#### **ORIGINAL PAPER**



# Prediction of endohedral borafullerenes $X@B_{32}C_{36}$ (X = CH<sub>4</sub>, BH<sub>4</sub><sup>-</sup>, H<sub>2</sub>O, and NH<sub>3</sub>) with a $B_{32}C_{36}$ shell isovalent with $C_{60}$

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## Abstract

**Context** Inspired by the newly synthesized endohedral fullerene  $T \operatorname{CH}_4 @\operatorname{C}_{60}(1)$  and based on extensive density functional theory calculations, we predict herein a series of endohedral borafullerenes  $C_3 \operatorname{CH}_4 @\operatorname{B}_{32} \operatorname{C}_{36}(4)$ ,  $T \operatorname{BH}_4 @\operatorname{B}_{32} \operatorname{C}_{36}^{-}(5)$ ,  $C_1 \operatorname{H}_2 \operatorname{O} @\operatorname{B}_{32} \operatorname{C}_{36}(6)$ ,  $C_3 \operatorname{NH}_3 @\operatorname{B}_{32} \operatorname{C}_{36}(7)$ , and  $T \operatorname{C}_8 @\operatorname{B}_{32} \operatorname{C}_{36}^{2^-}(8)$  which possess a  $\operatorname{B}_{32} \operatorname{C}_{36}(3)$  shell isovalent with  $\operatorname{C}_{60}$ , with the neutral  $D_2 \operatorname{C}_8 @\operatorname{B}_{24} \operatorname{C}_{44}(9)$  obtained from  $\operatorname{C}_8 @\operatorname{B}_{32} \operatorname{C}_{36}^{2^-}(8)$  by symmetric C–B substitutions. Detailed adaptive natural density partitioning (AdNDP) bonding analyses and iso-chemical shielding surfaces (ICSSs) calculations indicate that these core–shell species are spherically aromatic in nature, rendering high stability to the systems. More interestingly, based on the calculated effective donor–acceptor interaction between LP(O)  $\rightarrow$  LV(B@B\_3C\_3) in H<sub>2</sub>O@B\_{32}C\_{36}(6), we propose the concept of boron bond (BB) in chemistry which is defined as the in-phase orbital overlap between an electronegative atom A as lone-pair (LP) donor and an electron-deficient boron atom with a lone vacant (LV) orbital as LP acceptor. A boron bond appears to possess about 20 ~ 30% of the bond dissociation energy of a typical A-B covalent bond.

**Methods** Extensive density functional theory investigations at the hybrid M06-2X-D3 and PBE0-D3 levels with the basis set 6-311 + G(d) were employed to fully optimize the structures of endohedral  $C_3 \text{ CH}_4@B_{32}C_{36}$  (4),  $T \text{ BH}_4@B_{32}C_{36}^-$  (5),  $C_1 \text{ H}_2 O@B_{32}C_{36}$  (6),  $C_3 \text{ NH}_3@B_{32}C_{36}$  (7),  $T C_8@B_{32}C_{36}^{-2-1}$  (8), and  $D_2 C_8@B_{24}C_{44}$  (9), with natural bonding orbital (NBO) and adaptive natural density partitioning (AdNDP) analyses performed to analyze the bonding patterns of the concerned species and the non-covalent interactions reduced density gradient (NCI-RDG) approach utilized to identify the types of the intramolecular non-covalent bonding interactions.

Keywords Fullerene · Borafullerenes · Density functional theory · Core-shell structures · Bonding patterns · Boron bonds

# Introduction

With the diameter of about 7 Å,  $C_{60}$  can encapsulate various kinds of metal ions and small molecules inside comfortably to form stable endohedral fullerenes like Gd@C<sub>60</sub>, H<sub>2</sub>@C<sub>60</sub>, HF@C<sub>60</sub>, H<sub>2</sub>O@C<sub>60</sub>, and CH<sub>4</sub>@C<sub>60</sub> [1–7]. As the closest neighbors of carbon in the periodic table, boron and nitrogen have been used as doping atoms to form borafullerenes and azafullerenes, respectively. Kroto and coworkers

