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# The dodeca-coordinated $\text{La}@\text{B}_8\text{C}_4^{+/0/-}$ molecular wheels: conflicting aromaticity *versus* double aromaticity†

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The transition-metal centered boron molecular wheels have attracted the attention of chemists. The highest deca-coordination number for central metal atoms was observed in  $D_{10h}$   $\text{Ta}@\text{B}_{10}^-$  and  $\text{Nb}@\text{B}_{10}^-$  molecular wheels. Here, we report a theoretical study of  $\text{La}@\text{B}_8\text{C}_4^q$  ( $q = +1, 0, -1$ ) clusters with the dodeca-coordinated La atom. The  $\text{La}@\text{B}_8\text{C}_4^q$  clusters adopt fascinating molecular wheel structures, showing a La atom enclosed by a perfect  $\text{B}_8\text{C}_4$  monocyclic ring. The cationic  $\text{La}@\text{B}_8\text{C}_4^+$  cluster has a  $C_{4v}$  symmetry with the distinctly out-of-plane distortion of the La atom (0.70 Å), which is gradually flattened by the sequential reduction reaction. The distortion of the La atom from the plane in the neutral  $\text{La}@\text{B}_8\text{C}_4$  cluster decreases to 0.46 Å. The  $\text{La}@\text{B}_8\text{C}_4^-$  species turns out to be perfectly planar. Chemical bonding analyses indicate that the neutral  $\text{La}@\text{B}_8\text{C}_4$  and anionic  $\text{La}@\text{B}_8\text{C}_4^-$  possess  $10\sigma$  and  $9\pi/10\pi$  double aromaticity, respectively, obeying the principle of double aromaticity. However, the cationic  $\text{La}@\text{B}_8\text{C}_4^+$  has  $10\sigma$  and  $8\pi$  conflicting aromaticity, representing a counterexample in planar hyper-coordinated molecular wheels. The dodeca-coordination number in  $\text{La}@\text{B}_8\text{C}_4^q$  ( $q = +1, 0, -1$ ) clusters is unprecedented, which provides a new idea and concept for searching planar hyper-coordinated systems.

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## 1. Introduction

The electron-deficiency of boron results in unconventional geometries in its allotropes and chemical compounds.<sup>1–13</sup> The bare boron clusters like forming planar or quasi-planar (2D) structures over a wide range of sizes.<sup>4–6,9–17</sup> The  $D_{7h}$   $\text{B}_8^{2-}$  and  $D_{8h}$   $\text{B}_9^-$  clusters are intriguing, adopting the perfect molecular wheel shape with a central hepta- and octacoordinate boron atom,<sup>6</sup> and get their stability from the double ( $6\sigma + 6\pi$ ) aromaticity, fulfilling the  $4N_{\sigma/\pi} + 2$  Hückel rule ( $N_{\sigma} = N_{\pi} = 1$ ). Numerous transition-metal centred boron molecular wheels  $\text{M}@\text{B}_n^-$  with the central hypercoordinate metal atom in plane were designed and characterized according to the principle of double aromaticity.<sup>18–21</sup> At present, the highest coordination number in the planar systems has been limited in  $\text{Ta}@\text{B}_{10}^-$  and  $\text{Nb}@\text{B}_{10}^-$ .<sup>20,22</sup> Recently, the metal-centered monocyclic carbon wheel was theoretically investigated with record coordination number of thirteen.<sup>23</sup> Some main group metal centered boron molecular wheels have also been investigated theoretically.<sup>24,25</sup>

In view of the double aromaticity of  $\text{B}_8^{2-}$  and  $\text{B}_9^-$  molecular wheels, Wang and coworkers have suggested a general electronic design principle ( $n + x + q = K$ ) for transition-metal

centered boron molecular wheels  $\text{M}@\text{B}_n^{q-}$ ,<sup>26</sup> where  $n$  is the number of delocalized electrons supplied by the peripheral  $\text{B}_n$  ring,  $x$  is the formal valence of central metal atoms,  $q$  is the cluster's charge, and  $K$  is the total number of delocalized electrons. This electronic design principle is proved to be feasible in  $\text{M}@\text{B}_8^-$  ( $\text{M} = \text{Co}, \text{Re}$  and  $\text{Fe}$ ) and  $\text{M}@\text{B}_9^-$  ( $\text{M} = \text{Ru}, \text{Rh}, \text{Ir}, \text{Re}$  and  $\text{Fe}$ ) with  $K = 12$ .<sup>17–19</sup> The deca-coordinated  $\text{Ta}@\text{B}_{10}^-$  and  $\text{Nb}@\text{B}_{10}^-$  molecular wheels have a total delocalized electrons of  $K = 16$ , possessing  $10\sigma$  and  $6\pi$  double aromaticity.<sup>21</sup>

In the transition-metal centred boron molecular wheels, the partly filled d-orbitals of transition-metal atoms play a crucial role in describing the interaction between the central metal atom and peripheral ring. In contrast, the metal atoms without d-orbital electrons (or with full-filled d-orbital electrons) don't like to form stable molecular wheel geometries. For instance, the  $\text{AlB}_7^-$  and  $\text{AlB}_8^-$  clusters are inclined to form the umbrella-shaped geometries.<sup>27</sup> The Au atom with full-filled 5d-orbital electrons in  $\text{AuB}_{10}^-$  cluster like forming a covalent B–Au  $\sigma$  bond with the corner B atom, serving as H atom. The 5d-orbital electrons, existing in the five lone pairs, could not effectively participate in bonding with the peripheral boron ring. The  $\text{Au}@\text{B}_{10}^-$  molecular wheel is an extremely unstable local minimum (LM), being 1.95 eV higher in energy than the global minimum (GM) at B3LYP level.<sup>28</sup> Beyond that, the cavity of peripheral ring need match up with the volume of central metal atom in physics. The small cavity cannot accommodate a metal atom. If the cavity is too large, the B–M interaction would be

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weakened dramatically due to the increased B–M distances. The molecular wheels will fail in competing with the half-sandwich structures.<sup>29</sup> Therefore, it is a challenge to push the limit of coordination number in planar structures.

The present paper aims at breaking the record of deca-coordinated number in  $D_{10h}$   $Ta@B_{10}^-$  and  $Nb@B_{10}^-$  molecular wheels, which is realized in the  $La@B_8C_4^{+/0/-}$  clusters. The title clusters have the interesting molecular wheel shapes, showing a central La atom encircled with a closed  $-(BCB)_4-$  ring. The  $La@B_8C_4^+$  and  $La@B_8C_4$  species have the  $C_{4v}$  symmetry with an out-of-plane distortion of La atoms, whereas the  $La@B_8C_4^-$  is perfectly plane. Thus, sequential reduction reaction in the  $La@B_8C_4^q$  ( $q = +1, 0, -1$ ) results in the structural planarization. The chemical bonding analyses suggest that  $La@B_8C_4$  and  $La@B_8C_4^-$  molecular wheels have  $10\sigma$  and  $9\pi/10\pi$  delocalized electrons, respectively, faithfully fulfilling the general double aromaticity rule. Whereas, the  $La@B_8C_4^+$  cluster is a counterexample in planar molecular wheels. It possesses  $10\sigma$  and  $8\pi$  delocalized electrons, being the first hypercoordinate molecular wheel with conflicting aromaticity.

