Formation of the Quasi-planar B₅₀ Boron Cluster: Topological Path from B₁₀ and Disk Aromaticity

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(Abstract)

The lowest-lying isomer of the B₅₀ boron cluster is confirmed to have a quasi-planar shape with two hexagonal holes. By applying the topological (leap-frog) dual operation followed by a boron capping, we demonstrated that such a quasi-planar structure actually comes from the smallest elongated B₁₀²⁻, and its high thermodynamic stability is due to its inherent disk aromaticity arising from its 32 valent π electrons that fully occupy a disk configuration of $[(1\sigma)^2(1\pi)^4(1\delta)^4(2\sigma)^2(1\phi)^4(2\pi)^4(1\gamma)^4(2\delta)^4(1\eta)^4]$. The aromatic character of the quasi-planar B₅₀ is further supported by a strong diatropic magnetic current flow. The sudden appearance of a quasi-planar B₅₀ again points out that the growth pattern of pure boron clusters is still far from a complete understanding.

Keywords: B₅₀, Topological path; Leap-frog approach; Boron disk; Disk aromaticity; Magnetic ring current

The past decades have witnessed great advances in the cluster science, and as a result a large amount of non-classical structures have been revealed. Intensive experimental and theoretical investigations have been, and still are, carried out to gain more understanding on the relationships between geometrical shape, electronic structure and thermodynamic stability of elemental clusters, as well as their unusual properties. Owing to the wealth of available information, some design principles for novel cluster-based materials having tailored properties have been proposed.^{1,2,3,4,5,6,7,8,9}

Of the atomic clusters, the family of boron clusters appears to be as a special case due to the great diversity of its structural feature and chemical bonding phenomena. Actually the growth pattern of bare boron clusters still is a mystery. Previous landscape studies on small boron clusters B_n pointed out that a planar or quasi-planar shape is favoured for the size up to $n = 16$ for cations, and $n = 19$ for neutrals.^{10,11,12} However, the neutral B_{14} fullerene emerges as an exception of the planar shape tendency.¹³ Starting from the size B_{20} , a double ring tube connecting two B_n strings in an anti-prism form is found as the ground state of B_{20} , B_{22} , B_{24} and B_{26} clusters in the neutral state.¹⁴ More particularly, B_{27}^+ and B_{42} exhibit a triple ring tubular shape in which their geometry is constructed by superposing three B_9 and B_{14} strings in anti-prism fashion, respectively.^{15,16} These sizes show that a tubular shape is also an inherent structure of boron clusters beside the planar one. In growing further, both B_{28} and B_{29} turn out to have a cage-like structure rather than a planar or tubular shape emphasizing the unpredictability of boron cluster structures.^{17,18,19,20}

Then the appearance of bowl-shaped boron clusters brings in a surprise. Numerous studies demonstrated that the B_{26}^- , B_{30} , B_{32} , B_{33}^- , B_{34}^- , $B_{35}^{-/0}$ and B_{36} clusters are, among others, classified into a new bowl-like class which contains either one pentagonal or one hexagonal

hole.^{21,22,23,24,25} The following sizes B_{37}^- and B_{38}^- also exhibit bowl-shaped structures but with two hexagonal holes.²⁶ The appearance of many bowl-shaped structures led to an assumption that these small size boron clusters could be part of the boron sheets, and some kinds of planar structure were predicted to be favoured for subsequent sizes. However, a number of cage-like or fullerene structures have been found as global energy minimum isomers for the larger sizes including B_{39}^+ , B_{40} , B_{41}^+ , B_{42}^+ , B_{44} and B_{46} .^{27,28} Although the B_{46} was predicted to be a cage with an octagonal hole, subsequent calculations showed that a core-shell structure with four internal B atoms could be more stable.²⁹ The global minimum of B_{46} is not well established yet. More impressively, a double layer structure has been found for B_{48} suggesting a possibility of boron cluster to form two-dimensional bilayer phase.²⁹ The emergence of fullerene-like, core-shell and double-layer seems to suggest that the behaviour of boron clusters could be similar to that of isovalent aluminum clusters at larger sizes.^{30,31,32} Contrary to such an expectation, a quasi-planar structure **1** containing two hexagonal holes (Figure 1) has suddenly been found as the lowest-energy isomer for the B_{50} cluster.²⁹ This finding illustrates once more that the growth pattern of boron clusters is still far from regular and not fully understood yet.

