^1$-$\sigma^2$$^\dagger$). Furthermore, the simulated PES spectra of the global minima of B$_{12}$F$_n^{0/-}$ ($n = 1–6$) monoanions may facilitate their experimental characterization in the foreseeable future. Our work provides new examples for ribbon aromaticity and powerful support for the F/H/Au/BO analogy.

1. Introduction

As the prototype of electron deficient elements characterized with multicenter bonds in planar networks or cage-like structures, boron clusters have attracted almost unprecedented attention over the past decade in the area of cluster science. The joint photoelectron spectroscopy (PES) and high-level theoretical calculations have indicated that the global minima for B$_n^-$ exhibit planar or quasi-planar structures up to $n = 38$,\(^\ddagger\)\(^\dagger\) as well as B$_n^{0/-}$ that are unparalleled in any other elements in the periodic table. Furthermore, cationic B$_n^{+}$ and neutral B$_n$ clusters also were revealed to favor 2D structures at least up to $n = 16$\(^4\) and $n = 20$\(^5\), respectively.

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\(^\ddagger\) Electronic supplementary information (ESI) available: Low-lying isomers of B$_n$F$_n^{0/-}$ ($n = 1–6$), with their relative energies indicated in eV at CCSD(T)/B3LYP and B3LYP/6-311++G(d,p) (in italic) levels; low-lying isomers of B$_n$F$_n$ ($n = 1–6$), with their relative energies indicated in eV at CCSD(T)/B3LYP and B3LYP/6-311++G(d,p) (in italic) levels; simulated photoelectron spectra based on the global minimum C$_1$ B$_{12}$F$^{-}$ (7, 1A$^\dagger$) (a) and its low-lying isomer C$_1$ B$_{12}$F$^{-}$ (7.1, 1A) (b). The simulations were done by fitting the distribution of the calculated VDOSs with unit-area Gaussian functions of 0.1 eV halfwidth. See DOI: 10.1039/c7cp05658c

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3D icosahedral structures and the fluorinated boronene D_{inh} B_{12}F_{n} is energetically more favorable than its 3D counterpart at the B3LYP level.\textsuperscript{7}

However, according to our previous calculation experiences,\textsuperscript{10,17} B3LYP often overestimates the stability of 2D structures and the energetics from B3LYP deviate substantially from CCSD(T) for boron-based clusters. Moreover, to the best of our knowledge, few reports on the B_{12}F_{n} (n < 12) system have been published up to now, except for some study on polyboron fluorides B_{3}F_{m} (n \leq m)^{15,18} and fluoro-borane B_{12}H_{12-n}F_{n} \textsuperscript{2-} \textsuperscript{19,20} Initially, the nucelophilic substitution of hydrogen atoms in B_{12}H_{12} \textsuperscript{2-} by F up to B_{12}F_{12} \textsuperscript{2-} was studied.\textsuperscript{19} According to the structures of B_{12}H_{12-n}F_{n} \textsuperscript{2-} (n = 2, 4, 5, 6, 7, 8, 10, 12) and the results of quantum chemistry calculations of the charge distribution on relevant various isomers, \textit{closo}-B_{12}H_{12} \textsuperscript{2-} behaves in these substitution reactions as a spatial aromatic system. Furthermore, the fully fluorinated boron hydride B_{12}F_{12} \textsuperscript{2-} was synthesized firstly, which is similar to B_{12}H_{12} \textsuperscript{2-} and also possesses an icosahedral structure.\textsuperscript{19} Then the preparation and spectroscopic characterization of B_{12}H_{11}F_{2} \textsuperscript{2-} were reported.\textsuperscript{21} Owing to the reactivity of metal ions in M^{n+}(B_{12}F_{12}) salts similar to the corresponding gas-phase M^{n+} cation, B_{12}F_{12} \textsuperscript{2-}, that is called a superweak anion, creates new opportunities for delivery of highly reactive catalysts.\textsuperscript{22,23} Based on the above discussion, it is thus essential and of interest to systematically investigate partially fluorinated boron hydride B_{12}F_{n} (n < 12) species from the fundamental point of view for their application in the future.

Here we undertake an extensive density-functional theory (DFT) and coupled-cluster with single, double, and perturbative triple excitation [CCSD(T)] study on the partially fluorinated boron hydride B_{12}F_{n} \textsuperscript{0/-} (n = 1–6). Apart from the B_{12}F_{0/-} clusters maintaining the structural feature of quasi-planar C_{3v} B_{12},\textsuperscript{6} all B_{12}F_{n} \textsuperscript{0/-} (n = 2–6) species are confirmed to possess boron double chain (BDC) nanoribbon configurations. With more F atoms being attached to B_{12}, the true global minima of B_{12}F_{n} \textsuperscript{0/-} (n = 2–6) are characterized to consist of the central BDC unit with BF_{2} groups, rather than the alleged quasi-planar based on C_{3v} B_{12} or icosahedral configurations. Moreover, the 2D quasi-planar D_{inh} B_{12}F_{4} (6, 1, 1\textsuperscript{A}) is 0.60 eV less stable than the corresponding 3D icosahedral C_{2} B_{12}F_{4} (6, 1, 1\textsuperscript{A}) at the CCSD(T)/B3LYP level. For the sake of exploring the properties of these BDCs with BF_{2} groups, we analyzed their canonical molecular orbital (CMO) and adaptive natural density partitioning (AdNDP)\textsuperscript{24} and revealed that all of C_{2v} B_{12}F_{2} (2, 4\textsuperscript{A} \textsuperscript{A}), C_{s} B_{12}F_{3} (9, 4\textsuperscript{A} \textsuperscript{A}), C_{1} B_{12}F_{4} (4, 4\textsuperscript{A}) and C_{s} B_{12}F_{5} (11, 4\textsuperscript{A}) are ribbon aromatic systems in nature with 2(n + 1)\pi plus 2\pi delocalized electrons, whose total counting overall conform to the (n\pi + 2) Hückel rule. Meanwhile, the simulated photoelectron spectra (PES) of the global minima of B_{12}F_{n} \textsuperscript{0/-} (n = 1–6) may not only facilitate future experimental characterization, but also provide strong support for the F/H/Au/BO analogy.