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<sup>2</sup> Department of Chemistry, Xinzhou Normal University, Xinzhou 034000, China observed the first borafullerenes including  $C_{59}B$ ,  $C_{58}B_2$ , C<sub>57</sub>B<sub>3</sub>, C<sub>56</sub>B<sub>4</sub>, and C<sub>69</sub>B by atom-exchange in boron vapors, with higher doped borafullerenes  $C_{n-m}B_m$  (m > 1) predicted to be possible in experiments [8–10]. N-doped azafullerenes  $C_{59}N^+$  and  $C_{59}NH$  [11–13] and endohedral azafullerenes, Gd<sub>2</sub>@C<sub>79</sub>N, Y<sub>2</sub>@C<sub>79</sub>N, and Tb<sub>2</sub>@C<sub>79</sub>N have also been characterized in experiments [14, 15]. A series of U-doped endohedral borafullerenes U@C<sub>2n-1</sub>B (2n-1 = 27-59) were recently observed in gas-phase [16]. Jindal et. al. extended the borafullerene family to  $C_{60-n}B_n$  (n = 1-12) by first-principles theory calculations [17]. Jemmis et. al. investigated the stability of  $C_{50}B_{34}$  [ $C_2B_{10} + 12C_4B_2$ ] and  $C_{48}B_{36}^{2-}$  [ $B_{12}^{2-}$  + 12 $C_4B_2$ ] using the Wade's skeleton electron counting rules [18]. Based on extensive density functional theory (DFT) investigations, our group predicted the possibility of spherically aromatic borafullerenes  $C_{5h}$  $B_{20}C_{35}$ ,  $C_5 B_{20}C_{45}$ ,  $C_{5h} B_{20}C_{55}$ , and  $C_5 B_{20}C_{65}$  which are

isovalent with  $C_{50}$ ,  $C_{60}$ ,  $C_{70}$ , and  $C_{80}$  following the isolated  $B_4C_3$  hexagonal pyramid rule, respectively [19], icosahedral  $C_nB_{12-n}$ -stuffed mononuclear and binuclear borafullerenes and borospherenes (n = 0, 1, 2) with spherical aromaticity [20], and two-dimensional semiconducting  $B_4C_3$  monolayer isovalant with graphene [21]. However, investigations on  $CH_4$ -,  $BH_4^-$ -,  $H_2O$ -, or  $NH_3$ -doped endohedral borafullerenes, especially on the bonding patterns between the core and shell, have remained elusive in both experiments and theory to date.

Extensive DFT calculations performed in this work present the possibility of the endohedral borafullerenes T BH<sub>4</sub>@C<sub>60</sub><sup>-</sup> (2),  $C_3$  CH<sub>4</sub>@B<sub>32</sub>C<sub>36</sub> (4), T BH<sub>4</sub>@  $B_{32}C_{36}^{-}$  (5),  $C_1 H_2O@B_{32}C_{36}$  (6),  $C_3 NH_3@B_{32}C_{36}$  (7),  $TC_8@B_{32}C_{36}^{2-}(8)$  and  $D_2C_8@B_{24}C_{44}(9)$  with a perfect or slightly distorted  $(B_4C_3)_8C_{12}$  (3) shell isovalent with  $C_{60}$ . Detailed bonding pattern analyses indicate that these spherically aromatic core-shell species possess similar bonding patterns in different bond strengths. In particular, we define the concept of boron bonds in chemistry based on the effective donor-acceptor interaction between  $LP(O) \rightarrow LV (B@B_3C_3)$  in  $H_2O@B_{32}C_{36}(6)$  which appears to be similar to  $LP(O) \rightarrow BD^*$  (H–O) hydrogen bonds (HBs) in donor-acceptor bonding patterns but much weaker than an O-B covalent bond in bond dissociation energy.

## Computational methodology

The manually constructed borafullerene  $T B_{32}C_{36}$  (3) and endohedral borafullerenes  $C_3$  CH<sub>4</sub>@B<sub>32</sub>C<sub>36</sub> (4), T BH<sub>4</sub>@  $B_{32}C_{36}^{-}(5), C_1 H_2O@B_{32}C_{36}(6), C_3 NH_3@B_{32}C_{36}(7)$ , and  $T C_8 @B_{32}C_{36}^{2-}$  (8) were fully optimized in Fig. 1 at both the hybrid M06-2X [22] and PBE0 levels with 6-311+G(d)[23, 24] basis set using the Gaussian 16 program, with the D3 van der Waals corrections included [25]. Frequency calculations were performed to ensure that all low energy isomers obtained were true minima of the systems. To verify the dynamic stability of the concerned systems, extensive Born-Oppenheimer molecular dynamics (BOMD) simulations were performed on them at different temperatures for 30 ps using the CP2K program, with the GTH-PBE pseudopotential and DZVP-MOLOPT-SR-GTH basis set for boron, carbon, nitrogen, oxygen, and hydrogen [26]. Adaptive natural density partitioning (AdNDP) bonding pattern analyses were performed on them at M06-2X/6-31G(d) [27, 28]. Nucleus independent chemical shifts (NICSs) and iso-chemical shielding surfaces (ICSSs) were computed to reveal the spherical aromaticity of the concerned systems using the Multiwfn 3.8 software [29-32]. Natural bonding orbital (NBO) analyses were carried out utilizing the NBO 6.0 program at M06-2X/6-311G(d) [33]. The non-covalent interactions reduced density gradient (NCI-RDG) approach was used to explore the bonding nature and to identify the types of the intramolecular non-covalent