In attempts to understand such a structural diversity of boron clusters, different theoretical models have been proposed to emphasize the interplay between their geometrical feature, electronic structure and thermodynamic stability.^{15,33,34,35} The classical $(4N + 2)$ Hückel rule for aromaticity has initially been applied for π electrons of small planar boron clusters, and some successes have been recorded.¹² However, the Hückel electron count cannot be applied to many boron clusters having planar and tubular shapes.^{15,34,35,36} The simple models of a particle moving in a box associated with a specific cluster geometry provide us with an excellent interpretation not only for their electronic structure but also for their aromatic character. As a matter of fact, for

tubular clusters including B_{20} , B_{22} , B_{24} , B_{26} , B_{27}^+ and B_{42} , the model of a particle moving in hollow cylinder excellently reproduces the shapes and energy levels of the MOs of these clusters, and thereby establishing some novel electron counts.

In considering the model of a particle moving in a circular disk, the concept of disk aromaticity has been proposed and can successfully rationalize the stability for concentric (“ring-in-ring”) planar boron clusters including B_{18}^{2-} , B_{19}^- and B_{20}^{2-} .^{35,36} Some quantum rules have been put forward for the planar B_n up to size $n = 20$.^{36,37} The high stability of bowl-shaped clusters such as B_{30} , B_{32} , B_{36} and B_{42} can also be rationalized in terms of the disk aromaticity concept.^{16,38}

Of the boron clusters having a structural fluxionality, B_{50} thus appears to be a special case. While the 3D structures including fullerene, core-shell, triple ring and double layer... forms are dominant in the range of B_{40} - B_{48} , the B_{50} size suddenly emerges in a stable quasi-planar shape **1** (Figure 1). According to the previous report,²⁹ **1** can be regarded as an aromatic compound characterized by a negative NICS value. Although the NICS value is not a reliable magnetic indicator for aromatic character due to the fact that it is estimated at a fixed point whereas the aromatic property is dynamically induced by freely delocalized electrons over the entire skeleton,^{39,40} it can suggest a certain aromatic character. In this context, we set out to investigate in the present work two different intrinsic aspects of **1**, namely where it comes from, and why it is so thermodynamically stable. For this purpose, we demonstrate a topological relationship between the stable elongated B_{10}^{2-} cluster and **1** by using an approach derived from the graph theory and popularly known as the leap-frog approach. We then carefully analyze the electronic structure, chemical bonding and aromatic character of B_{50} **1** by mean of the disk aromaticity concept and magnetic ring current maps. The molecular orbitals (MOs) of B_{50} **1** are carefully rationalized using the model of electron in a circular disk. To elucidate the aromatic character of

1, a magnetic indicator, namely the gauge-including magnetically induced current (GIMIC), is used for probing the electron motion over the whole molecular skeleton.⁴¹

Topological Leap-frog Approach: Formation of Quasi-planar B₅₀ from Elongated B₁₀.

Let us first demonstrate the formation of B₅₀ **1** through a topological path starting from an elongated B₁₀ form, known as the leapfrog operation [**L**]. This mathematical operation which was first suggested as a generating scheme to yield large stable fullerenes (C_n),⁴² consists of a combination of an omni-capping [**O**] and a dual [**D**] operation. Afterwards, this approach was applied to the boron cages (B_n) with an addition of boron caps, denoted as operation [**C**], on all new hexagons to generate B_{4n}-fullerenes that exhibit properties similar to C_{3n}-fullerenes.⁴³