2. Theoretical methods

Initial structures of B_{12}F_{n} \textsuperscript{0/-} (n = 1–6) clusters were constructed based on quasi-planar B_{12},\textsuperscript{6} icosahedral B_{12}H_{12} \textsuperscript{2-} \textsuperscript{7-12} and the corresponding B_{12}H_{n} \textsuperscript{+} cations (n = 0–12).\textsuperscript{12} More extensive and unbiased global minimum searches were performed utilizing the Basin-Hopping procedure.\textsuperscript{25} We optimized and analyzed the vibrational frequencies of B_{12}F_{n} \textsuperscript{0/-} (n = 1–6) series using the hybrid DFT method of B3LYP\textsuperscript{26,27} with the 6-311+G(d,p)\textsuperscript{28} basis set as implemented in the Gaussian 09 program.\textsuperscript{29} An additional single-point coupled cluster method including triple excitation (CCSD(T))\textsuperscript{30} calculations with the 6-311+G(d,p) basis set was used at the B3LYP/6-311+G(d,p) geometries to further evaluate the relative energies. Our calculations proved that B3LYP indeed overestimates the stability of 2D quasi-planar isomers of B_{12}F_{n} \textsuperscript{0/-} (n = 1–6) and its energetics are substantially inconsistent with CCSD(T). As a comparison, we also optimized some representative isomers of B_{12}F_{n} \textsuperscript{0/-} (n = 1–6) clusters at the PBE1PBEx.\textsuperscript{30} The AdNDP analyses were performed to elucidate the bonding patterns using the Multiwfn program.\textsuperscript{31} AdNDP bonding patterns in Fig. 5 were visualized using the Molekel 5.4 software.\textsuperscript{32} Excitation energies of the neutral B_{12}F_{n} (n = 1–6) species were calculated with the time-dependent DFT (TD-DFT) method\textsuperscript{33} at the ground-state structures of the corresponding B_{12}F_{n} \textsuperscript{-} (n = 1–6) monoanions. The adiabatic detachment energies (ADEs) of the anions were calculated as the energy differences between the anions and the corresponding neutrals at their ground-state structures, whereas the vertical detachment energies (VDEs) were calculated as the energy differences between the ground states of the anions and the ground states of neutrals at the anionic geometries.

3. Results and discussion

3.1 The global minima and low-lying isomers of B_{12}F_{n} \textsuperscript{0/-} (n = 1–6)

Combining B3LYP and CCSD(T) calculations, we obtain the global minima of B_{12}F_{n} \textsuperscript{0/-} (n = 1–6) and summarize their structures, symmetries, electronic states and relative energies in eV at CCSD(T)/B3LYP and B3LYP in Fig. 1. Both their typical 2D quasi-planar isomers based on C_{2v} B_{12} and 3D icosahedral isomers are also depicted in Fig. 1. The top 8 low-lying isomers of B_{12}F_{n} (n = 1–6) and B_{12}F_{n} (n = 1–6) clusters are summarized in Fig. S1–S6 and S7–S12 in the ESI,\textsuperscript{†} respectively. The energy differences of B_{12}F_{n} \textsuperscript{0/-} (n = 1–6) between global minima and 2D quasi-planar isomers and between global minima and 3D icosahedral isomers are shown in Fig. 2. And the CCSD(T)/B3LYP results are mainly discussed, unless stated otherwise.

As shown in Fig. 1, we start from the global minima of B_{12}F_{n} \textsuperscript{0/-}, C_{1} B_{12}F_{1} (1, 1\textsuperscript{A}), C_{1} B_{12}F_{2} (7, 1\textsuperscript{A}), which are almost iso-energetically isomers of C_{1} B_{12}F_{2} (1, 1\textsuperscript{A}) and C_{1} B_{12}F_{2} (7, 1\textsuperscript{A}) with the energy differences of less than 0.09 eV, respectively, all of them are derived from the global minima of the B_{12} cluster with the F atom bonded to its periphery, similar to B_{12}X\textsuperscript{0/-} (X = H/Au/BO).\textsuperscript{34} Among alternative low-lying structures identified for B_{12}F_{0/-} in Fig. S1 and S7 (ESI),\textsuperscript{1} the BDC isomers C_{1} B_{12}F_{4} (1.5, 2\textsuperscript{A}), C_{1} B_{12}F_{7} (7.5, 1\textsuperscript{A}) are 0.58 and 0.75 eV higher in energy, respectively. The well-known 3D icosahedral isomers C_{1} B_{12}F_{1} (1.7, 1\textsuperscript{A}) and C_{1} B_{12}F_{2} (7.7, 1\textsuperscript{A}) lie even higher above their global minima.
It is clear in Fig. 1 that the global minima \( C_{2v} B_{12} F_2 \) \((2.1, 1A_1)\) and \( C_{2v} B_{12} F_2^- \) \((8.5, 2A_2)\) all possess BDC nanoribbon structures, closely resembling the global minima of \( B_{12} H_2^0/C_0 \) and \( B_{12}(BO)_{2}\) \({35–37}\).