**Fig. 1** Optimized structures of  $T \operatorname{CH}_4 @ \operatorname{C}_{60}(1)$ ,  $T \operatorname{BH}_4 @ \operatorname{C}_{60}^-(2)$ ,  $T \operatorname{B}_{32}\operatorname{C}_{36}(3)$ ,  $C_3 \operatorname{CH}_4 @ \operatorname{B}_{32}\operatorname{C}_{36}(4)$ ,  $T \operatorname{BH}_4 @ \operatorname{B}_{32}\operatorname{C}_{36}^-(5)$ ,  $C_1 \operatorname{H}_2 \operatorname{O} @ \operatorname{B}_{32}\operatorname{C}_{36}(6)$ ,  $C_3 \operatorname{NH}_3 @ \operatorname{B}_{32}\operatorname{C}_{36}(7)$ ,  $T \operatorname{C}_8 @ \operatorname{B}_{32}\operatorname{C}_{36}^{2^-}(8)$ , and  $D_2 \operatorname{C}_8 @ \operatorname{B}_{24}\operatorname{C}_{44}(9)$  at both M06-2X/6-311 + G(d)-D3 and PBE0/6-311 + G(d)-D3 levels

bonding interactions using the Multiwfn program [34]. The visualization for the isosurfaces of various DFT functions was realized with VMD software [35]. The IR and Raman spectra of the concerned species were simulated at M062x/6-31G(d)-D3.

# **Results and discussions**

### **Structures and stabilities**

As indicated in Fig. 1, the experimentally observed CH<sub>4</sub>@ C<sub>60</sub> (1) has a perfect *T* symmetry with the calculated smallest vibration frequency of  $\nu_{min} = 261.17 \text{ cm}^{-1}$ , HOMO–LUMO gap of  $\Delta E_{gap} = 4.48 \text{ eV}$ , and CH<sub>4</sub>-C<sub>60</sub> core–shell interaction energies of  $E_c = 0.68 \text{ eV}$  at M06-2X-D3. Replacing CH<sub>4</sub> with BH<sub>4</sub><sup>-</sup> in 1 via isovalent substitution, the perfect *T* BH<sub>4</sub>@C<sub>60</sub><sup>-</sup> (2) were obtained with  $\nu_{min} = 178.86 \text{ cm}^{-1}$ ,  $\Delta E_{gap} = 4.43 \text{ eV}$ , and  $E_c = -1.75 \text{ eV}$ , indicating its high chemical stability (Table S1).

The optimized borafullerene  $T B_{32}C_{36}$  (3) with  $\nu_{\rm min} = 208.2 \text{ cm}^{-1}$  and  $\Delta E_{\rm gap} = 4.29 \text{ eV}$  was obtained by isovalent substitution of eight symmetrically distributed  $C_6$  hexagons in an  $I_h C_{60}$  with eight  $\eta^6$ -B-centered inwardbuckled B@B<sub>3</sub>C<sub>3</sub> hexagonal pyramids. Such a designed high-symmetry model molecule isovalent with C<sub>60</sub> with the cage diameter of 6.25 Å can also encapsulate  $CH_4$ ,  $BH_4^-$ ,  $H_2O_1$ , and  $NH_3$  inside to form the concerned endohedral  $C_3$  $CH_4@B_{32}C_{36}(4), TBH_4@B_{32}C_{36}^{-}(5), C_1H_2O@B_{32}C_{36}(6),$ and  $C_3 \text{ NH}_3 @B_{32}C_{36}$  (7) which all prove to be true minima of the systems without imaginary vibrational frequencies (see Table S1), with the calculated HOMO-LUMO gaps of  $\Delta E_{gap} = 5.26, 5.36, 4.34, and 4.46 eV and core-shell inter$ action energies of  $E_c = -0.77, -5.87, -1.66, \text{ and } -2.46 \text{ eV},$ respectively. To satisfy the dangling bonds on the eight B@  $B_3C_3$  units in  $B_{32}C_{36}$  (3), we introduce a  $C_8$  cube into the system to form the  $C_8@B_{32}C_{36}^{2-}(8)$  dianion which has a perfect T symmetry as a true minimum of the system. The dynamically highly stable  $D_2 C_8 @B_{24}C_{44}$  (9), a true minimum of the neutral with  $v_{\rm min} = 272.17$  cm<sup>-1</sup> and  $\Delta E_{\rm gap} = 5.97$  eV, can be obtained from  $C_8@B_{32}C_{36}^{2-}(8)$  by symmetric substitutions of eight tetracoordinate periphery  $\eta^4$ -B atoms in eight B<sub>3</sub>C<sub>3</sub> hexagons with eight periphery  $\eta^4$ -C atoms.