## 2. Theoretical methods

We searched the GM structures for cationic and anionic  $La@B_8C_4^{+/0/-}$  clusters using the Coalescence Kick (CK) algorithm<sup>30,31</sup> at B3LYP/LanL2DZ level, as well as the manual structural constructions. More than 3000 stationary points for each species were probed on their potential energy surfaces. The low-lying isomers ( $\Delta E < 60$  kcal mol<sup>-1</sup>) of  $La@B_8C_4^{+/0/-}$  and their corresponding neutral structures were reoptimized using B3LYP functional in Gaussian 09 package.<sup>32</sup> The Stuttgart ECP28MWB\_ANO basis set with the corresponding energy-consistent relativistic pseudopotential ECP28MWB was used for La, and 6-311+G\* basis set for boron and carbon.<sup>33</sup> This basis set combination is reasonable for current system according to the literature on transition-metal doped boron clusters.<sup>34</sup> The vibrational frequencies were calculated at the same level to verify that the isomers presented are true minima. The relative energies of the top five lowest-lying isomers of  $La@B_8C_4^{+/0/-}$  were further refined at the single-point CCSD(T) level using the same basis set combination of B3LYP level.<sup>35</sup> The top isomers of  $La@B_8C_4^q$  ( $q = +1, 0, -1$ ) clusters are independently checked at the PBE0 level as well.

All electronic property calculations were performed at the same theory level with structural optimizations. The Wiberg bond indices (WBIs) and natural atomic charges of  $La@B_8C_4^q$  ( $q = +1, 0, -1$ ) clusters were calculated using the NBO 6.0 program.<sup>36</sup> The chemical bonding was elucidated using the canonical molecular orbital (CMO) analyses, the electron localization functions (ELFs)<sup>37,38</sup> and adaptive natural density partitioning (AdNDP).<sup>39</sup> Since the neutral  $La@B_8C_4$  is an open-shell system, the AdNDP analysis is performed using the unrestricted AdNDP (UAdNDP) version. The anisotropy of current-induced density (ACID) analyses was carried out using ACID code.<sup>40</sup> The ring-current images were visualized using the POV-Ray 3.7.<sup>41</sup> and the ELFs and AdNDP data were visualized using Molekel 5.4.0.8.<sup>42</sup>

## 3. Results and discussion

### 3.1. The geometries and energies of $La@B_8C_4^q$ ( $q = +1, 0, -1$ )

The alternative low-lying isomers (sixty-seven structures) of cationic  $La@B_8C_4^+$  cluster are shown in Fig. S1 (ESI†). The GM structure, as shown in Fig. 1 and S1,† adopts an interesting molecular wheel style with a symmetry of  $C_{4v}$  ( $^1A_1$ ), showing a dodeca-coordinated La atom surrounded by a fascinating  $-(BCB)_4-$  ring. The central La atom has a little bulge with respect to the peripheral  $B_8C_4$  ring. Its Cartesian coordinates are given in Table S1 (ESI†). The closest competitor has a symmetry of  $C_s$  ( $^1A'$ ), being 0.23 and 0.34 eV higher in energy than GM at single-point CCSD(T) and B3LYP levels, respectively, whose centered La atom is nona-coordinated with the  $B_5C_4$  ring. The third and fourth isomers also adopt the molecular wheel structures, albeit with an inferior arrangement of  $B_8C_4$  ring, which are at least 0.50 eV higher than GM at both levels. In particular, the fifth isomer ( $C_{4v}$ ,  $^3A_1$ ) with a triplet ground state, possessing the same geometry with the GM, is 0.89 and 0.70 eV higher than GM at the CCSD(T) and B3LYP levels, respectively. Thus, the GM is clearly defined on its potential energy surface at the B3LYP and CCSD(T) levels.

The GM and low-lying isomers of neutral  $La@B_8C_4$  cluster are presented in Fig. 1 and S2 (ESI†). All of them possess fascinating molecular wheel geometries. The GM ( $C_{4v}$ ,  $^2B_1$ ) of neutral  $La@B_8C_4$  cluster adopts the similar architecture with cationic species, whose nearest competitor has a  $C_s$  ( $^2A'$ ) symmetry, being 0.19 and 0.18 eV higher in energy at the CCSD(T) and B3LYP levels.

As for anionic  $La@B_8C_4^-$  cluster, the potential energy surface appears to be more complicated. There are four isomeric geometries within 0.10 eV at the CCSD(T) and B3LYP levels (Fig. S3, ESI†), and the calculated energies are highly consistent at both levels. The GM structure of  $La@B_8C_4^-$  cluster adopts a  $C_s$  symmetry with the  $^1A'$  electronic state, which is identical with that of the closest competitor of neutral  $La@B_8C_4$  and the fourth isomer of cationic  $La@B_8C_4^+$ . The perfectly planar  $D_{4h}$  ( $^1A_{1g}$ ) isomer (Fig. 1) of  $La@B_8C_4^-$  cluster turns out to be a LM, which is only 0.04 eV higher in energy than GM at both CCSD(T) and B3LYP levels. We mainly focus on the perfect LM structure in this paper. The  $T_1$  diagnostic factors of CCSD(T) for three perfect molecular wheels are 0.022, 0.026 and 0.018, respectively, indicating the reliable CCSD(T) data.

### 3.2. The bond distances, Wiberg bond indices and natural atomic charges

The bond distances for GM ( $C_{4v}$ ,  $^1A_1$ ) of  $La@B_8C_4^+$  cluster are shown in Fig. 1. The GM has the equivalent B–B (1.57 Å) and B–C (1.38 Å) bond distances. The B–B bonds are distinctly shorter than the standard B–B single bond (1.70 Å),<sup>43</sup> and being comparable with the B=B double bond (1.56 Å). The B–C bonds are even shorter than the B=C double bond (1.45 Å), being close to the B≡C triple bond (1.33 Å). The B–La and C–La bond distances are 2.91 and 2.84 Å, respectively. The central La atom is 0.70 Å out of  $B_8C_4$  ring (not shown).