The corresponding icosahedral \( D_{5d} B_{12} F_2 \) \((2.6, 1A_1)\) and \( C_s B_{12} F_2^- \) \((8.7, 2A_0)\) are much less stable with a relative energy of 1.56 eV, respectively. The \( C_s B_{12} F_2 \) \((2.7, 1A')\) and \( C_s B_{12} F_2^- \) \((8.6, 2A')\) isomers with a central BDC \( B_{11} \) unit and one BF\(_2\) group bonded to its periphery lie 1.51 and 0.91 eV higher in energy than their corresponding global minima, separately. Other isomers of \( B_{12} F_2^0/C_0 \) are also displayed in Fig. S2 and S8 (ESI†). When another F atom is introduced to \( B_{12} F_2^0/C_0 \), \( C_s B_{12} F_3 \) \((3.0, 2A_0)\) and \( C_s B_{12} F_3^- \) \((9.0, 1A_0)\), accompanied by the structural feature of BDC with one F atom and one BF\(_2\) group bonding to the central \( B_{11} \) unit, turn out to be their global minima, respectively.

Fig. 1 Optimized global-minimum structures, typical 2D quasi-planar and 3D icosahedral isomers at the B3LYP level for (a) \( B_{12} F_n \) and (b) \( B_{12} F_n^- \) \((n = 0 – 6)\). The symmetry, electronic state and relative energy in eV at CCSD(T)//B3LYP, B3LYP/6-311++G(d,p) \(\text{italic}\) and CCSD(T)//PBE1PBE (in curly brackets, for some isomers) are labeled under each structure. Boron is in blue, and F is in light green.
However, as shown in Fig. S3 and S9 (ESI†), the BDC planar nanoribbons without BF₂ groups Cₓ B₁₂F₃ (3.1, 1A) and Cₓ B₁₂F₃⁻ (9.1, 1A) are proved to be the second candidates with the relative energy values of 0.31 and 0.74 eV. Among higher isomers are 2D quasi-planar C₁ B₁₂F₃ (3.5, 2A) and C₁ B₁₂F₃⁻ (9.7, 1A), situating at 0.79 and 1.35 eV above Cₓ B₁₂F₃ (3, 2A) and Cₓ B₁₂F₃⁻ (9, 1A), respectively. Similarly, the typical icosahedral isomers Cₓ B₁₂F₃ (3, 2A) and Cₓ B₁₂F₃⁻ (9.6, 1A) are all at least 0.74 eV above their global minima. It is a remarkable fact that 3D icosahedral Cₓ B₁₂F₃ (3, 2A) and Cₓ B₁₂F₃⁻ (9.6, 1A) have been found to be more stable than 2D quasi-planar C₁ B₁₂F₃ (3.5, 2A) and C₁ B₁₂F₃⁻ (9.7, 1A) at the CCSD(T) level, respectively. In fact, C₁ B₁₂F₃ (3.5, 2A) and C₁ B₁₂F₃⁻ (3.7, 1A) can be viewed as isoenergetic isomers.