A leapfrog operation proceeds as follows: first each face of the parent geometry is capped. This omni-capping operation [**O**] transforms a parent ring into a triangular tessellated geometry. It is then followed by another operation, called dual [**D**], that changes all faces into vertices and vertices into faces, and rotate each edge of the parent geometry by 90 degree. The leapfrog operation [**L**] applied to a parent geometric cage P can be summarized as follows:

$$\mathbf{L}\{\mathbf{P}_n\} = \mathbf{D.O}\{\mathbf{P}_n\} = \mathbf{P}_{3n} \text{ for C-fullerenes,}^{42} \text{ and}$$

$$\mathbf{L}\{\mathbf{P}_n\} = \mathbf{C.D.O}\{\mathbf{P}_n\} = \mathbf{C P}_{3n} = \mathbf{P}_{4n} \text{ for B-fullerenes,}^{43}$$

where **L**, **D**, and **O** stand for leap-frog, dual and omni-capping operations, respectively. **C** represents a capping of all new hexagons in order to compensate for boron electron deficiency in which caps boron atoms are added on each new hexagons obtained after the dual transformation.^{43,44}

In this section we show that this topological approach can be extended to the smallest elongated B_{10}^{2-} structure to generate the global minimum geometry of B_{50} **1**. The different steps of this operation applied to an B_{10} form to establish B_{50} are illustrated in Figure 2. Actually, the most stable form of the dianion B_{10}^{2-} seen in Figure 2b is considered as the smallest elongated aromatic boron cluster comprising 4-centre-2-electron bonds.³⁷ This B_{10}^{2-} geometry is formed upon overlapping of two capped hexagons (Figure 2a).^{45,46} If one converts each face of this elongated cluster B_{10}^{2-} to a vertex, and then each of its vertex becomes a face (Figure 2c), this operation, called dual operation **[D]** (see above), leads to a new geometry having ten hexagons (Figure 2c).⁴⁴ The two internal boron atoms of B_{10} actually coincide to both capped B atoms, resulting from operation **[O]** and are transformed into empty hexagons, while the eight surrounding B atoms are capped B atoms (Figure 2d). The resulting geometry of this operation is a B_{40} planar geometry, being thus four times as large as the number of atoms of the parent geometry. Because the boron element is electron deficient, its clusters do not like having empty corner spaces such as the case of carbon clusters on their peripheral ring. Therefore, ten additional boron atoms forming 6 x B_4 patterns are needed to homogenously be distributed on the peripheral by applying the **[C]** operation (cf. equations above) in order to form a disk-like geometry to compensate the inherent electron deficiency of B (Figure 2e-f). This finally yields the B_{50} cluster **1** (Figure 1) exhibiting a high symmetry D_{2h} as illustrated in Figures 2g-h, which contains two fused empty hexagons and eight capped hexagons.

The global energy minimum geometry of B_{50} was determined from previous investigations,²⁹ and we now reoptimize it using density functional theory with the hybrid TPSSh functional in conjunction with the 6-311+G(d) basis set. Our geometry optimizations actually confirm that **1** corresponds well to the energetically most stable isomer of B_{50} . As given in

Figure 3, electron population analysis using NBO calculations of **1** also shows that all additional B atoms are indeed the mostly positively charged centers, indicating that those B atoms are transferring their electrons to the dual B₄₀ form. Accordingly, the most remarkable result is that a leap-frog topological path starting from the most stable form of B₁₀²⁻ leads to the most stable form of B₅₀.

Electronic Structure of B₅₀ **1**.

Let us now examine the electronic structure of the quasi-planar B₅₀ **1** under the light of the disk aromaticity concept. This concept has recently been introduced on the basis of a model of a particle freely moving in a circular disk, and successfully rationalized the interplay between the electronic structure and stability of several planar and quasi-planar and bowl-shaped clusters.^{34,35}