As shown in Fig. S1, extensive BOMD simulations indicate that  $T \text{ BH}_4 @ \text{C}_{60}^-$  (2),  $\text{B}_{32}\text{C}_{36}$  (3),  $C_3 \text{ CH}_4 @ \text{B}_{32}\text{C}_{36}$ (4),  $T \text{ BH}_4 @ \text{B}_{32}\text{C}_{36}^-$  (5),  $C_1 \text{ H}_2\text{O} @ \text{B}_{32}\text{C}_{36}$  (6),  $C_3 \text{ NH}_3 @$  $\text{B}_{32}\text{C}_{36}$  (7),  $T \text{ C}_8 @ \text{B}_{32}\text{C}_{36}^{-2^-}$  (8), and  $D_2 \text{ C}_8 @ \text{B}_{24}\text{C}_{44}$ (9) are all highly dynamically stable in 30 ps at 1200, 1300, 1000, 1300, 300, 1200, 800, and 1200 K, with the calculated average root-mean-square-deviations of RMSD = 0.06, 0.09, 0.08, 0.09, 0.04, 0.08, 0.07 and 0.09 Å and maximum bond length deviations of MAXD = 0.19, 0.32, 0.28, 0.32, 0.13, 0.27, 0.26 and 0.31 Å, respectively. There were no obvious bond breakages or structural distortions observed during the simulations.

#### **Electronic structures and bonding analyses**

To better understand the high stability of the concerned species, detailed AdNDP bonding analyses was performed on them in Fig. 2. As shown in Fig. 2(a) and (b),  $T \operatorname{CH}_4@C_{60}$ (1) and  $T BH_4 @C_{60}^{-}(2)$  possess the same bonding patterns on the  $C_{60}$  shell, with 4 2c-2e C-H  $\sigma$  bonds and 4 2c-2e B-H  $\sigma$  bonds inside the CH<sub>4</sub> and BH<sub>4</sub><sup>-</sup> cores, respectively. Similar to  $C_{60}$ ,  $T B_{32}C_{36}$  (3) has 42 2c-2e C–C and B-C  $\sigma$  bonds on the borafullene framework and 48 3c-2e B-B-C  $\sigma$  bonds on the eight equivalent  $B@B_3C_3$  units, with the remaining 60 valence electrons forming 6 localized 2c-2e C = C  $\pi$  bonds and 24 delocalized 7c-2e  $\pi$  bonds over eight equivalent B@  $B_3C_3$  units. As can be seen from Fig. 2(a), (b), (d), and (e), T  $CH_4@C_{60}(1), TBH_4@C_{60}^{-}(2), C_3CH_4@B_{32}C_{36}(4), and T$  $BH_4@B_{32}C_{36}^{-}(5)$  as isovalent systems possess similar bonding patterns, with the differences mainly occurring inside the cores, with the  $CH_4$  core in both  $CH_4@C_{60}(1)$  and  $CH_4@$  $B_{32}C_{36}$  (4) possessing 4 2c-2e C-H  $\sigma$  bonds, the BH<sub>4</sub><sup>-</sup> core in  $BH_4@C_{60}^{-}(2)$  having 4 2c-2e B-H  $\sigma$  bonds, while  $BH_4^{-}$  in  $BH_4@B_{32}C_{36}^{-}(5)$  having 4 3c-2e B-H-B hydrogen-bridgebonds delocalized between the core and shell with ON = 1.98lel. Such  $3c-2e \sigma$  interactions demonstrate the unique and non-negligible contributions of the  $\eta^6$ -B atoms in B@B<sub>3</sub>C<sub>3</sub> units to the core-shell interaction in  $BH_4@B_{32}C_{36}^{-}(5)$ which effectively enhance the core-shell interaction energy to  $E_c = -5.87$  eV, the largest in the series. The bonding patterns of the  $B_{32}C_{36}$  shell in both  $CH_4@B_{32}C_{36}$  (4) and T  $BH_4@B_{32}C_{36}^{-}(5)$  are consistent with that of borafullerene  $T B_{32} C_{36} (\mathbf{3}).$ 