With more F atoms being attached to B₁₂⁻⁻, the global minima of B₁₁F₄⁻⁻ are similar to that of B₁₂⁻⁻. Our sufficient calculations show that C₁ B₁₂F₄ (4, 1A) and C₁ B₁₂F₄⁻ (10, 2A) are the most stable structures with the BDC B₁₁ unit which is bonded with two F atoms directly and one BF₂ group by one B–B bond at its periphery. Compared with other low-lying isomers with a BDC motif for the B₁₂F₄ cluster in Fig. S4 (ESI†), both C₂B₁₂F₄ (4.6, 1A) consisting of the BDC B₁₀ unit with two BF₂ groups and C₂B₁₂F₄ (4.7, 1A) composed of the BDC B₁₂ unit with four B–F bonds are at least 0.67 eV above the global-minimum C₁ B₁₂F₄ (4, 1A). The popular 2D quasi-planar isomer C₂B₁₂F₄ (4.4, 1A) and 3D icosahedral isomer C₁ B₁₂F₄ (4.5, 1A) are 0.58 and 0.65 eV higher in energy, respectively. For B₁₂F₄⁻, the Cₓ B₁₂F₄ (10.1, 2A) BDC isomer with two BF₂ groups is found to be nearly degenerate with the global-minimum C₁ B₁₂F₄⁻ (10, 2A) and the energy difference is merely 0.09 eV. C₂ B₁₂F₄⁻ (10.6, 2A), as the other available BDC isomer, lies 1.53 eV higher in energy. As indicated in Fig. 1, the 3D icosahedral C₁ B₁₂F₄⁻ (10.5, 2A) becomes more stable than the 2D quasi-planar C₁ B₁₂F₄⁻ (10.7, 2A) in spite of both of them being at least 1.00 eV less stable than the global-minimum Cₓ B₁₂F₄⁻ (10, 2A). With one more F atom being attached to B₁₂⁻⁻, the global minimum searches in conjunction with full structural optimizations found that Cₓ B₁₂F₅ (5, 2A) and Cₓ B₁₂F₅⁻ (11, 1A) are the global minima of B₁₂F₅⁻⁻ species, which are derived from the BDC B₁₀ unit with two BF₂ groups and one F atom bonding to its periphery. The fact is that the global minima of B₁₂F₅⁻⁻ closely resemble the counterparts of B₁₂F₄⁻⁻. As shown in Fig. 1 and Fig. S5, S12 (ESI†), both the 3D icosahedral C₁ B₁₂F₅ (5.1, 2A) and Cₓ B₁₂F₅⁻ (11.2, 1A) nearly become the lowest-lying isomers and lie 0.28 and 0.36 eV higher in energy, respectively. However, the 2D quasi-planar C₁ B₁₂F₅ (5.6, 2A) and C₁ B₁₂F₅⁻ (11.6, 1A) are proved to be 1.31 and 1.58 eV less stable than their corresponding global minima. When the total number of F atoms reaches six, we found that the true minima C₁ B₁₂F₆ (6, 1A) and C₁ B₁₂F₆⁻ (12, 2A) stem from the global minima C₁ B₁₂F₅ (5, 2A) and C₁ B₁₂F₅⁻ (11, 1A) by means of breaking a B–B bond in the central B₁₀ unit and forming a new BF₂ group. Surprisingly, the well-known 3D icosahedral or called cage-like Cₓ B₁₂F₆ (6.1, 1A) and Cₓ B₁₂F₆⁻ (12.1, 2A) turn out to be the nearest isomers with the relative energy values of 0.14 and 0.10 eV, respectively. In contrast, the popular 2D quasi-planar D₁₂h B₁₂F₆ (6.7, 1A) and Cₓ B₁₂F₆⁻ (12.7, 2A) are confirmed to be the most unstable isomers among the top 8 low-lying candidates, which are 0.74 and 2.05 eV above their corresponding global minima. As shown in Fig. 1, we also found that the relative energy orders of B₁₂F₄⁻⁻ (n = 1–4) and B₁₂F₄⁻⁻ (n = 1–5) species at the PBE1PBE level are almost consistent with that at CCSD(T)//B3LYP. Moreover, except for B₁₂F₃⁻⁻ (8.7) (its symmetry is Cₓ at B3LYP but C₁ at PBE1PBE), the geometries of B₁₂F₄⁻⁻ (n = 1–6) species at PBE1PBE well agree with their counterparts at B3LYP. However, the PBE1PBE results show that the 2D quasi-planar C₁ B₁₂F₃⁻⁻ (9.7, 1A) is slightly more stable than the 3D icosahedral C₁ B₁₂F₃⁻⁻ (9.6, 1A). The 3D icosahedral C₁ B₁₂F₅ (5.1, 2A) is more stable than the BDC nanoribbon Cₓ B₁₂F₃ (5, 2A) and 2D quasi-planar C₁ B₁₂F₅ (5.6, 2A) at the PBE1PBE level, with the relative energy values of 0.33 and 1.10 eV, respectively. Similarly, the 3D icosahedral B₁₂F₄⁻⁻ species are proved to be the most stable isomers with respect to their BDC nanoribbon and 2D quasi-planar isomers. After the single point calculations for Bₓ B₁₂F₄⁻⁻, Bₓ B₁₂F₅ and Bₓ B₁₂F₅⁻⁻ species based on their optimized structures at PBE1PBE, we verified that the relative energies from CCSD(T)//PBE1PBE are in good agreement with the CCSD(T)//B3LYP results,
as displayed in Fig. 1. Therefore, there is no large effect on their relative energies obtained using the B3LYP or PBE1PBE method as long as the single-point CCSD(T) calculations are performed at the corresponding geometries eventually. In addition, the 3D icosahedral \( \text{C}_3 \, \text{B}_{12} \text{F}_2 \) (6, 1, \( ^1 \text{A} \)) is more stable than BDC nanoribbon \( \text{C}_1 \, \text{B}_{12} \text{F}_2 \) (6, \( ^1 \text{A} \)) and 2D quasi-planar \( D_{3h} \, \text{B}_{12} \text{F}_2 \) (6.7, \( ^1 \text{A} \)) at the MP2/6-311++G(d,p) level, with the relative energy values of 0.90 and 1.15 eV, respectively. However, at the CCSD(T)//MP2 level, the BDC nanoribbon \( \text{C}_1 \, \text{B}_{12} \text{F}_2 \) (6, \( ^1 \text{A} \)) is proved to be 0.12 and 0.74 eV more stable than 3D icosahedral \( \text{C}_3 \, \text{B}_{12} \text{F}_2 \) (6, \( ^1 \text{A} \)) and 2D quasi-planar \( D_{3h} \, \text{B}_{12} \text{F}_2 \) (6.7, \( ^1 \text{A} \)), respectively. It can be seen that the CCSD(T)/MP2 results are also well consistent with the CCSD(T)//B3LYP results.