In considering a free particle moving in a circular disk, the corresponding Schrödinger equation in polar coordinates can be written as follows (equation 1):

$$-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \varphi^2} \right) \Psi(\varphi, r) = E \Psi(\varphi, r) \quad (1)$$

where $r = R$ is radius of the disk, $\hbar$ the Plank constant and μ the mass of the particle. Within the circular symmetry, $\Psi(\varphi, r)$ can be written as:

$$\Psi(\varphi, r) = R(r) \cdot \Phi(\varphi)$$

where $\Phi(\varphi) = \exp(im\varphi) / (2\pi)^{1/2}$. The angular part should be periodic due to the requirement of boundary conditions. Therefore, the cylindrical quantum number must be integer, namely $m = 0, \pm 1, \pm 2, \dots$. Substitution of the wavefunction into the Schrödinger equation (1) gives us the radial part, with $\hbar^2 k^2 = 2\mu E$ (equation 2):

$$\frac{\partial^2 R(r)}{\partial r^2} + \frac{1}{r} \frac{\partial R(r)}{\partial r} + \left(k^2 - \frac{m^2}{r^2} \right) R(r) = 0 \quad (2)$$

Equation (2) is well known as the Bessel's differential equation whose solutions are the integer Bessel function $J_m(kr)$.⁴⁷ The potential wall at $r = R$ requires the radial function to vanish at the boundary of the box, $J_m(k,R) = 0$ are termed as zeros of Bessel's functions. The radii associated with such zeroes of Bessel's function are denoted as $a_{m,n}$. The eigenvalues of the solutions are determined as follows (equation 3):

$$E = \frac{\hbar^2 (a_{m,n})^2}{2\mu R^2} \quad n = 1, 2, 3, \dots; m = 0, \pm 1, \pm 2, \pm 3, \dots \quad (3)$$

The rotational quantum numbers m are usually denoted by Greek letters as σ ($m = 0$), π ($m = \pm 1$), δ ($m = \pm 2$), ϕ ($m = \pm 3$), γ ($m = \pm 4$), η ($m = \pm 5$) etc... The eigenstates with non-zero value of m are twofold degenerate. The lowest eigenstates in an ascending ordering are thus denoted as 1σ , 1π , 1δ , 2σ , 1ϕ , 2π , etc... Within the framework of the phenomenological shell model, a molecular system whose number of electrons fully occupies the eigenstates of the disk is classified as a disk aromatic compound, and according to equation (3), these electron numbers are counted being equal to 2, 6, 10, 12, 16, 20, 24, 28, ... While the first values correspond to the Hückel ($4N + 2$) electron count, the subsequent values no longer satisfy it.

Aromaticity of B₅₀ 1.

The energies of frontier MOs of B₅₀ **1** computed at the TPSSh/6-311+G(d) level are given in Table S1 of the Supplementary Information (ESI) file. **1** contains 32 π electrons that are

distributed in 16 delocalized MOs. Therefore, it is formally classified as anti-aromatic according to the Hückel rule. This assignment is in conflict with a previous conclusion²⁹ based on NICS calculations which pointed out a negative NICS value for **1**. Actually, delocalized π -MOs of B₅₀ **1** are well reproduced by the model of a particle moving in circular disk. A comparison of the shapes of delocalized π -MOs of **1** with those of eigenstates of disk model is shown in Figure 4 and Figure S2 (ESI file). According to the corresponding eigenstates of the relevant π MOs, the 32 π electrons of B₅₀ **1** turn out to fill a disk configuration as $[(1\sigma)^2(1\pi)^4(1\delta)^4(2\sigma)^2(1\phi)^4(2\pi)^4(1\gamma)^4(2\delta)^4(1\eta)^4\dots]$. Indeed, both HOMO-38 and HOMO-14 of **1** are associated with both 1σ and 2σ eigenstates, and each of them is occupied by two electrons. HOMO-36 and HOMO-37 are well represented by the 1π eigenstates, and similarly, HOMO-13, and HOMO-11 correspond to the 2π level. On the basis of eigenstates, the HOMO-34 and HOMO-33 of **1** are associated with the disk 1δ eigenstates, while HOMO-7 and HOMO-4 are reproduced by the disk 2δ level. HOMO-10 and HOMO-8 have a same representation as that of 1ϕ eigenstate, and two MOs constitute the 1ϕ level are occupied by 4 electrons for disk configuration. Similarly, the 1γ disk level is actually appeared in the HOMO-7 and HOMO-4. Finally, both HOMO-1 and HOMO are assigned as the 1η eigenstate fulfilled by 4 electrons. Hence, the 32 π valent electrons of B₅₀ **1** are fully populating the levels of a disk configuration, and thereby give rise to a high thermodynamic stability for this cluster. In term of electron counting, the 32 π electrons of **1** satisfy the counting rule of the disk aromaticity (cf. equation (3)) rather than that of the $(4N+2)$ Hückel count.

