

Cite this: *Nanoscale*, 2012, 4, 2567

www.rsc.org/nanoscale

## COMMUNICATION

Superatomic orbitals in sixteen-coordinate  $M@Li_{16}$  bonded by metallic bondsXiao Gu,<sup>\*a</sup> Guo-hong Chen,<sup>b</sup> Min Ji,<sup>c</sup> Yong-xin Yao<sup>c</sup> and Xin-gao Gong<sup>b</sup>

Received 7th January 2012, Accepted 10th February 2012

DOI: 10.1039/c2nr00056c

Based on density-functional calculation and genetic algorithm structure search, we propose a series of 16-coordinate core-shell clusters:  $M@Li_{16}$  ( $M = Ca, Sr, Ba, Ti, Zr, Hf$ ). A tetrahedral ( $T_d$ ) structure with an outer shell of 16 lithium atoms and one enclosed heavy atom is found to be the global minimum in the structural exploration of  $BaLi_{16}$  based on genetic algorithm. This structure also has lower energy compared to the other isomers we employed in all the  $MLi_{16}$  clusters. In this structure, the atoms are bonded together by metallic bonds with alkali (IA) and alkaline-earth (IIA) metal atoms. Their corresponding first electronic shells are closed with significant energy gaps because their total numbers of valence electrons fulfil the 18-electron rule. Such a combination could be extended to 20-electron systems by enclosing IVB elements. With simple valence electrons and highly symmetric structures, superatomic molecular orbitals are identified in all of the  $T_d$  clusters.

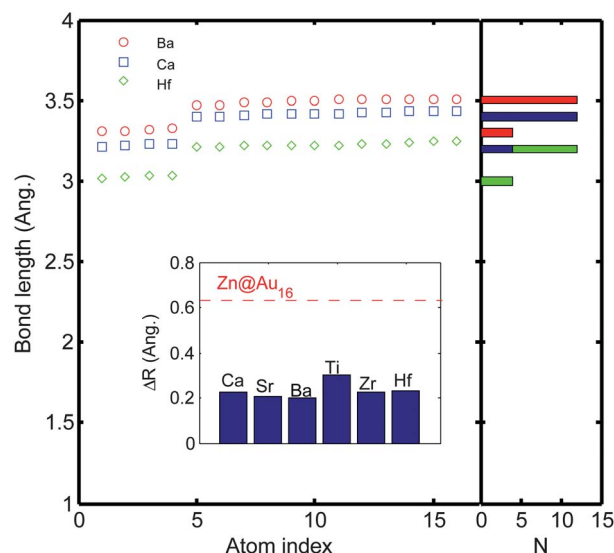
How many coordinations a core could handle is one of the key issues in coordination compounds, and important for both fundamental science and applications. There are many systems with high coordination numbers ( $N > 12$ ). Most of them are based on covalent bonds because the rigid bonds could hold the cage-like shell structure, such as  $M@Si_{16}$ <sup>1,2</sup> and  $M@C_{28}$ .<sup>3</sup> Metal hydride is another interesting system with complicated interactions. Raab *et al.* has performed both theoretical calculations and experimental matrix spectroscopy of a 16-coordinate complex of  $U-H_4(H_2)_6$ , whereas the 6  $H_2$  molecules are 'moieties interact' with the central atom.<sup>4</sup> Recently, a similar fifteen-coordinate complex,  $[Th(H_3BNMe_2BH_3)_4]$ , has been synthesized.<sup>5</sup> Another recent search for the highest coordination number predicted a 15-coordinate compact structure in the  $Pb@He_N^{2+}$  systems.<sup>6</sup> It is certainly interesting to explore various compact structures, which could accommodate even more coordinates.