As shown in Fig. 2(f) and (g), both  $C_1 H_2O@B_{32}C_{36}$  (6) and  $C_3 NH_3@B_{32}C_{36}$  (7) appear to inherit the  $\sigma$  and  $\pi$  bonding patterns of  $B_{32}C_{36}$  (3) over the  $B_{32}C_{36}$  shell. The  $H_2O$ core in  $H_2O@B_{32}C_{36}$  (6) has 1 1c-2e lone pair on O towards the  $\eta^6$ -B atom in  $B@B_3C_3$ , 1 1c-2e lone pair in the opposite direction, and two typical 2c-2e O–H  $\sigma$  bonds on the two sides (Fig. 2(f)), while the NH<sub>3</sub> core in NH<sub>3</sub>@B<sub>32</sub>C<sub>36</sub> (7) possesses 1 1c-2e lone pair towards the  $\eta^6$ -B atom in B@  $B_3C_3$  and three typical 2c-2e N–H  $\sigma$  bonds symmetrically distributed along the  $C_3$  molecular axis (Fig. 2(g)). The  $C_8$  core in  $C_8@B_{24}C_{44}$  (9) participates in 12 2c-2e C–C  $\sigma$ bonds on the cubic framework and 8 B-C  $\sigma$  bonds between the  $C_8$  core and  $B_{24}C_{44}$  shell to help stabilize the system (Fig. 2S(a)).

The isochemical-shielding surfaces (ICSSs) of  $T B_{32}C_{36}(3)$ ,  $T BH_4@B_{32}C_{36}^-(5)$ ,  $C_1 H_2O@B_{32}C_{36}(6)$ ,  $C_3 NH_3@B_{32}C_{36}(7)$ , and  $D_2 C_8@B_{24}C_{44}(9)$  are plotted in Fig. 3 based on their calculated NICS-ZZ components, in comparison with the experimentally known spherically aromatic  $I_h C_{60}$  in which the yellow areas with negative



**Fig. 2** AdNDP bonding patterns of (a)  $T \operatorname{CH}_4@C_{60}$ , (b)  $T \operatorname{BH}_4@C_{60}^-$ , (c)  $T \operatorname{B}_{32}C_{36}$ , (d)  $C_3 \operatorname{CH}_4@B_{32}C_{36}$ , (e)  $T \operatorname{BH}_4@B_{32}C_{36}^-$ , (f)  $C_1 \operatorname{H}_2O@B_{32}C_{36}$ , and (g)  $C_3 \operatorname{NH}_3@B_{32}C_{36}$ , with the occupation numbers (ON) indicated



**Fig. 3** Calculated NICS-ZZ surfaces of (**a**)  $I_h C_{60}$ , (**b**)  $T B_{32}C_{36}$  (**3**), (**c**)  $T BH_4 @B_{32}C_{36}$ .<sup>-</sup> (**5**), (**d**)  $C_1 H_2 O @B_{32}C_{36}$  (**6**), (**e**)  $C_3 NH_3 @B_{32}C_{36}$  (**7**), and (**f**)  $D_2 C_8 @B_{24}C_{44}$  (**9**)

NICS-ZZ values inside the shell and within about 1.0 Å above the cage surface in the vertical direction belong to chemical shielding regions, while the green regions with positive NICS-ZZ values like a belt around the waist in horizontal directions belong to chemical de-shielding regions. The ICSSs of the concerned endohedral borafullerenes all appear to be similar with that of the  $I_h C_{60}$  (Fig. S2), indicating that they are all spherically aromatic in nature, rendering high stability to the systems.

## Donor-acceptor orbital overlapping

To better interpret the donor–acceptor orbital overlapping patterns in endohedral  $BH_4@B_{32}C_{36}^{-}(5)$ ,  $H_2O@B_{32}C_{36}(6)$ , and  $NH_3@B_{32}C_{36}(7)$ , we performed detailed natural bond orbital (NBO) analyses on them in Fig. 4 at M06-2X/6-311G(d) level using the second-order perturbation theory of the Fock matrix. In-phase donor–acceptor orbital overlaps cause electron transfer from the fully occupied Lewis NBOs to empty non-Lewis NBOs. The electron donors are lone pairs (LP) or bonds (BD) and the corresponding LP acceptors are antibonding (BD\*) or lone vacant (LV) orbitals [36].