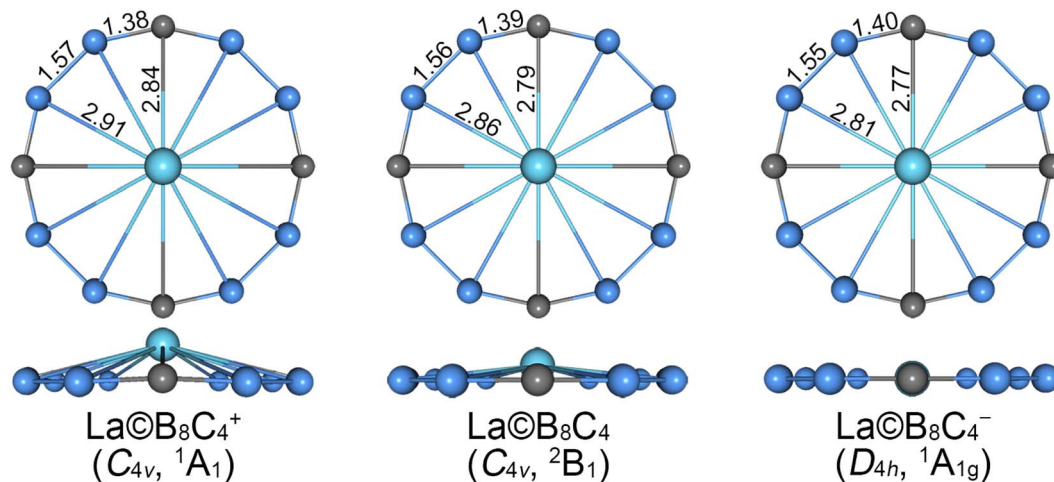


Fig. 1 Optimized geometry for  $C_{4v}$  ( $^1A_1$ ) global-minimum (GM) of  $\text{La@B}_8\text{C}_4^+$ ,  $C_{4v}$  ( $^2B_1$ ) GM of  $\text{La@B}_8\text{C}_4$  and  $D_{4h}$  ( $^1A_{1g}$ ) local-minimum (LM) of  $\text{La@B}_8\text{C}_4^-$  clusters at the B3LYP level. The bond distances are shown in Å.

The GM ( $C_{4v}$ ,  $^2B_1$ ) of neutral  $\text{La@B}_8\text{C}_4$  and LM ( $D_{4h}$ ,  $^1A_{1g}$ ) of  $\text{La@B}_8\text{C}_4^-$  are almost identical with the GM of  $\text{La@B}_8\text{C}_4^+$  species. The B–B and B–C bond distances of  $\text{La@B}_8\text{C}_4$  are 1.56 and 1.39 Å, and those of  $\text{La@B}_8\text{C}_4^-$  are 1.55 and 1.40 Å, respectively, showing slight decrease for B–B bonds and increase for B–C bonds (within 0.01–0.02 Å) compared to  $\text{La@B}_8\text{C}_4^+$ . Overall, the peripheral  $\text{B}_8\text{C}_4$  ring enlarges by 0.04 Å for  $\text{La@B}_8\text{C}_4$  and 0.08 Å for  $\text{La@B}_8\text{C}_4^-$  clusters compared with that of  $\text{La@B}_8\text{C}_4^+$  cluster. By contrast, the B–La and C–La bond distances shrink markedly (0.05–0.10 Å for the B–La bonds and 0.05–0.07 Å for C–La bonds). The B–La and C–La bond distances in  $\text{La@B}_8\text{C}_4$  are 2.86 and 2.79 Å, and those in  $\text{La@B}_8\text{C}_4^-$  are 2.81 and 2.77 Å. The expansion of  $\text{B}_8\text{C}_4$  ring and reduction of B–La/C–La links planarize the  $\text{La@B}_8\text{C}_4$  and  $\text{La@B}_8\text{C}_4^-$  clusters. The out-of-plane distortion of central La reduces to 0.46 Å for  $\text{La@B}_8\text{C}_4$ . The  $\text{La@B}_8\text{C}_4^-$  turns into a perfectly planar structure.

The above bond distances are rationalized by the calculated WBIs (Fig. S4, ESI†) and natural charge (Fig. S5, ESI†) data from NBO analyses at the B3LYP level. In GM of  $\text{La@B}_8\text{C}_4^+$  cluster, the B–B and B–C bonds have the WBIs of 1.19 and 1.62, being distinctly greater than 1.0 (the latter in particular), implying that  $\text{B}_8\text{C}_4$  ring is controlled by the delocalized  $\sigma/\pi$  bonds beyond the Lewis B–B/B–C two-center two-electrons (2c–2e)  $\sigma$  single bond. The covalent interaction of B–C bonds are markedly stronger than that of B–B ones, hinting that the delocalized electrons are mainly located at the B–C bonds of peripheral ring. Whereas, the covalent interaction between the central La and peripheral  $\text{B}_8\text{C}_4$  ring is somewhat weak, with the small WBIs of 0.18 for B–La and 0.23 for C–La links. The WBIs of B–C, B–La and C–La bonds in neutral  $\text{La@B}_8\text{C}_4$  and anion  $\text{La@B}_8\text{C}_4^-$  are consistent with those in  $\text{La@B}_8\text{C}_4^+$  cluster (within 0.01). The variations of WBIs among three structures are mainly occurred in B–B bonds, showing a gradual increase by 0.08. It implies that the extra one electron in  $\text{La@B}_8\text{C}_4$  and two electrons in  $\text{La@B}_8\text{C}_4^-$  clusters are primarily dispersed on B–B bonds of  $\text{B}_8\text{C}_4$  rings (see Section 3.4). Moreover, the total WBIs of

centered La atom in  $\text{La@B}_8\text{C}_4^{+/0/-}$  clusters are 2.34, 2.41 and 2.45, respectively, indicating a negligible increase.

As for the natural charges (Fig. S5, ESI†), in  $\text{La@B}_8\text{C}_4^+$  cluster, the C atom carries a plentiful negative charge of  $-0.92 |e|$ , whereas the B atom is positively charged by  $+0.38 |e|$ , meaning the natural charges are markedly localized at C sites. Overall, the  $\text{B}_8\text{C}_4$  ring has a collective negative charge of  $-0.64 |e|$ . It should be noted that the charge distribution on  $\text{B}_8\text{C}_4$  ring is in line with their distinct electronegativity of B (2.04) and C (2.55) elements. The central La atom possesses a positive charge of  $+1.67 |e|$  with the electronic configuration of  $[\text{Xe}] 6s^{0.05} 4f^{0.10} 5d^{1.16} 6p^{0.01} 5f^{0.01} 6d^{0.02}$ , indicating an obvious charge transfer from the La atom to  $\text{B}_8\text{C}_4$  ring, hinting a robust electrostatic attraction among them. The interaction between the central La and  $\text{B}_8\text{C}_4$  ring is governed by both electrostatics and covalent interaction. In neutral  $\text{La@B}_8\text{C}_4$  and anion  $\text{La@B}_8\text{C}_4^-$  clusters, the La atoms almost maintain the same positive charge with that in  $\text{La@B}_8\text{C}_4^+$ . In contrast, the total charges of  $\text{B}_8\text{C}_4$  rings increase to  $-1.64 |e|$  of  $\text{La@B}_8\text{C}_4$  and  $-2.64 |e|$  of  $\text{La@B}_8\text{C}_4^-$ . Specifically, the carrying charge of C atoms slightly decreases to  $-0.89 |e|$  of  $\text{La@B}_8\text{C}_4$  and  $-0.86 |e|$  of  $\text{La@B}_8\text{C}_4^-$ , and that of B atoms distinctly increases to  $+0.24 |e|$  and  $+0.10 |e|$ , which are corresponding with the bond distances and WBIs data of B–B/B–C bonds.