According to the disk model the strict order for the upper part of the occupied orbitals is given by:

$$\dots 1\phi < 2\pi < 1\gamma < 2\delta < 3\sigma < 1\eta < 2\phi \dots \quad (4)$$

In B₅₀ **1** it is seen that the ordering of both 1 η and 3 σ levels has been inverted, and coincides with the HOMO-LUMO gap. In the disk model these levels are very close in energy, and the inversion is due to the presence of two hexagonal voids in the center, which will raise the 3 σ level. The a₁ LUMO (considering C_{2v} point group) can indeed be associated with the 3 σ disk level, while the next LUMO+1 and LUMO+2 have the nodal patterns of the 2 ϕ function, as predicted by the disk model (Table S1, ESI file).

To illustrate further the aromaticity of **1**, its magnetic current density is performed using the GIMIC method.^{48,49} The magnetic field is oriented perpendicularly to the molecular plane. The direction of the magnetic field is chosen in such a way that the diatropic ring current, associated with an aromatic feature, circle in the clockwise direction, and reversely the paratropic ring currents, giving an anti-aromatic character, are in the anticlockwise direction. Nuclear magnetic resonance shielding for GIMIC calculations are performed using the Gaussian 09 package.⁵⁰

The magnetic ring current map of B₅₀ is shown in Figure 5. Accordingly, B₅₀ **1** produces a diatropic current with respect to a magnetic response, and as a result this cluster is an aromatic species. The disk aromaticity constitutes a reason for the quasi-planar shape as well as the high thermodynamic stability of the B₅₀ cluster **1**.

To gain more insights into the electronic structure of **1**, its electron distribution is examined by means of electron localization function (ELF) map.⁵¹ As shown in Figure 6, at the bifurcation value of ELF = 0.70, electrons are delocalized over its whole skeleton. With ELF = 0.75 and 0.80, all of localization domains are associated to trisynaptic V(B,B,B) basins, and B atoms of the middle strings are involved in three-center bonds with inner and outer strings. Formation of delocalized bonds in **1** thus gives rise to its high stability.

Using a topological approach, it is shown that B_{50} can be formed from an elongated B_{10} whose dianion is an aromatic species according to ring current calculations.⁵² Interestingly, from a B_{10} aromatic cluster, a topological transformation ends up in a quasi-planar B_{50} disk which is also aromatic. This result strongly suggests that a topological operation from an aromatic species can lead to a larger aromatic counterpart. The π valent electrons of B_{10}^{2-} apparently obeys the classical $(4N+2)$ counting rule whereas those of B_{50} rather follow a different $4N$ count of the circular disk. However, the electron numbers in both structures can consistently be accounted for by the disk levels.