In particular, metal clusters may also be good choices since they usually tend to form compact structures. Small 12-coordinate icosahedral aluminium clusters are the typical examples of stable metal

clusters, also regarded as 'superatoms', by accommodating an additional core atom, either Al itself<sup>7,8</sup> or other elements.<sup>9</sup>  $W@Au_{12}$ ,  $Pu@Pb_{12}$  and  $M@Au_{12}$  also show extraordinary stability and interesting properties, because of their high symmetry and large energy gaps between highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO).<sup>10–13</sup> Previous studies by joint experimental and theoretical methods found that the  $Au_{16}$  cage<sup>14</sup> can accommodate transition metal elements.<sup>15,16</sup> However, the radial distribution shows a difference of 0.6 Å between the core atom and two different Au sites; and Au–Au bonds show mixing character of covalent and metallic bonding due to the relativistic effect.<sup>17–19</sup>

In this letter, we propose a new series of compact clusters,  $M@Li_{16}$  ( $M = Ca, Sr, Ba, Ti, Zr, Hf$ ). They have a core-shell structure, where the big atoms (M) occupy the core site coordinated with 16 lithium atoms as the outer shell.

As shown in Fig. 1, there are two kinds of lithium atoms according to the radial distribution. Similar to the two groups of icosahedral sites in  $Au_{32}$ ,<sup>18</sup> the lithium atoms could also be divided into two groups of tetrahedral sites, with 4 Li1 and 12 Li2 atoms, respectively. In this combination of simple metals, the deviation of the two sites is



**Fig. 1** The bond length distribution of the tetrahedral structure  $M@Li_{16}$  ( $M = Ca, Ba, Hf$ ). On the right panel,  $N$  is the integration of the number of atoms with a interval of 0.1 Å. The inset shows the difference ( $\Delta R$ ) between the maximum and minimum of the bond lengths. All the bond lengths between M and Li are very similar: within a difference of 0.2 Å.

<sup>a</sup>Key Laboratory of Computational Physical Sciences, Ministry of Education, Department of Environmental Sciences and Engineering, Fudan University, Shanghai 200433, China. E-mail: gx@fudan.edu.cn; Fax: +86-21-55665515; Tel: +86-21-65643775

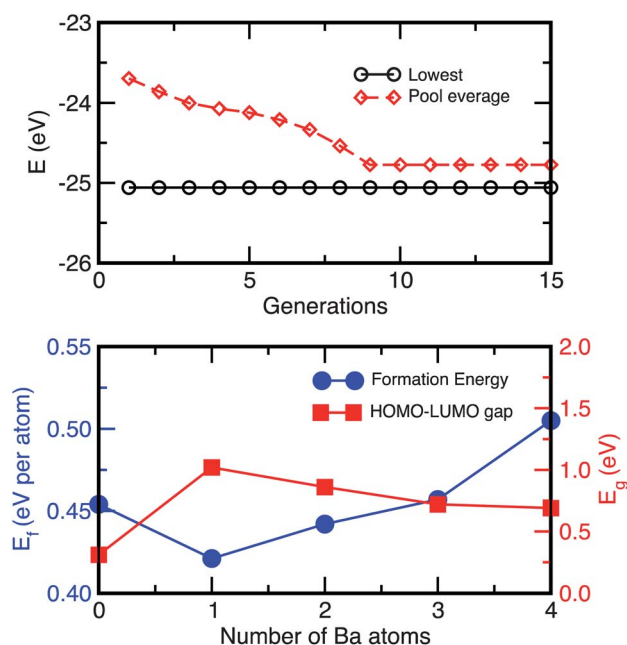
<sup>b</sup>Key Laboratory of Computational Physical Sciences, Ministry of Education, Surface Physics Laboratory & Department of Physics, Fudan University, Shanghai 200433, China. E-mail: xggong@fudan.edu.cn

<sup>c</sup>Department of Physics and Astronomy, Iowa State University, Ames Laboratory, US DOE, Ames, IA 50011, USA