### 3.3. The stabilities of $\text{La@B}_8\text{C}_4^{+/0/-}$ along with out-of-plane distortion of La atom

The  $\text{B}_8\text{C}_4$  rings of  $\text{La@B}_8\text{C}_4^+$  and  $\text{La@B}_8\text{C}_4$  are slightly small, cannot accommodate the large La atom, leading to a tiny hump of central La atom. In order to quantitatively evaluate the relative stabilities of  $\text{La@B}_8\text{C}_4^{+/0/-}$  molecular wheels with different La height relative to the  $\text{B}_8\text{C}_4$  rings, we performed the potential energy scanning as the La atoms move along with their  $C_4$  axes, prescribed by the  $\text{La}\cdots\text{B}_8\text{C}_4$  angle  $\theta$ , as shown in Fig. 2. The perfect  $D_{4h}$  structure of  $\text{La@B}_8\text{C}_4^+$  is a one-order saddle point with the imaginary frequency of  $73.93i \text{ cm}^{-1}$ , which is 0.17 eV above the  $C_{4v}$  GM  $\text{La@B}_8\text{C}_4^+$ . In essence, the  $D_{4h}$  structure is the



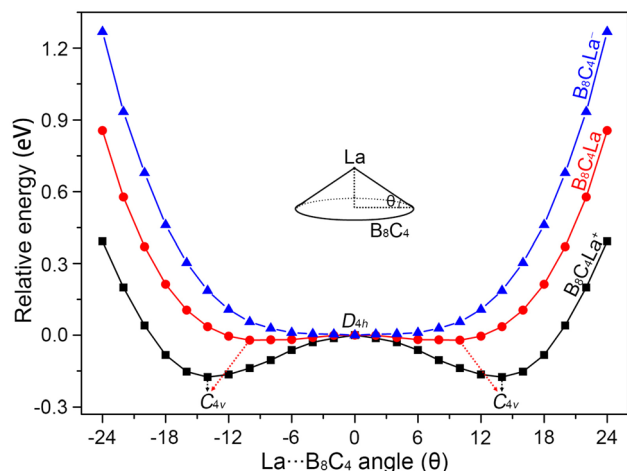


Fig. 2 The potential energy curves of  $C_{4v}$  ( $^1A_1$ ) GM  $\text{La@B}_8\text{C}_4$ ,  $C_{4v}$  ( $^2B_1$ ) GM  $\text{La@B}_8\text{C}_4$ , and  $D_{4h}$  ( $^1A_{1g}$ ) LM  $\text{La@B}_8\text{C}_4$  clusters along with the out-of-plane distortion central La atom.

transition state (TS) structure for the La atom traversing the  $\text{B}_8\text{C}_4$  ring. The  $C_{4v}$  GM of  $\text{La@B}_8\text{C}_4^+$  has the  $\theta$  value of  $\pm 14.19^\circ$ , being corresponding to a La height of  $0.70 \text{ \AA}$  above the center of  $\text{B}_8\text{C}_4$  ring. The potential energy curve of  $\text{La@B}_8\text{C}_4$  is flatter than that of  $\text{La@B}_8\text{C}_4^+$ , whose  $D_{4h}$  structure (with a small imaginary frequency of  $49.82i \text{ cm}^{-1}$ ) is only  $0.03 \text{ eV}$  higher in energy than  $C_{4v}$  GM of  $\text{La@B}_8\text{C}_4$ , which is attribute to its enlarged  $\text{B}_8\text{C}_4$  ring and reduced B–La/C–La bond distances. The potential energy curve of  $\text{La@B}_8\text{C}_4^-$  indicates that the  $D_{4h}$  structure is the true minimum.

### 3.4. Chemical bonding

In view of the similar molecular wheel structures of  $\text{La@B}_8\text{C}_4^{+/0/-}$  clusters, the chemical bonding analyses are mainly focused on the close-shelled  $\text{La@B}_8\text{C}_4^+$  and  $\text{La@B}_8\text{C}_4^-$  species. The  $\text{La@B}_8\text{C}_4^+$  cluster has 42 valence electrons, occupying 21 valence CMOs (Fig. S6, ESI<sup>†</sup>). These occupied CMOs are divided into three subsets based on their constituent atomic orbitals (AOs). The twelve CMOs in subset (a) are primarily composed of 2s and tangential 2p AOs of B/C, which can be reasonably localized into eight 2c–2e B–C and four 2c–2e B–B Lewis  $\sigma$  bonds in  $\text{B}_8\text{C}_4$  ring. The five delocalized  $\sigma$  CMOs in subset (b) are composed of the radial 2p AOs of B/C and 5d AOs of La ( $d_{x^2-y^2}$  in HOMO and  $d_{xy}$  in HOMO-2). It should be noted that the HOMO and HOMO-2  $\sigma$  CMOs are formally degenerated. These five CMOs constitute the delocalized  $\sigma$  framework, resulting in the  $10\sigma$  aromaticity of  $\text{La@B}_8\text{C}_4^+$ , according to  $(4N_\sigma + 2)$  Hückel rule ( $N_\sigma = 2$ ). There are four delocalized  $\pi$  CMOs in subset (c), being composed of the vertical 2p AOs of B/C and 5d AOs of La ( $d_{xz}$  in HOMO-4 and  $d_{yz}$  in HOMO-4'), constructing the  $\pi$  framework of  $\text{La@B}_8\text{C}_4^+$ , and leading to its  $8\pi$  antiaromaticity in view of  $(4N_\pi)$  Hückel rule ( $N_\pi = 2$ ). Overall,  $\text{La@B}_8\text{C}_4^+$  molecular wheel is a system of  $10\sigma$  and  $8\pi$  conflicting aromaticity. Following Boldyrev, the term conflicting aromaticity refers to the systems with simultaneous presence of aromaticity and antiaromaticity in orthogonal planes, there is aromaticity in one plane and anti-aromaticity in

the plane orthogonal to it.<sup>14,44</sup> In nature, the four delocalized  $\pi$  CMOs can be appropriately recombined four three-center two-electrons (3c–2e) –BCB– island  $\pi$  bonds (see the ELF and AdNDP analyses), being in line with its  $C_{4v}$  symmetry.