For a better comparison with the representative 2D quasi-planar and 3D icosahedral isomers of the \( \text{B}_{12} \text{F}_n \) (\( n = 1–6 \)) system, we plotted relative energy difference curves as a function of the number of F atoms \( n \). As clearly shown in Fig. 2, no matter what species, either \( \text{B}_{12} \text{F}_n \) or \( \text{B}_{12} \text{F}_n^- \), both the variation trend of the energy difference between global minima and 2D quasi-planar isomers and the relevant trend between global minima and 3D icosahedral isomers at the CCSD(T) level are in good agreement with that at the B3LYP level, and it can be described as the relative stabilities of 3D icosahedral isomers gradually increase but the relative stabilities of 2D quasi-planar ones decrease step by step, along with the increasing of F atoms. Compared with the CCSD(T) and B3LYP results, there is no doubt that B3LYP distinctly overestimates the relative energy values of 2D and 3D isomers. For \( \text{B}_{12} \text{F}_n \) (\( n = 1–6 \)), the 2D quasi-planar isomers are more stable than their corresponding 3D icosahedral isomers at the B3LYP level, however, as can be seen from the figure at more accurate CCSD(T) level, when the number of F atoms equals to 3–4, 3D \( \text{C}_3 \, \text{B}_{12} \text{F}_2 \) (3.7, \( ^2 \text{A} \)) and \( \text{C}_6 \, \text{B}_{12} \text{F}_4 \) (4.5, \( ^1 \text{A} \)) turn out to be energetically competitive with 2D \( \text{C}_1 \, \text{B}_{12} \text{F}_3 \) (3.5, \( ^2 \text{A} \)) and \( \text{C}_{2n} \, \text{B}_{12} \text{F}_4 \) (4.4, \( ^1 \text{A} \)), respectively, and when \( n \) is greater than 4, 3D isomers become more stable. For the \( \text{B}_{12} \text{F}_n^- \) (\( n = 1–6 \)) system, similar to the case of \( \text{B}_{12} \text{F}_n \) at B3LYP, the 2D quasi-planar \( \text{B}_{12} \text{F}_n^- \) (\( n = 1–5 \)) are proved to be at least 0.14 eV more stable than their 3D icosahedral isomers, only the 3D icosahedral \( \text{C}_1 \, \text{B}_{12} \text{F}_6^- \) (12.1, \( ^2 \text{A} \)) turns out to be favored in energy (0.32 eV) over the 2D quasi-planar \( \text{C}_{2n} \, \text{B}_{12} \text{F}_6^- \) (12.7, \( ^2 \text{A} \)). Nevertheless, we further calculated the relative energy of \( \text{B}_{12} \text{F}_6^- \) using the more accurate CCSD(T) method at B3LYP structures and found that the 3D and 2D structures of \( \text{B}_{12} \text{F}_6^- \) can be practically viewed as iso-energetic isomers. When \( n > 3 \), the 3D icosahedral isomers are energetically more favored than their 2D quasi-planar counterparts. Based on the above theoretical calculation results, the fact is B3LYP undisputedly overestimates the stability of the 2D quasi-planar structures of \( \text{B}_{12} \text{F}_n \) (\( n = 1–6 \)).

3.2 \( \text{B}_{12} \text{F}_n^- \) (\( n = 1–6 \)): quasi-planar vs. icosahedral isomers

The 2D quasi-planar and 3D icosahedral \( \text{B}_{12} \text{H}_n \) (\( n = 1–6 \)) clusters have been investigated in our previous work, and herein we have extended the research to \( \text{B}_{12} \text{F}_n \) (\( n = 1–6 \)) by using F instead of H atoms, although they are not the true minima on their potential energy surfaces. As a matter of fact, a similar work about \( \text{B}_{12} \text{F}_n \) has been reported at the B3LYP level, however, it is indispensable to further verify its accuracy according to our calculation experiences for boron clusters.

As a comparison, we also plotted the total energy difference between 2D quasi-planar and 3D icosahedral isomers at the CCSD(T) level is in good agreement with that at B3LYP and our calculation results on the variation trend of the energy difference between 2D and 3D isomers of \( \text{B}_{12} \text{F}_n \) (\( n = 1–6 \)) at the B3LYP level in Fig. 3(a) are in good accord with the reported results for \( \text{B}_{12} \text{F}_n \) clusters, which show that the 2D quasi-planar clusters with up to six H atoms are more stable than the corresponding 3D icosahedral structures. However, our CCSD(T) results verify that the 2D quasi-planar clusters of \( \text{B}_{12} \text{F}_n \) (\( n = 1, 2 \)) are proved to be 1.78 and 0.89 more stable than their 3D icosahedral structures, respectively. The 2D quasi-planar and 3D icosahedral isomers of \( \text{B}_{12} \text{F}_n \) (\( n = 3, 4 \)) can be viewed as energetically competitive configurations with a 0.05–0.07 eV energy difference. Conversely, the 2D quasi-planar structures of \( \text{B}_{12} \text{F}_n \) (\( n = 5, 6 \)) are 1.03 and 0.60 eV less stable than their corresponding 3D icosahedral isomers, respectively. Therefore, a 2D-to-3D structural transition actually occurs at \( n = 5 \) in partially fluorinated \( \text{B}_{12} \text{F}_n \) (\( n = 1–6 \))
series, while a similar structural reverse occurs at \( n = 4 \) in the \( \text{B}_{12}\text{H}_n \) system.\(^{10} \) Considering that B3LYP overestimates the robustness of 2D quasi-planar configurations as it takes into account the electron correlation energy less sufficient than CCSD(T), hereinto we mainly discuss the CCSD(T) results for \( \text{B}_{12}\text{F}_n^- \) \(( n = 1–6 \) species in Fig. 3(b). Our calculation results establish that \( \text{B}_{12}\text{F}_n^- \) preferentially forms 2D quasi-planar structures in the size range between \( n = 1–2 \), whereas \( \text{B}_{12}\text{F}_n^- \) \(( n = 3–6 \) tend to form 3D icosahedral cages. A stability conversion actually occurs from \( \text{B}_{12}\text{F}_3^- \), with the distorted 3D icosahedral \( \text{C}_n \text{B}_{12}\text{F}_3^- \) \(( 9.6, 1\text{A}^\text{a} ) \) being 0.08 eV more stable than the corresponding 2D quasi-planar \( \text{C}_1 \text{B}_{12}\text{F}_3^- \) \(( 9.7, 1\text{A}^\text{a} ) \) at the CCSD(T) level. Similar to \( \text{B}_{12}\text{H}_n^o \), both the 2D planar \( \text{D}_{3h} \text{B}_{12}\text{F}_6 \) \(( 6.7, 1\text{A}^\text{a} ) \) and \( \text{C}_{2v} \text{B}_{12}\text{F}_6^- \) \(( 12.7, 2\text{A}^\text{a} ) \) are just high-lying local minima of the system and can also be safely ruled out from experiments under normal conditions. Therefore, it is unfeasible to design larger boron-based nanomaterials starting from 2D planar \( \text{B}_{12}\text{F}_6^o \) building blocks. Simultaneously, we found that the partial fluorination cannot reverse the relative stability of the corresponding 2D quasi-planar boron hydride counterparts.