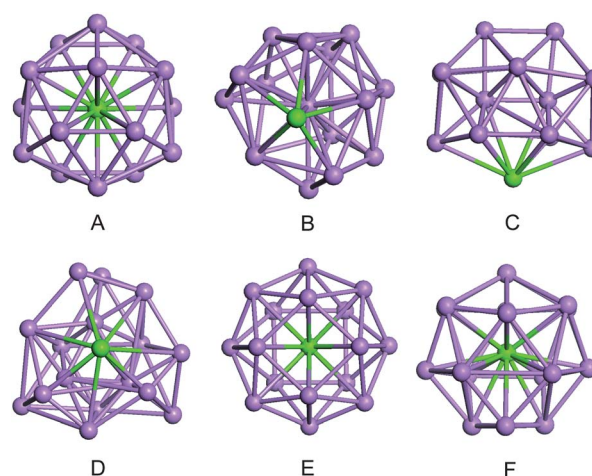
much smaller than the  $\text{Au}_{16}$ . As shown in the inset of Fig. 1, most of the deviations are within  $0.2 \text{ \AA}$ , which indicates that these clusters are more spherical and compact.

Our calculations were carried out based on density functional theory, using the generalized gradient approximation<sup>20</sup> for the exchange and correlation effects. The pseudo-potentials of projector augmented wave method<sup>21</sup> were used for describing the interactions between the core and valence electrons. Only the gamma point was used to sample the k-space, as the super cell size was as large as  $32 \times 32 \times 32 \text{ (\AA)}$ . The energy cutoff for the plane-waves was set to  $450 \text{ eV}$ . All of the features were implemented in the Vienna *Ab initio* Simulation Package (VASP).<sup>22</sup>

To identify the global minimum structure of the  $\text{BaLi}_{16}$  cluster, we have employed the genetic algorithm (GA). Details of GA implementation are described in ref. 23 and 24. In Fig. 2 upper panel, we show one example of a GA search history. The lowest energy structure is located even at the first generation and the average pool energy demonstrates the convergence of the exploration after 9 generations. This kind of extremely quick GA search suggests that these systems have a fairly simple phase space and could be globally explored by GA. In order to investigate the stability of this core-shell structure, we have compared a bunch of isomers identified by GA with high or low symmetries, as depicted in Fig. 3. The calculated properties are listed in Table 1. According to the results, the tetrahedral structure (*A*) has the lowest binding energy, the largest HOMO–LUMO energy gap and the highest symmetry. Cores with different numbers of lithium atoms have been investigated. Isomers *B*, *C* and *D* have one, two and three lithium atoms in the core and the calcium/barium atoms are placed on the surface. We studied another core-shell structure, *E*, which is similar to the tetrahedral one (*A*),



**Fig. 2** Upper panel shows one typical GA history of  $\text{BaLi}_{16}$  structure search. Lower panel shows formation energies ( $E_f$ ) and corresponding energy gaps ( $E_g$ ) with different numbers of Ba ( $\text{Ba}_X\text{Li}_{18-2X}$ ,  $X = 0, 1, 2, 3, 4$ ).  $E_f$  is defined as  $E_{\text{tot}} - N_{\text{Ba}} \times \mu_{\text{Ba}} - N_{\text{Li}} \times \mu_{\text{Li}}$ , where the chemical potential  $\mu_{\text{Ba}}$ ,  $\mu_{\text{Li}}$  are the calculated cohesive energy of bulk barium and lithium, respectively.



**Fig. 3** The isomers of  $\text{Ca@Li}_{16}$ . The green atom is calcium; others are lithium. Their calculated properties are listed in Table 1. *A*: the tetrahedral one with spherical shell. *B*: the calcium atom is on the surface; one lithium atom makes the core. *C*: two lithium atoms as the core. *D*: three lithium atoms as the core. *E*: another core-shell structure with symmetry of  $D_{4d}$ . *F*: 'two-shell' structure from ref. 6.

except the  $\text{Li}_{16}$  shell has  $D_{4d}$  symmetry. This isomer also has the closest binding energy and energy gap with the tetrahedral one. Structure *F* is the one found in  $\text{Pb@He}_{15}^{2+}$ <sup>6</sup> and its energy is very close to that of *E*. The thermal stability of the tetrahedral structure is further confirmed by the thermodynamics simulation. The core-shell structure is sustainable up to  $600 \text{ K}$ . When the heated cluster is cooled down and optimized, it comes back to the  $T_d$  structure.