The  $\text{La@B}_8\text{C}_4^-$  cluster is a system with 44 valence electrons, occupying 22 CMOs (Fig. S7, ESI<sup>†</sup>). It has one more full-filled  $\pi$  CMO (HOMO) than  $\text{La@B}_8\text{C}_4^+$ . The five delocalized  $\pi$  CMOs in subset (c) are one-to-one corresponding with the  $\sigma$  CMOs in subset (b), following the same spatial distribution. Thus,  $\text{La@B}_8\text{C}_4^-$  cluster is double aromatic with  $10\sigma$  and  $10\pi$  delocalized electrons. The  $\sigma$  CMOs (HOMO-1/HOMO-4) and  $\pi$  CMOs (HOMO/HOMO-2) also are formally degenerated, being similar to the  $\sigma$  CMOs (HOMO/HOMO-2) of  $\text{La@B}_8\text{C}_4^+$  in Fig. S6(b) (ESI<sup>†</sup>). The energy gap between the HOMO and HOMO-2 is  $1.83 \text{ eV}$ , which hints the out-of-plane distortion of central La atom in neutral  $\text{La@B}_8\text{C}_4$  and cationic  $\text{La@B}_8\text{C}_4^+$  molecular wheels is not due to the Jahn–Teller effect. The electron density of HOMO is mainly dispersed on four B–B bonds, which leads to decrease of bond distances by  $0.02 \text{ \AA}$  (Fig. 1) and increase of WBIs by  $0.16$  compared with those in  $\text{La@B}_8\text{C}_4^+$  wheel (Fig. S4, ESI<sup>†</sup>).

The CMOs bonding pattern of  $\text{La@B}_8\text{C}_4$  cluster (Fig. S8, ESI<sup>†</sup>) is similar to that of  $\text{La@B}_8\text{C}_4^-$  cluster, albeit possessing a single occupied  $\pi$  molecular orbital (that is the SOMO). Thus,  $\text{La@B}_8\text{C}_4$  molecular wheel is dominated by  $10\sigma$  and  $9\pi$  double aromaticity. The delocalized  $\pi$  frameworks in  $\text{La@B}_8\text{C}_4^{+/0/-}$  clusters are compared with the  $D_{4h}$   $\text{B}_8\text{C}_4^{4-}$  ring and planar aromatic  $D_{10h}$   $\text{C}_{10}\text{H}_{10}$  (annulene) model molecule (see Fig. 3). Note that the  $D_{4h}$   $\text{B}_8\text{C}_4^{4-}$  ring and  $D_{10h}$   $\text{C}_{10}\text{H}_{10}$  are not the true minimums.<sup>45</sup> The delocalized  $\pi$  CMOs in  $\text{La@B}_8\text{C}_4$  and  $\text{La@B}_8\text{C}_4^-$  clusters are one to one corresponding to those in  $D_{4h}$   $\text{B}_8\text{C}_4^{4-}$  ring and  $D_{10h}$   $\text{C}_{10}\text{H}_{10}$  model. Importantly, the SOMO in  $\text{La@B}_8\text{C}_4$  and HOMO in  $\text{La@B}_8\text{C}_4^-$  facilitate the  $\pi$  electron delocalization on  $\text{B}_8\text{C}_4$  ring and enhance the interaction of B–La links, which would obviously shorten the B–La bond distances, and make the molecular wheels planarization.

It should be pointed out that the coordination interaction between the La atom and  $\text{B}_8\text{C}_4$  ring is mainly attributed to the d–p (La  $5d_{x^2-y^2}/5d_{xy}$  AOs and B/C radial 2p AOs)  $\sigma$  CMOs (HOMO/HOMO-2 in  $\text{La@B}_8\text{C}_4^+$  and HOMO-1/HOMO-4 in  $\text{La@B}_8\text{C}_4^-$ ) and d–p (La  $5d_{xz}/5d_{yz}$  AOs and B/C vertical 2p AOs)  $\pi$  CMOs (HOMO-4/4' in  $\text{La@B}_8\text{C}_4^+$  and HOMO-5/5' in  $\text{La@B}_8\text{C}_4^-$ ). The coordination interactions of d–p  $\sigma$  CMOs with the relatively large orbital component of La 5d AOs are a little bit stronger than those of d–p  $\pi$  CMOs. Quantitatively, the HOMO and HOMO-2 in  $\text{La@B}_8\text{C}_4^+$  (Fig. S6, ESI<sup>†</sup>) have a 19.89% La  $5d_{x^2-y^2}$  and 10.39% La  $5d_{xy}$  AOs contribution, respectively. In  $\text{La@B}_8\text{C}_4^-$ , the La  $5d_{x^2-y^2}$  AO contributes by 14.58% to HOMO-1, and La  $5d_{xy}$  AO contributes by 8.42% to HOMO-4 (Fig. S7, ESI<sup>†</sup>). For the d–p  $\pi$  CMOs, the La  $5d_{xz}/5d_{yz}$  AOs contributes merely by 6.72% in HOMO-4/4' of  $\text{La@B}_8\text{C}_4^+$ , and 8.11% in HOMO-5/5' of  $\text{La@B}_8\text{C}_4^-$ .

The CMOs bonding images of  $\text{La@B}_8\text{C}_4^{+/0/-}$  molecular wheels are faithfully confirmed by the ELF analyses. As shown in Fig. 4, the ELF $_\sigma$  patterns of  $\text{La@B}_8\text{C}_4^+$  and  $\text{La@B}_8\text{C}_4^-$  clusters are almost identical, showing twelve localized 2c–2e B–B/B–C  $\sigma$  bonds (left panels) and strong global delocalized  $\sigma$  electron