### 3.3 Chemical bonding analyses

In order to shed further light on the stability of the global minima of \( \text{B}_{12}\text{F}_n^- \) \(( n = 1–6 \) ), we analyzed their delocalized \( \pi \) and \( \sigma \) CMOs and performed chemical bonding analysis using AdNDP in the Multiwfn program\(^{31} \) that represents the electronic structure of a molecule in terms of \( n \)-centre two-electron bonds \((n\text{-}2\text{e}) \) with \( n \) ranging from one to the total number of atoms in the molecule. Because the AdNDP method handles only closed-shell systems, we chose \( \text{C}_{2h} \text{B}_{12}\text{F}_2 \) \(( 2, 1\text{A}_g \) ), \( \text{C}_s \text{B}_{12}\text{F}_3^- \) \(( 9, 1\text{A}^a \) ), \( \text{C}_1 \text{B}_{12}\text{F}_4 \) \(( 4, 1\text{A} \) ), \( \text{C}_2 \text{B}_{12}\text{F}_5^- \) \(( 11, 2\text{A}^a \) ), and \( \text{C}_1 \text{B}_{12}\text{F}_6 \) \(( 6, 1\text{A} \) ) with 25, 29, 32, 36, and 39 electron pairs for the purpose of bonding analyses, respectively. The delocalized \( \pi \) and \( \sigma \) CMOs are presented in Fig. 4 and the detailed AdNDP results are summarized in Fig. 5.

As revealed from the CMOs in Fig. 4, the BDC nanoribbon \( \text{C}_{2h} \text{B}_{12}\text{F}_2 \) \(( 2, 1\text{A}_g \) ), \( \text{C}_s \text{B}_{12}\text{F}_3^- \) \(( 9, 1\text{A}^a \) ), \( \text{C}_1 \text{B}_{12}\text{F}_4 \) \(( 4, 1\text{A} \) ) and \( \text{C}_s \text{B}_{12}\text{F}_5^- \) \(( 11, 2\text{A}^a \) ) all possess three delocalized \( \pi \) CMOs and two delocalized \( \sigma \) CMOs, which conform the common electron configuration \(( \pi^2{n+1})\sigma^{2n} \) of ribbon aromaticity\(^{17} \) and the total number of delocalized electrons amounts to the \(( 4n + 2 \) ) Hückel rule. The key mechanism of ribbon aromaticity is that the optimal delocalized \( \pi \) and \( \sigma \) bondings within the \( \text{B}_3 \) or \( \text{B}_4 \) unit effectively reduce the intramolecular electrostatic repulsion in the BDC nanoribbon configuration. The ribbon aromatic system satisfies the common electron configuration of \(( \pi^{2n+1})\sigma^{2n} \) with \( (n + 1) \) delocalized \( \pi \) CMOs and \( n \) delocalized \( \sigma \) CMOs. Therefore, the total number of delocalized electrons amounts to \( 2(n + 1)n + 2n\sigma \) that is the \(( 4n + 2 \) ) Hückel rule. In fact, all delocalized \( \pi \) and \( \sigma \) CMOs in the BDC nanoribbons originate from the overlaps between \( \text{B} \text{2p} \) atomic orbitals of neighboring atoms in the single \( \text{B} \) chains. Moreover, the delocalized \( \pi \) and \( \sigma \) CMOs are highly mixed in sequence based on their energies, into which the available valence electrons in the system successively fill. When two electrons occupy a \( \pi \) CMO, the next two electrons would fill in a \( \sigma \) CMO. Because the ribbon aromaticity in the BDC structures may be conveniently achieved either by an appropriate number of \( \text{B} \) atoms, or by charging, or both of them, \( \text{C}_1 \text{B}_{12}\text{F}_6 \) \(( 6, 1\text{A} \) ) with a \( \text{B}_5 \) \( \text{BCD} \) unit does not belong to the ribbon.

![Fig. 4 Delocalized \( \pi \) and \( \sigma \) CMOs of the global-minima of \( \text{B}_{12}\text{F}_n \) \(( n = 2, 4, 6 \) ) and \( \text{B}_{12}\text{F}_n^- \) \(( n = 3, 5 \) ). The orbitals are aligned according to their shapes.](image-url)
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Aromatic system with two delocalized \( \pi \) CMOs (HOMO--1(a) and HOMO--4(a)) and two delocalized \( \sigma \) CMOs (HOMO(a) and HOMO--3(a)) which satisfies the Hückel 4\( n \) rule.