A comparison between the bowl-shaped B_{30} and B_{36} and the planar B_{42} disks points out an interesting relationship between them in terms of aromaticity. In previous investigations, the concentric $B_n@B_{2n}@B_{3n}$ with $n = 5, 6$ and 7 quasi-planar clusters were identified as disk aromatic compounds according to disk electron counts as well as magnetic ring current calculations.¹⁶ The bowl-shaped B_{30} cluster contains 20π electrons populated in a disk configuration of $[(1\sigma)^2 (1\pi)^4 (1\delta)^4 (2\sigma)^2 (1\phi)^4 (2\pi)^4 \dots]$, while the disk configuration of B_{36} is identified as $[(1\sigma)^2 (1\pi)^4 (1\delta)^4 (2\sigma)^2 (1\phi)^4 (2\pi)^4 (1\gamma)^4 \dots]$ which is established by simply adding the $(1\gamma)^4$ eigenstate to that of B_{30} , giving rise to 24π electrons. The electron configuration of B_{42} is established by adding the $(2\delta)^4$ level to that of B_{36} and thus occupied by 28π electrons. Therefore, as for an extension, the next member of this disk aromatic family should exhibit 32π electrons with a disk configuration of $[(1\sigma)^2 (1\pi)^4 (1\delta)^4 (2\sigma)^2 (2\pi)^4 (1\phi)^4 (1\gamma)^4 (2\delta)^4 (1\eta)^4 \dots]$ which turns out to be the shell configuration of B_{50} **1** as mentioned above. Hence, it is beyond any doubt that the quasi-planar B_{50} **1** is a member of family of disk aromatic compounds.

In summary, we confirmed in the present theoretical study that the B_{50} cluster is the largest size boron cluster to date which is thermodynamically stable in a quasi-planar shape. By

applying the topological leap-frog dual operation followed by boron capping, which is derived from the graph theory, we demonstrated that such a quasi-planar structure actually comes from the smallest elongated B_{10}^{2-} , and its high thermodynamic stability is due to its inherent disk aromaticity arising from its 32 valent π electrons.

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Conflict of Interest.

There is no conflict of interest to declare.

Figure 1. Three different views of the quasi-planar B₅₀ boron cluster **1**.

a)

b)

c)

d)

e)

f)

g)

h)

Figure 2. A topological leapfrog operation applied to B_{10} leading to B_{50} : a) B_{10} formed from two overlapped hexagons. b) an elongated B_{10} , c) dual operation **[O]** and **[D]**, d) the resulting B_{40} , e) and f) B-capping, g) and h) the resulting B_{50} .

Figure 3. NBO charge populations of B_{50} **1**. A scale from positive to negative charges associates with green to red.

Figure 4: Calculated π -MOs of B_{50} **1** (TPSSH/6-311+G(d), lower panel) and disk eigenstates including 1ϕ , 1γ and 1η of the model of a particle on circular box (upper panel).

Figure 5: Ring current map of B₅₀ 1. Current density (GMIC) is obtained using TPSSh/6-311+G(d) calculation.

Figure 6: ELF iso-surface of B₅₀ **1** plotted at different bifurcation values ELF. Electron density is obtained from TPSSh/6-311+G(d) calculation.