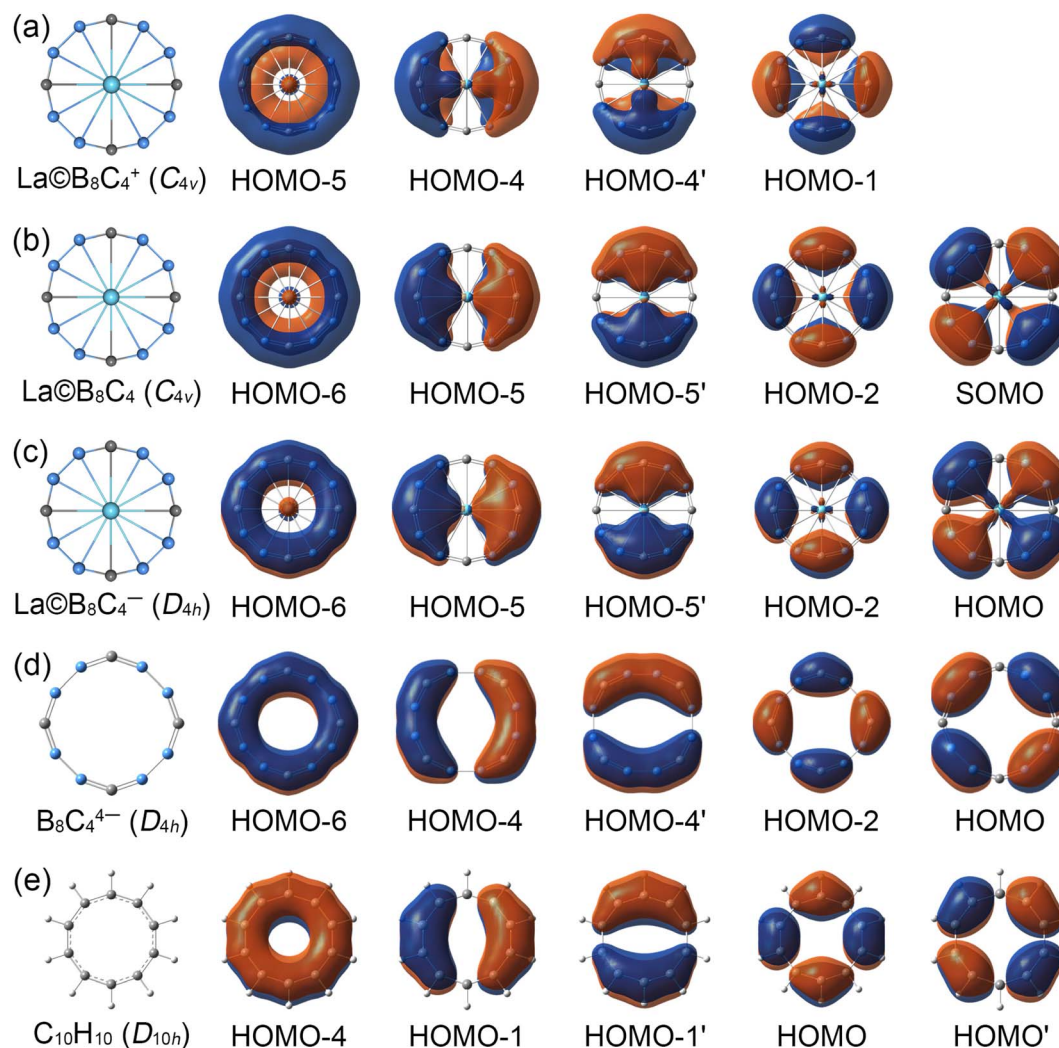


Fig. 3 Comparison of the delocalized canonical molecular orbitals (CMOs) between (a)  $C_{4v}$  ( $^1A_1$ ) GM  $\text{La@B}_8\text{C}_4$ , (b)  $C_{4v}$  ( $^2B_1$ ) GM  $\text{La@B}_8\text{C}_4$ , (c)  $D_{4h}$  ( $^1A_{1g}$ ) LM  $\text{La@B}_8\text{C}_4^-$  clusters, (d)  $D_{4h}$  ( $^1A_{1g}$ )  $\text{B}_8\text{C}_4^{4-}$  and (e)  $D_{10h}$   $\text{C}_{10}\text{H}_{10}$  (annulene) model molecule.

density (middle panels). Obviously, two molecular wheels mainly differ in  $\text{ELF}_\pi$  patterns. The  $\pi$  electron density of  $\text{La@B}_8\text{C}_4^+$  is clearly segmented into four  $\text{-BCB-}$  islands (right panels), but that of  $\text{La@B}_8\text{C}_4^-$  is continuous, and being smoothly distributed on the whole  $\text{B}_8\text{C}_4$  ring, which firmly supports the above assessments of  $8\pi$  antiaromaticity for  $\text{La@B}_8\text{C}_4^+$  and  $10\pi$  aromaticity for  $\text{La@B}_8\text{C}_4^-$ .

The chemical bonding patterns in both  $\text{La@B}_8\text{C}_4^{+/-}$  molecular wheels are accurately elucidated by the AdNDP analyses. The AdNDP results for  $\text{La@B}_8\text{C}_4^+$  (Fig. 5) reveal eight localized  $2c-2e$  B-C  $\sigma$  bonds and four localized  $2c-2e$  B-B  $\sigma$  bonds in peripheral  $\text{B}_8\text{C}_4$  ring, which are related to the CMOs in Fig. S6(a) (ESI $^\dagger$ ). There are four  $3c-2e$   $\text{-BCB-}$  island  $\sigma$  bonds and one thirteen-center two-electrons ( $13c-2e$ )  $\sigma$  bond in  $\text{B}_8\text{C}_4$  ring, supporting its  $10\sigma$  aromaticity. Meanwhile, the four  $3c-2e$   $\text{-BCB-}$  island  $\pi$  bonds are in line with  $8\pi$  antiaromaticity. The island version for four  $3c-2e$   $\sigma$  and  $\pi$  bonds are fully supported by the ELF analyses. The AdNDP results for  $\text{La@B}_8\text{C}_4^-$  (Fig. 6) show the identically localized B-B/B-C  $\sigma$  bonds and delocalized

$\sigma$  framework on  $\text{B}_8\text{C}_4$  ring with  $\text{La@B}_8\text{C}_4^+$ . Differently, it has one more fully delocalized  $13c-2e$   $\pi$  bond except for four  $3c-2e$   $\text{-BCB-}$  island  $\pi$  bonds, firmly confirmed its  $10\pi$  aromaticity. It should be noted that the occupation numbers (ON) of the  $3c-2e$   $\text{-BCB-}$   $\sigma$  and  $\pi$  bonds in both  $\text{La@B}_8\text{C}_4^+$  and  $\text{La@B}_8\text{C}_4^-$  clusters ( $1.88/1.87$  versus  $1.85$ ) are less than 2, hinting a small degree of covalent interaction between the  $\text{B}_8\text{C}_4$  ring and the central La atom, which is consistent with the small WBIs of B-La/C-La links. The AdNDP data of  $\text{La@B}_8\text{C}_4$  cluster (obtained from UAdNDP version) are indicated in Fig. S9 (ESI $^\dagger$ ), showing one global delocalized  $13c-1e$   $\pi$  bond. In addition, the AdNDP chemical bonding images (four  $3c-2e$  island  $\sigma/\pi$  bonds plus one  $13c-2e$  delocalized  $\sigma/\pi$  bond) of  $\text{La@B}_8\text{C}_4^{+/-}$  molecular wheels are reasonable, which is in line with the structural data, and rationalizes the delocalized  $\sigma$  and  $\pi$  frameworks as well.