Figure 4(a) clearly shows that the BD(B-H)  $\rightarrow$  LV(B@  $B_3C_3$ ) in-phase donor-acceptor orbital overlaps in  $BH_4@$  $B_{32}C_{36}^{-}(5)$  include four equivalent delocalized 3c-2e B–H–B interactions. Figure 4(b) indicates that the LP(O)  $\rightarrow$  LV (B@  $B_3C_3$ ) in-phase donor-acceptor orbital overlap in  $H_2O@$  $B_{32}C_{36}(6)$  mainly originates from the interaction between the lone pair  $P_{z}$  orbital of O atom in  $H_{2}O$  and lone vacant  $P_{z}$ orbital of  $\eta^6$ -B atom in B@B<sub>3</sub>C<sub>3</sub>. Similar LP(N)  $\rightarrow$  LV (B@  $B_3C_3$ ) in-phase orbital overlap LP(N)  $\rightarrow$  LV(B@B<sub>3</sub>C<sub>3</sub>) exists in  $NH_3@B_{32}C_{36}$  (7) (Fig. 4(c)). Based on the fact that the  $LP(O/N) \rightarrow LV(B@B_3C_3)$  in-phase donor-acceptor orbital overlapping patterns in  $H_2O@B_{32}C_{36}(6)$  is similar with that of the  $LP(O) \rightarrow BD^*$  (H–O) hydrogen bonds (HBs) in  $(H_2O)_n$  (n = 1-6) clusters where the antibonding orbital BD\* serves as the LP acceptor [37], we propose the concept of boron bond (BB) in chemistry which is defined as the inphase orbital overlap between an electronegative atom (O in H<sub>2</sub>O) as lone-pair (LP) donor and an electron-deficient B atom ( $\eta^{6}$ -B in B@B<sub>3</sub>C<sub>3</sub>) with a lone vacant (LV) orbital as LP acceptor. Boron bonds are similar with HBs in donor–acceptor bonding patterns, but much stronger than the latter in bond dissociation energies [37]. However, with the bond dissociation energies of 1.66 eV in H<sub>2</sub>O@B<sub>32</sub>C<sub>36</sub>(6) at M06-2X level, a LP(O)  $\rightarrow$  LV(B) boron bond possesses only about 20.0% of the dissociation energy (8.35 eV) of a typical O-B covalent bond, indicating that a boron bond much weaker than a covalent O-B bond in bond strength. Similar LP(N)  $\rightarrow$  LV(B) donor–acceptor interaction exists in NH<sub>3</sub>@B<sub>32</sub>C<sub>36</sub>(7).

## Non-covalent interactions-reduced density gradient analyses

The NCI-RDG approach which enables the weak interactions to be graphically visualized has been widely used to identify the types of non-covalent interactions in concerned systems. Johnson et al. developed the reduced density gradient (RDG) approach and defined RDG(r) in the following equation [34]:

$$RDG(r) = \frac{1|\nabla\rho(r)|}{2(3\pi^2)^{\frac{1}{3}}\rho(r)^{\frac{4}{3}}}$$

Figure 5 shows RDG ~  $\sin(\lambda_2)\rho$  plots of  $T \operatorname{CH}_4@\operatorname{C}_{60}(1)$ ,  $T \operatorname{BH}_4@\operatorname{C}_{60}(2)$ ,  $C_3 \operatorname{CH}_4@\operatorname{B}_{32}\operatorname{C}_{36}(4)$ ,  $T \operatorname{BH}_4@\operatorname{B}_{32}\operatorname{C}_{36}(5)$ ,  $C_1 \operatorname{H}_2\operatorname{O}@\operatorname{B}_{32}\operatorname{C}_{36}(6)$ , and  $C_3 \operatorname{NH}_3@\operatorname{B}_{32}\operatorname{C}_{36}(7)$ . The light green spike 1 around -0.015 a.u. for  $\operatorname{CH}_4@\operatorname{C}_{60}(1)$  in Fig. 5(a) corresponds to the color-filled light green RDG isosurface between  $\operatorname{CH}_4$  and  $\operatorname{C}_{60}$  in Fig. 5(a'), indicating the existence of nonclassical hydrogen bond interactions  $\operatorname{C-H}_{\cdot\cdot\pi}$  between C-H bonds and C<sub>6</sub> rings, in consistent with the previously reported results [38]. As isovalent system,  $T \operatorname{BH}_4@\operatorname{C}_{60}(2)$  also exhibits a light green spike 1 at around -0.015 a.u which represents the nonclassical hydrogen bond interactions B-H·· $\pi$  (spike 1) between BH<sub>4</sub><sup>-</sup> and C<sub>6</sub> rings (Fig. 5(b, b')). The four green spikes 1, 2, 3, and 4 around -0.02 ~ 0.00 a.u. for  $C_3 \operatorname{CH}_4@\operatorname{B}_{32}\operatorname{C}_{36}(4)$  represent four different kinds of weak van der Waals interactions between the CH<sub>4</sub> core and