Detailed AdNDP analyses also unravel their bonding patterns in Fig. 5. Similar to \( \text{B}_{12} \text{H}_{2} \), \( \text{C}_{2n} \text{B}_{12} \text{F}_{2} (2, 1A_{g}) \) possesses two 2c-2e \( \sigma \)-bonds (ON = 2.00 [e]) along the peripheral B–B bonds, two 2c-2e \( \sigma \)-bonds with ON = 1.80 [e] and three 4c-2e \( \pi \)-bonds with ON = 1.80–1.81 [e] which form the unique \( \sigma \) plus \( \pi \) double conjugation and play critical roles in its stability. Owing to the existence of two \( F \) atoms, \( \text{B}_{12} \text{F}_{2} (2, 1A_{g}) \) also has six 1c-2e lone-pairs (ON = 1.85–1.99 [e]) around the \( F \) atoms. With the addition of \( F \) atoms, both \( C_{n} \text{B}_{12} \text{F}_{3} (9, 1A') \) and \( C_{1} \text{B}_{12} \text{F}_{4} (4, 1A') \) form one \( BF_{2} \) group at the corner of the central \( B_{11} \) unit and have similar bonding patterns. The \( BF_{2} \) group is a common structural unit with high stability, which has been observed repeatedly in the crystallographic experiment of polyboron fluorides.\(^{15,16,18}\) \( C_{n} \text{B}_{12} \text{F}_{3} (9, 1A') \) possesses nine 1c-2e lone-pairs with ON = 1.87–1.99 [e], three 2c-2e \( \sigma \)-bonds (ON = 2.00 [e]), twelve 2c-2e and 3c-2e \( \sigma \)-bonds (ON = 1.78–1.98 [e]) along the peripheral B–B bonds, two 4c-2e \( \pi \)-bonds with ON = 1.80 [e] and three 4c-2e \( \pi \)-bonds with ON = 1.80–1.81 [e] which form the unique \( \sigma \) plus \( \pi \) double conjugation and play critical roles in its stability.

Owing to the increasing of the \( F \) atom, \( \text{B}_{12} \text{F}_{4} (11) \) only adds three 1c-2e lone-pairs and one 2c-2e \( \sigma \)-bond in comparison with \( \text{B}_{12} \text{F}_{4} (4) \). It is obvious that all of \( \text{B}_{12} \text{F}_{2} (2), \text{B}_{12} \text{F}_{3} (9), \text{B}_{12} \text{F}_{4} (4) \) and \( \text{B}_{12} \text{F}_{5} (11) \) are ribbon aromatic systems, where regular \( \sigma \) versus \( \pi \) alternation of the delocalized electron clouds along the BDC nanoribbons contributes to their stability from the AdNDP analyses in Fig. 5. The electron clouds distribute almost evenly on each part of the BDC nanoribbons, which maintain the optimal delocalized \( \pi \) or \( \sigma \) bonding within the \( \text{B}_{3}/\text{B}_{4}/\text{B}_{5} \) units and effectively reduce the intramolecular electrostatic repulsion in the BDC systems. For \( C_{1} \text{B}_{12} \text{F}_{5} (6, 1A) \), it has eighteen 1c-2e lone-pairs with ON = 1.85–1.99 [e] on the six \( F \) atoms, six 2c-2e \( \sigma \)-bonds (ON = 2.00 [e]) and eleven 2c-2e and 3c-2e \( \sigma \)-bonds (ON = 1.74–1.96 [e]) around the peripheral B–B framework. The remaining one 3c-2e \( \sigma \)-bond with ON = 1.85 [e], one 4c-2e \( \sigma \)-bond with ON = 1.85 [e] and two 4c-2e \( \pi \)-bonds (ON = 1.71–1.79 [e]) form the \( \pi \) plus \( \sigma \) double conjugation along the BDC \( B_{6} \) unit but do not conform the electron counting rule of ribbon aromaticity.

Therefore, there are two reasons for the stability of the global minima of \( \text{B}_{12} \text{F}_{n}^{0/-} (n = 1–6) \). On one hand, the ribbon aromaticity of the BDC nanoribbon \( \text{B}_{12} \text{F}_{n}^{0/-} (n = 1–6) \) play a prominent role by means of reducing the intramolecular electrostatic repulsion to some extent. On the other hand, a mass of peripheral 2c-2e B-B \( \sigma \)-bonds exists in the BDC nanoribbons, which is an extremely vital stabilizing factor for planar boron clusters.

Fig. 5 The AdNDP bonding patterns of the global-minima of \( \text{B}_{12} \text{F}_{n} (n = 2, 4, 6) \) and \( \text{B}_{12} \text{F}_{n}^{-} (n = 3, 5) \).

\[ C_{n} \text{B}_{12} \text{F}_{n}^{+} (A_{g}) \quad \text{2x1c-2e lone-pairs ON=1.99[e]} \quad \text{2x1c-2e lone-pairs ON=1.92[e]} \]
\[ C_{n} \text{B}_{12} \text{F}_{n}^{+} (A') \quad 3x1c-2e lone-pairs ON=1.98-1.99[e] \quad 3x1c-2e lone-pairs ON=1.93-1.95[e] \]
\[ C_{n} \text{B}_{12} \text{F}_{n}^{-} (A_{g}) \quad 4x1c-2e lone-pairs ON=1.98-1.99[e] \quad 4x1c-2e lone-pairs ON=1.89-1.94[e] \]
\[ C_{n} \text{B}_{12} \text{F}_{n}^{-} (A') \quad 5x1c-2e lone-pairs ON=1.98-1.99[e] \quad 5x1c-2e lone-pairs ON=1.91-1.95[e] \]
\[ C_{n} \text{B}_{12} \text{F}_{n}^{+} (A_{g}) \quad 6x1c-2e lone-pairs ON=1.99[e] \quad 6x1c-2e lone-pairs ON=1.94[e] \]
\[ C_{n} \text{B}_{12} \text{F}_{n}^{+} (A') \quad 6x1c-2e lone-pairs ON=1.99[e] \quad 6x1c-2e lone-pairs ON=1.94[e] \]
3.4 Simulated photoelectron spectroscopy of the global minima of B_{12}F_n^− (n = 1–6)

To aid the future experimental characterization of B_{12}F_n^− (n = 1–6) global minima, we also calculated herein the adiabatic and vertical detachment energies (ADE and VDE) of the ground-state B_{12}F_n^− monoanions (n = 1–6) at TDDFT and simulated their photoelectron spectra. The simulated PES spectra are depicted in Fig. 6 and Fig. S13 (ESI†), where the spectra are constructed by fitting the distributions of 0.1 eV half-width and the electronic binding energies of the species well fall within the energy range of conventional excitation lasers (0–7 eV) in PES measurements.