The anisotropy of current-induced density (ACID) analyses was performed to probe the ring currents of  $\text{La@B}_8\text{C}_4^+$  and  $\text{La@B}_8\text{C}_4^-$  clusters, induced by an external magnetic field being vertical to molecular wheels. The decomposed  $\sigma$  and  $\pi$ -ring



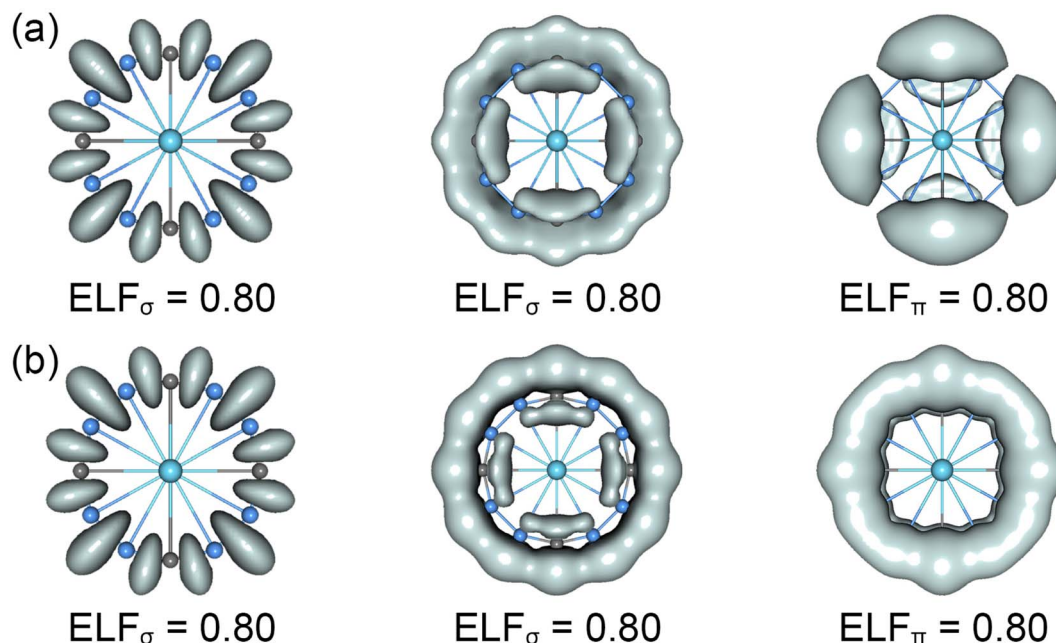


Fig. 4 Electron localization functions (ELFs) for (a) the  $C_{4v}$  ( $^1A_1$ ) GM of  $La@B_8C_4^+$  and (b) the  $D_{4h}$  ( $^1A_{1g}$ ) LM of  $La@B_8C_4^-$  clusters.

current images with a high-resolution are depicted in Fig. S10 (ESI†). The  $La@B_8C_4^+$  molecular wheel shows the robust  $\sigma$ -ring current (Fig. S10(a)†) on whole  $B_8C_4$  peripheral ring. In contrast, its  $\pi$ -ring current is clearly localized on four  $-BCB-$  units, showing local circulation for vector of induced current density. The direction of  $\pi$ -ring current is opposite to that of  $\sigma$ -ring currents, supporting the  $10\sigma$  and  $8\pi$  conflicting aromaticity.

The  $La@B_8C_4^-$  molecular wheel shows the robust  $\sigma$  and  $\pi$ -ring current (Fig. S10(b)†), perfectly elucidating the  $10\sigma$  and  $10\pi$  double aromaticity.

The thermal stabilization for  $La@B_8C_4^{+/0/-}$  molecular wheels is mainly attributed to the cyclic electron delocalization in peripheral  $B_8C_4$  ring, albeit the  $La@B_8C_4^+$  cluster possesses  $8\pi$  antiaromaticity. Furthermore, we calculated the bond

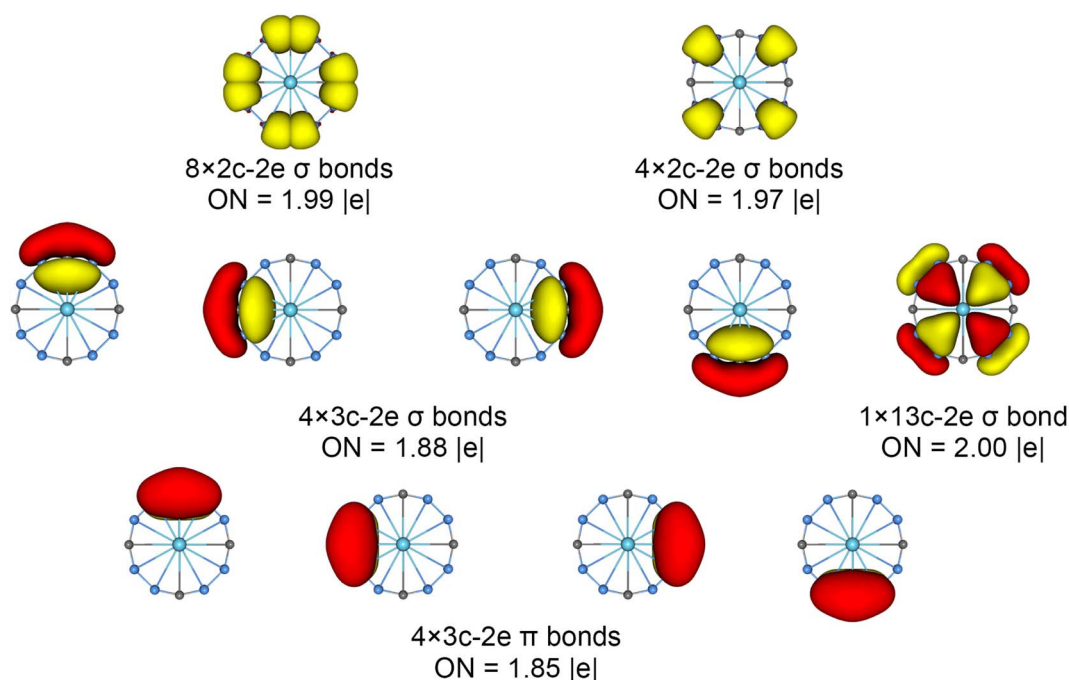


Fig. 5 Chemical bonding pattern of the  $C_{4v}$  ( $^1A_1$ ) GM  $La@B_8C_4^+$  cluster based on the adaptive natural density partitioning (AdNDP) analysis. Occupation numbers (ONs) are indicated.