**Fig. 4** Donor–acceptor orbital overlapping patterns of the 3c-2e B-H-B bonds in  $T \text{ BH}_4$ @  $B_{32}C_{36}^{-1}$ (**5**) (**a**) and 2c-2e boron bonds in  $C_1 \text{ H}_2\text{O}@B_{32}C_{36}$ (**6**) (**b**) and  $C_3 \text{ NH}_3@B_{32}C_{36}$ (**7**) (**c**)



4\*3c-2e BD(B-H)→LV (B@B<sub>3</sub>C<sub>3</sub>)



 $LP(O) \rightarrow LV (B@B_3C_3)$ 

(b)  $C_1$  H<sub>2</sub>O(*a*)B<sub>32</sub>C<sub>36</sub>



(c) C<sub>3</sub>NH<sub>3</sub>@B<sub>32</sub>C<sub>36</sub>

1\*2c-2e LP(N)→LV (B@B<sub>3</sub>C<sub>3</sub>)



**Fig. 5** Calculated RDG ~ sign( $\lambda_2$ ) $\rho$  plots (**a**, **b**, **c**, **d**, **e**, and **f**) and color-filled RDG isosurfaces (a', b', c', d', e', and f') of the endohedral *T* CH<sub>4</sub>@ C<sub>60</sub>, *T* BH<sub>4</sub>@C<sub>60</sub>, *C*<sub>3</sub> CH<sub>4</sub>@B<sub>32</sub>C<sub>36</sub>, *T* BH<sub>4</sub>@B<sub>32</sub>C<sub>36</sub>, *C*<sub>1</sub> H<sub>2</sub>O@B<sub>32</sub>C<sub>36</sub>, and C<sub>3</sub> NH<sub>3</sub>@B<sub>32</sub>C<sub>36</sub>

B<sub>32</sub>C<sub>36</sub> shell (Fig. 5(c, c')). Interestingly, *T* BH<sub>4</sub>@B<sub>32</sub>C<sub>36</sub><sup>−</sup>(**5**) exhibits obviously a blue spike 1 with an obviously more negative  $sin(λ_2)\rho$  value of around -0.070 a.u which indicates the existence of the effective BD(B-H) → LV(B@B<sub>3</sub>C<sub>3</sub>)

donor-acceptor interaction in the system, well supporting the four equivalent 3c-2e B-H-B bonds in Fig. 2(c) and four equivalent BD(B-H)  $\rightarrow$  LV(B@B<sub>3</sub>C<sub>3</sub>) in-phase orbital overlaps in Fig. 4(a).

In sharp contrast, as shown in Fig. 5(e), (e'), (f), and (f),  $C_1 H_2 O@B_{32}C_{36}$  (6) exhibits clearly a deep blue spike 1 with the much more negative  $\sin(\lambda_2)\rho$  value of -0.11a.u. in Fig. 5(e) which corresponds to the color-filled blue RDG isosurface between the  $H_2O$  core and  $B_{32}C_{36}$  shell in Fig. 5(e'), while  $C_3 \text{ NH}_3 @B_{32}C_{36}$  (7) also has a deep blue spike 1 with an even more negative sign $(\lambda_2)\rho$  value of -0.13a.u. in Fig. 5(f) which corresponds to the blue isosurface between the NH<sub>3</sub> and  $B_{32}C_{36}$  in Fig. 5(f'). These deep blue spikes between  $-0.11 \sim -0.13$  a.u. further evidence the existence of boron bonds LP(O)  $\rightarrow$  LV (B@B<sub>3</sub>C<sub>3</sub>) in H<sub>2</sub>O@B<sub>32</sub>C<sub>36</sub> (7) in Fig. 4(b) and similar LP(N) $\rightarrow$ LV (B@B<sub>3</sub>C<sub>3</sub>) interactions in  $NH_3@B_{32}C_{36}$  (7) in Fig. 4(c). As shown in Fig. S4, boron bonds also exist in the optimized  $C_s$  H<sub>2</sub>O-BH<sub>3</sub> and  $C_{3y}$  $H_3B-NH_3$  which have the deep blue spikes at around -0.07a.u. and -0.11 a.u. corresponding to the color-filled deep blue isosurfaces between the fragments in the systems, respectively. Similar situations occur in the newly observed boron carbonyl aromatics (BCAs)  $B_{13}(CO)_n^+$  (n = 1-7) in which the CO ligands serve as LP donors and the periphery B atoms serve as LP acceptors, in which the average LP(CO) $\rightarrow$ LV(B) bond dissociation energy of 1.26 eV is about 27.1% of the corresponding value (4.63 eV) of a C-B covalent bond [39].