The ADEs and VDEs of 2D quasi-planar C_s B_{12}F^- (7, 1A') and its iso-energetic isomer C_1 B_{12}F^- (7.1, 1A) that is similar to the global minima of B_{12}X^- (X = H/Au/BO)\(^{34}\) are predicted to be ADE = 3.92, 3.50 eV and VDE = 4.11, 3.68 eV, respectively, where the ADEs also represent the electron affinity (EAs) of C_s B_{12}F (1.3, 2A') and C_1 B_{12}F (1.1, 2A). It is more difficult to detach one

Fig. 6  Simulated photoelectron spectra based on the global minimum structures of B_{12}F_n^− (n = 1–6) series. The simulations were done by fitting the distribution of the calculated VDEs with unit-area Gaussian functions of 0.1 eV halfwidth.
electron from $C_s B_{12}F^-$ (7, 1'A), thus $C_s B_{12}F^-$ (7, 1'A) is electronically robust. In Fig. S13 (ESI†), the X-A gaps between the ground-state band (X) and the first excited-state band (A) of $C_s B_{12}F^-$ (7, 1'A) and $C_s B_{12}F^-$ (7.1, 1'A) are 0.44 and 0.91 eV, respectively. Thus, the simulated photoelectron spectrum suggests that the 2D quasi-planar $C_s B_{12}F^-$ (1, 1') is a more stable electronic structure and inert in chemistry. Similarly, the calculated ground state ADEs and VDEs for BDC $B_{12}F_{n-}$ ($n = 2–6$) series at the B3LYP/6-311++G(d,p) level are ADE = 3.06, 3.97, 3.28, 3.57, 3.40 eV and VDE = 3.22, 4.11, 3.48, 3.76, 3.60 eV, respectively. The ADEs of BDC $B_{12}F_{n-}$ ($n = 2–6$) corresponding to the EAs of their corresponding neutral species can be utilized to facilitate their future spectroscopic investigations. As shown in Fig. 6, the X–A gaps of $C_{2h} B_{12}F_{2-}$ (8, 2A) is 1.10 eV, extremely close to the gaps (0.91, 0.99, and 1.11 eV) of $C_1 B_{12}F^-$ (7.1, 1'A), $C_{s} B_{12}F_2$ (11, 1'A), and $C_{1} B_{12}F^-_6$ (12, 2A). However, the simulated PESs of $C_{s} B_{12}F^-_3$ (9, 1'A) and $C_{s} B_{12}F^-_4$ (10, 2'A) are also depicted in Fig. 6(c) and (d), which exhibit a small energy gap (0.36 and 0.53 eV) between the first and second detachment transitions at the TD-DFT level. We hope that the simulated spectra will facilitate future PES characterization of the global minima of $B_{12}F_{n-}$ ($n = 1–6$) by taking full advantage of their VDEs and difference of X–A gaps.

3.5 F/H/Au/BO analogy

Nowadays, there is abundant theoretical and experimental evidence to confirm the H/Au/BO analogy.34,37–40 In order to elucidate the validity of our theoretical prediction and explore the relationship between F and H/Au/BO, we compared the theoretical ADEs of $B_{12}X^- (X = F/H/Au/BO)$ systems at the B3LYP/6-311++G(d,p) level. It is worthwhile to state that similar to $B_{12}X^- (X = F/H/BO)$, the most stable $B_{12}Au^-_2$ also possesses a trans nanoribbon structure with two terminal Au bonding to the corners of the BDC $B_{12}$ unit. As demonstrated in Fig. 7, the ADEs gradually increase from H to Au, F and BO in $B_{12}X^- (X = 3h B_{12}F_6$ (6.7, 1'A) also has a high-lying local minimum on the potential energy surface and almost can be ruled out from experiments under normal conditions. Our extensive and unbiased global minimum searches confirmed that with the exception of $B_{12}F_0^- (n = 1–6)$ species and found that it is unfeasible to reverse the relative stability of boron hydride $B_{12}H_n$ ($n = 1–6$) clusters by taking advantage of partial fluorination. Similar to previously reported perfectly planar $D_{3h} B_{12}H_6$ which is called as aromatic borozene, the planar fluorinated $D_{3h} B_{12}F_6$ clusters (6.7, 1'A) also has a high-lying local minimum on the potential energy surface and almost can be ruled out from experiments under normal conditions. Our extensive and unbiased global minimum searches confirmed that with the exception of $B_{12}F_0^- (n = 1–6)$ species adopt BDC nanoribbon structures and start to form an extremely stable BF2 group from $n = 3$. Comparing their representative 2D quasi-planar and 3Dicosahedral isomers, a 2D-to-3D structural transformation occurs at $n = 5$ and $n = 3$ for $B_{12}F_4$ and $B_{12}F_6^-$ ($n = 1–6$) species, respectively. Bonding analyses reveal that the peripheral 2c-2e B–B σ-bonds and ribbon aromaticity play an indispensable role in stabilizing the $B_{12}F_0^-$ system. Our results also provide new cases for ribbon aromaticity that seems to be a general concept in nanoribbon systems. The simulated PES spectra of $B_{12}F_{n-}$ ($n = 1–6$) may not only facilitate further experimental and
computational explorations, but also provide convincing evidence for the F/H/Au/BO analogy.

Conflicts of interest
The authors declare no competing financial interest.

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