References

- 1 P. Jena and Q. Sun, *Chem. Rev.* 2018, **118**, 5755-5870.
- 2 A. C. Reber and S. N. Khana, *Acc. Chem. Res.*, 2017, **50**, 255-263.
- 3 Z. Luo and A. W. Castleman, *Acc. Chem. Res.*, 2014, **47**, 2931-2940.
- 4 Z. Luo, A. W. Castleman and S. N. Khanna, *Chem. Rev.*, 2016, **116**, 14456-14492.
- 5 S. Mitzinger, L. Broeckaert, W. Massa, F. Weigend and S. Dehnen, *Nat. Comm.*, 2016, **7**, 10480.
- 6 X. Roy, C. H. Lee, A. C. Crowther, C. L. Schenck, T. Besara, R. A. Lalancette, T. Siegrist, P. W. Stephens, L. E. Brus, P. Kim, M. L. Steigerwald and C. Nuckolls, *Science*, 2013, **341**, 154-157.
- 7 A. Pinkard, A. M. Champsaur, X. Roy, *Acc Chem Res.* 2018, **51**, 919-929.
- 8 A. M. Champsaur, A. Velian, D. W. Paley, B. Choi, X. Roy, M. L. Steigerwald and C. Nuckolls, *Nano.Lett.*, 2016, **16**, 5273-5277.
- 9 C. Tan, X. Cao, X. J. Wu, Q. He, J. Yang, X. Zhang, J. Chen, W. Zhao, S. Han and G. H. Nam, *Chem. Rev.* 2017, **117**, 6225-6331.
- 10 E. Oger, N. R. Crawford, R. Kelting, P. Weis, M. M. Kappes and R. Ahlrichs, *Angew. Chem. Int. Ed.* 2007, **46**, 8503-8506.
- 11 T. B. Tai, N. M. Tam and M. T. Nguyen, *Theoret. Chem. Acc.* 2012, **131**, 1241 (15 pages) and references therein.
- 12 A. P. Sergeeva, I. A. Popov, Z. A. Piazza, W. L. Li, C. Romanescu, L. S. Wang and A. I. Boldyrev, *Acc. Chem. Res.*, 2014, **47**, 1349-1358.
- 13 L. Cheng, *J. Chem. Phys.*, 2012, **136**, 104301.
- 14 T. B. Tai and M. T. Nguyen, *Phys. Chem. Chem. Phys.*, 2015, **17**, 13672-13679.
- 15 L. V. Duong, H. T. Pham, N. M. Tam and M. T. Nguyen, *Phys. Chem. Chem. Phys.*, 2014, **16**, 19470-19478.
- 16 H. T. Pham, L. V. Duong, N. M. Tam, M. P. P. Ho, M. T. Nguyen, *Chem. Phys. Lett.*, 2014, **608**, 295-302.
- 17 J. Zhao, X. Huang, R. Shi, H. Liu, Y. Su and R. B. King, *Nanoscale*, 2015, **7**, 15086-15090.
- 18 H. R. Li, T. Jian, W. L. Li, C. Q. Miao, Y. J. Wang, Q. Chen, X. M. Luo, K. Wang, H. J. Zhai, S. D. Li and L. S. Wang, *Phys. Chem. Chem. Phys.*, 2016, **18**, 29147 – 29155,

-
- 19 Y. J. Wang, Y. F. Zhao, W. L. Li, T. Jian, Q. Chen, X. R. You, T. Ou, X. Y. Zhao, H. J. Zhai, S. D. Li, J. Li and L. S. Wang, *J. Chem. Phys.*, 2016, **144**, 064307.
- 20 L. Pei, H. R. Li, M. Yan, Q. Chen, Y. W. Mu, H. G. Lu, Y. B. Wu and S. D. Li, *Phys. Chem. Chem. Phys.*, 2018, **20**, 15330-15334.
- 21 X. M. Luo, T. Jian, L. J. Cheng, W. L. Li, Q. Chen, R. Li, H. J. Zhai, S. D. Li, A. I. Boldyrev, J. Li, L. S. Wang, *Chem. Phys. Lett.*, 2017, **683**, 336–341.
- 22 Q. Chen, W. L. Li, X. Y. Zhao, H. R. Li, L. Y. Feng, H. J. Zhai, S. D. Li and L. S. Wang, *Eur. J. Inorg. Chem.*, 2017, 4546–4551.
- 23 W. L. Li, Q. Chen, W. J. Tian, H. Bai, Y. F. Zhao, H. S. Hu, J. Li, H. J. Zhai, S. D. Li and L. S. Wang, *J. Am. Chem. Soc.*, 2014, **136**, 12257–12260.
- 24 T. B. Tai and M. T. Nguyen, *Chem. Commun.*, 2016, **52**, 1653-1656.
- 25 Z. A. Piazza, H. S. Hu, W. L. Li, Y. F. Zhao, J. Li and L. S. Wang, *Nat. Comm.*, 2014, **5**, 3113-3118.
- 26 Q. Chen, W. J. Tian, L. Y. Feng, H. G. Lu, Y. W. Mu, H. J. Zhai and S. D. Li and L. S. Wang, *Nanoscale*, 2017, **9**, 4550-4557.
- 27 Q. Chen, S. Y. Zhang, H. Bai, W. J. Tian, T. Gao, H. R. Li, C. Q. Miao, Y. W. Mu, H. G. Lu, H. J. Zhai and S. D. Li, *Angew. Chem. Int. Ed.* 2015, **54**, 8160 –8164.
- 28 X. Y. Zhao, Q. Chen, H. R. Li, Y. W. Mu, H. G. Lu and S. D. Li, *Phys. Chem. Chem. Phys.*, 2017, **19**, 10998 -11003.
- 29 L. Sai, X. Wu, N. Gao, J. Zhao and R. B. King, *Nanoscale*, 2017, **9**, 13905–13909.
- 30 N. Drebov and R. Ahlrichs, *J. Chem. Phys.*, 2010, **132**, 164703 – 164710.
- 31 B. K. Rao and P. Jena, *J. Chem. Phys.*, 1999, **111**, 1890-1906.
- 32 A. Aguado and José M. López, *J. Chem. Phys.*, 2009, **130**, 064704-06413.
- 33 H. T. Pham, D. V. Long and M. T. Nguyen, *J. Phys. Chem. C*, 2014, **118**, 24181–24187.
- 34 T. B. Tai, A. Ceulemans, M. T. Nguyen, *Chem. Eur. J.*, 2012, **18**, 4510-4512.
- 35 T. B. Tai, R. W. A. Havenith, J. L. Teunissen, A. R. Dok, S. D. Hallaert, M. T. Nguyen and A. Ceulemans, *Inorg. Chem.*, 2013, **52**, 10595-10600.
- 36 A. G. Arvanitidis, T. B. Tai, M. T. Nguyen and A. Ceulemans, *Phys. Chem. Chem. Phys.*, 2014, **16**, 18311-18318.