#### **IR and Raman spectral simulations**

Infrared photodissociation (IR-PD) has proved to be an effective approach to characterize gas-phase clusters [40, 41]. The infrared (IR) and Raman spectra of  $T B_{32}C_{36}$  (4), T  $BH_4@B_{32}C_{36}^{-}(5), C_1H_2O@B_{32}C_{36}(6), and D_2C_8@B_{24}C_{44}$ (9) were simulated at the M06-2X/6-31G(d)- $D_3$  level in Fig. S5 to facilitate their future spectral characterizations. As shown in Fig. S5(a),  $TB_{32}C_{36}$  exhibits strong IR active peaks at 737 (t), 1045 (t), 1274 (t), 1317 (t) and Raman spectral features at 218 (e), 336 (a), 456 (a), 1125 (a), 1568(a) cm<sup>-1</sup>, respectively, with a typical radial breathing mode (RBM) [42] at 336 cm<sup>-1</sup>.  $T BH_4 @B_{32}C_{36}^{-}$  (5) possesses three major IR-active peaks at 1204 (t), 1300 (t), 2264 cm<sup>-1</sup> (t) and five major Raman-active modes at 228(e), 325 (t), 374 (a), 459 (a), 1041 (a), 1595  $\text{cm}^{-1}$  (e), with a RMB peak at 374  $\text{cm}^{-1}$ (Fig. S5(b)). The IR and Raman spectra of  $C_1$  H<sub>2</sub>O@B<sub>32</sub>C<sub>36</sub> (6) appear to be similar with that of the  $T BH_4 @B_{32}C_{36}^{-}(5)$ (Fig. S5(c)).  $D_2 C_8 @B_{24}C_{44}$  (9) exhibits strong IR peaks at 867 (b<sub>1</sub>), 1249 (b<sub>2</sub>), 1299 (b<sub>3</sub>), 1321 cm<sup>-1</sup> (b<sub>1</sub>) and Raman active peaks at 302 (a), 453 (a), 881 (a), 1524 cm<sup>-1</sup> (a), and 453 cm<sup>-1</sup> (Fig. S5(d)).

## Conclusions

Extensive DFT calculations performed in this work present the viability of the highly stable endohedral  $C_3 CH_4@B_{32}C_{36}$ (4),  $T BH_4@B_{32}C_{36}^-$  (5),  $C_1 H_2O@B_{32}C_{36}$  (6),  $C_3 NH_3@$   $B_{32}C_{36}(7)$ ,  $TC_8@B_{32}C_{36}^{2-}(8)$ , and  $D_2C_8@B_{24}C_{44}(9)$  which turn out to be spherically aromatic in nature. As demonstrated in the case of the LP(O)  $\rightarrow$  LV(B@B<sub>3</sub>C<sub>3</sub>) interaction in H<sub>2</sub>O@  $B_{32}C_{36}$  (6), boron bonds are used to describe the unique inphase donor-acceptor orbital overlaps between an electronegative atom A as lone-pair (LP) donor and an electron-deficient boron atom with a lone vacant (LV) orbital as LP acceptor which appear to be much weaker than the corresponding A-B covalent bonds in bond dissociation energies. Boron bonds are expected to exist in a wide range of boron-involved systems due to the prototypical electron-deficiency of boron which may serve as unique and effective LP acceptors to react with various LP donors like CO, H2O, and NH3. Further experimental and theoretical investigations are invited to synthesize and characterize these endohedral borafullerenes to enrich the chemistry of both boron and heterofullerenes.

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**Data availability** No datasets were generated or analysed during the current study.

#### Declarations

Competing interests The authors declare no competing interests.

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