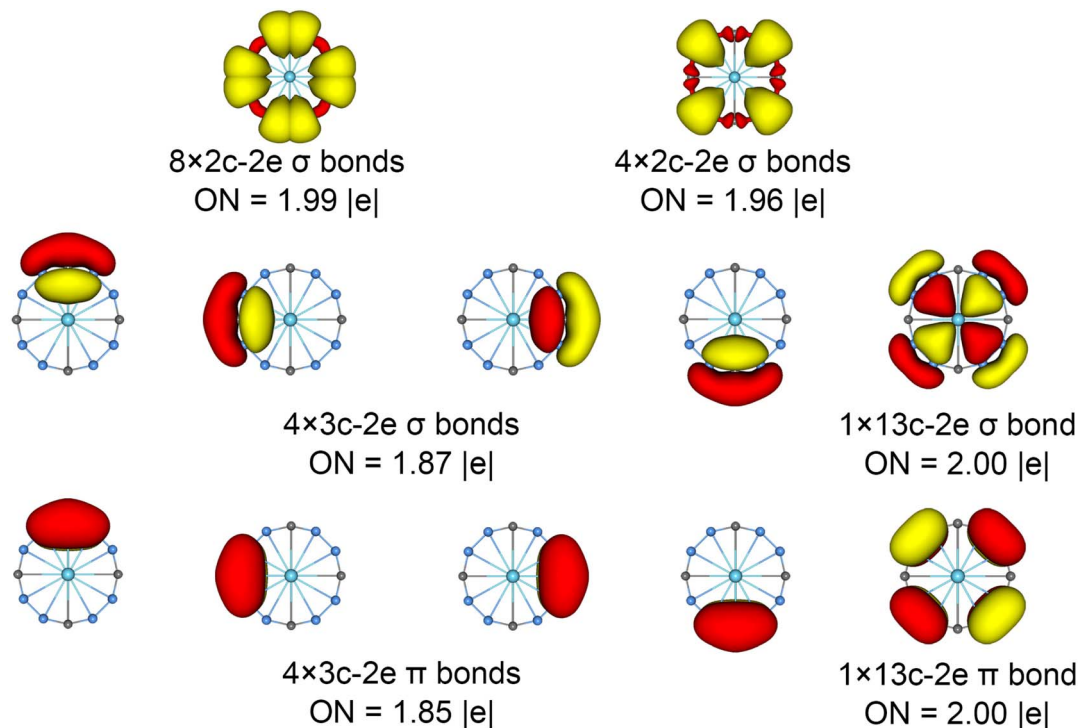


Fig. 6 Chemical bonding pattern of the  $D_{4h}$  ( $^1A_{1g}$ ) LM  $\text{La@B}_8\text{C}_4^-$  cluster based on the AdNDP analysis. The ONs are indicated.

dissociation energy (BDE) and inherent interaction energy of  $\text{La@B}_8\text{C}_4$  between the central La atom and  $\text{B}_8\text{C}_4$  motif according to the below formulas.

$$\text{La@B}_8\text{C}_4 (C_{4v}, ^2B_1) = \text{B}_8\text{C}_4 (\text{LM}, D_{4h}, ^1A_{1g}) + \text{La}$$

$$\text{La@B}_8\text{C}_4 (C_{4v}, ^2B_1) = \text{B}_8\text{C}_4 (\text{frozen}, D_{4h}, ^1A_{1g}) + \text{La}$$

where, the  $\text{B}_8\text{C}_4$  (LM,  $D_{4h}$ ,  $^1A_{1g}$ ) has a square geometry, a true local minimum on its potential surface. Rather, the  $\text{B}_8\text{C}_4$  (frozen,  $D_{4h}$ ,  $^1A_{1g}$ ) represents the frozen fragment form  $\text{La@B}_8\text{C}_4$  molecular wheel, which is a second-order saddle point. The  $\text{B}_8\text{C}_4$  (LM,  $D_{4h}$ ,  $^1A_{1g}$ ) and  $\text{B}_8\text{C}_4$  (frozen,  $D_{4h}$ ,  $^1A_{1g}$ ) are calculated at B3LYP/6-311+G\* level, the La atom is done at B3LYP/ECP28MWB\_ANO level, respectively. The BDE and inherent interaction energies are as high as  $-178.99$  and  $-208.59$  kcal mol $^{-1}$ , respectively, confirming the stabilization of dodeca-coordinated  $\text{La@B}_8\text{C}_4$  molecular wheel. The energy difference between the BDE and inherent interaction energy describes the isomerization energy of  $\text{B}_8\text{C}_4$  motif from the square geometry to a circular one in nature (Fig. S11, ESI†).

### 3.5. The electronic counting rule in $\text{La@B}_8\text{C}_4^q$ molecular wheels

The fascinating transition-metal centered boron molecular wheels  $\text{M@B}_n^{q-}$  is controlled by the double ( $\sigma$  and  $\pi$ ) aromaticity, following the electronic design principle ( $n + x + q = K$ ) proposed by Wang and coworkers.<sup>26</sup> In intriguing  $\text{La@B}_8\text{C}_4^{+/0/-}$  boron-carbon molecular wheels, each C atom can provide two delocalized electrons, one more than B atom. Thus, an update

version of electronic design principle for  $\text{M@B}_m\text{C}_n^{q-}$  molecular wheels is proposed, that is  $m + 2n + x \pm q = K$ , where the  $m$  and  $n$  is the number of peripheral B and C atoms,  $x$  is the formal valence of central metal atoms,  $q$  is the cluster's charge. The  $\text{La@B}_8\text{C}_4^{+/0/-}$  molecular wheels are unprecedented with the highest dodeca-coordination number in plane, following  $m + 2n + x \pm q = 18, 19$  and  $20$  electronic counting principles, respectively. The anionic  $\text{La@B}_8\text{C}_4^-$  molecular wheel has  $(10\sigma + 10\pi)$  double aromaticity, following  $(4N_{\sigma/\pi} + 2)$  Hückel rule with  $N_{\sigma} = N_{\pi} = 2$ , respectively. The neutral  $\text{La@B}_8\text{C}_4$  molecular wheel is an open-shell system with a single occupied  $\pi$  orbital, possessing the  $10\sigma$  and  $9\pi$  double aromaticity. Interestingly, the cationic  $\text{La@B}_8\text{C}_4^+$  cluster is a conflicting aromatic system of with  $10\sigma$  and  $8\pi$  delocalized electrons ( $K = 18$ ), obeying the  $(4N_{\sigma} + 2)$  and  $(4N_{\pi})$  Hückel rule with  $N_{\sigma} = N_{\pi} = 2$ , respectively. Thus,  $\text{La@B}_8\text{C}_4^+$  represents a counterexample for double aromaticity in planar hypercoordinate molecular wheels.

## 4. Conclusions

In summary, we have theoretically predicated three dodeca-coordinated  $\text{La@B}_8\text{C}_4^{+/0/-}$  molecular wheels, featuring a central La atom enclosed by a perfectly planar  $\text{B}_8\text{C}_4$  ring, which is viable in the  $-(\text{BCB})_4^-$  form. The  $\text{La@B}_8\text{C}_4^+$  and  $\text{La@B}_8\text{C}_4$  molecular wheels have the  $C_{4v}$  symmetry with a slightly out-of-plane distortion of La atom. The  $\text{La@B}_8\text{C}_4^-$  molecular wheel is perfectly planar. The stabilizations of  $\text{La@B}_8\text{C}_4^{+/0/-}$  molecular wheels are benefit from their unique chemical bonding. The  $\text{La@B}_8\text{C}_4$  and  $\text{La@B}_8\text{C}_4^-$  molecular wheels have  $10\sigma$  and  $9\pi/10\pi$  delocalized electrons, obeying the universal





principle of double aromaticity, whereas, the  $\text{La}@\text{B}_8\text{C}_4^+$  molecular wheel is a counterexample, which has the conflicting aromaticity with  $10\sigma$  and  $8\pi$  delocalized electrons. The  $\text{La}@\text{B}_8\text{C}_4^{+/0/-}$  molecular wheels with dodeca-coordination number are unprecedented for a planar system in coordination chemistry.

## Conflicts of interest

There are no conflicts to declare.

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