-
- 37 A. G. Arvanitidis, K. Z. Lim, R. W. A. Havenith and A. Ceulemans, *Int. J. Quant. Chem.* 2018, **118**, e25575.
- 38 I. Patouossa, J. T. Muya, A. Arvanitidis, M. T. Nguyen and A. Ceulemans, *Phys. Chem Chem. Phys.* 2018, in press.
- 39 F. Nejad, *Theor. Chem. Acc.*, 2015, **134**, 8-16.
- 40 P. Bultinck, S. Fias, M. Mandado, R. Ponc, in *Aromaticity and Metal Clusters*, P. K. Chattaraj (Ed.), Chapter 13, CRC Press, London, U.K., **2012**, pp. 245–270 and references therein.
- 41 H. Fliegl, S. Taubert, O. Lehtonen and D. Sundholm, *Phys. Chem. Chem. Phys.*, 2011, **13**, 20500-20518.
- 42 P. W. Fowler, D. E. Manolopoulos, *An Atlas of Fullerenes*, Clarendon Press, Oxford, 1995.
- 43 J. T. Muya, G. Gopakumar, M. T. Nguyen, A. Ceulemans, *Phys. Chem. Chem. Phys.*, 2011, **13**, 7524-7533.
- 44 P.W. Fowler and A. Ceulemans, *J. Phys. Chem.*, 1995, **99**, 508-510.
- 45 T. B. Tai, D. J. Grant, M. T. Nguyen and D. A. Dixon, *J. Phys. Chem. A* 2010, **114**, 994–1007
- 46 A. P. Sergeeva, D. Y. Zubarev, H. J. Zhai, A. I. Boldyrev, L.S. Wang, *J. Am. Chem. Soc.* **2008**, *130*, 7244-7246
- 47 E. Steiner, *The Chemistry Maths Book*, Oxford University Press, Oxford, UK, 2008. p. 391.
- 48 J. Juselius, D. Sundholm and J. Gauss, *J. Chem. Phys.*, 2004, **121**, 3952-3963.
- 49 H. Fliegl, St. Taubert, O. Lehtonen and D. Sundholm, *Phys. Chem. Chem. Phys.*, 2011, **13**, 20500–20518.
- 50 M.J. Frisch, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. Millam, J. *et al.*, Gaussian 09 Revision: **A.01**; Gaussian, Inc.: Wallingford, CT, 2009.
- 51 B. Silvi and A. Savin, *Nature*, 1994, **371**, 683-686.
- 52 H. T. Pham, K. Z. Lim, R. W. A. Havenith and M. T. Nguyen, *Phys. Chem. Chem. Phys.* 2016, **18**, 11919-11931.