We have carried out further structure searches based on the 18-electron rule, where different combinations of the barium and lithium atoms ( $\text{Ba}_X\text{Li}_{18-2X}$ ,  $X = 0, 1, 2, 3$  and  $4$ ) are considered. All of the searches can converge within 15 generations and locate ground state structure. Formation energies are used to compare the relative stabilities of these clusters. The formation energy is defined as the calculated total energy subtract the corresponding chemical potential, which is calculated from the cohesive energy of bulk barium and lithium. As shown in the lower panel of Fig. 2,  $\text{Ba@Li}_{16}$  has the lowest formation energy. In all these structures, one Ba atom is located in the core site and an additional Ba will join outer shell of Li

**Table 1** Calculated properties of the  $\text{CaLi}_{16}$  and  $\text{BaLi}_{16}$  isomers (all units in eV). The total energies refer to that of isomer *A* for both  $\text{CaLi}_{16}$  and  $\text{BaLi}_{16}$ , respectively. For  $\text{BaLi}_{16}$ , the isomers are further optimized by Gaussian<sup>25</sup> with B3LYP.<sup>26–28</sup> The total energies in the brackets are calculated with CCSD with the optimized structures. SDD is used as the basis set

| Isomers  | Point group | Total energies |                | Energy gaps |                |
|----------|-------------|----------------|----------------|-------------|----------------|
|          |             | Ca             | Ba             | Ca          | Ba             |
| <i>A</i> | $T_d$       | 0              | 0 (0)          | 0.57        | 1.02           |
| <i>B</i> | $C_s$       | 1.39           | 1.69 (1.98)    | 0.33        | 0.31           |
| <i>C</i> | $C_{2v}$    | 0.60           | 0.94 (1.09)    | 0.16        | 0.12           |
| <i>D</i> | $C_1$       | 0.97           | 1.68 (1.98)    | 0.40        | 0.31           |
| <i>E</i> | $D_{4d}$    | 0.11           | 0.12 (0.13)    | 0.47        | 0.89           |
| <i>F</i> | $C_1$       | 0.12           | — <sup>a</sup> | 0.50        | — <sup>a</sup> |

<sup>a</sup> Relaxation shows isomer *F* of  $\text{Ba@Li}_{16}$  transits into isomer *A*.

atoms. Therefore more Ba atoms will lower the structure symmetry in comparison with  $T_d$  Ba@Li<sub>16</sub>. Interestingly, the Ba@Li<sub>16</sub> also has the largest HOMO–LUMO energy gap among the global minima of Ba<sub>X</sub>@Li<sub>18–2X</sub> ( $X = 0, 1, 2, 3$  and 4).

All the above calculations strongly suggest that this system could be described by ‘jellium model’, which is successfully applied to the electronic configurations of highly symmetrical clusters by metal elements. Similar to the atomic orbitals, the number of electrons each energy level can accommodate is determined by the angular quantum number  $l$ . Therefore it matches the  $2(N+1)^2$  rule as long as the next  $s$  orbital comes in.<sup>29,30</sup> M@Li<sub>16</sub> ( $M = \text{Ca, Sr and Ba}$ ) clusters can be considered as 18-electron systems, and they all have closed shells with considerable HOMO–LUMO gaps as listed in Table 2. Among these 18-electron clusters, the Ba@Li<sub>16</sub> has the largest gap of about 1.02 eV. Fig. 4 shows the calculated eigenvalues of the molecular orbitals of Ba@Li<sub>16</sub>. The orbital around  $-30$  eV is the semi-core  $5s$  states from the barium, and  $5p$  for those around  $-17$  eV. The valence electrons ( $6s$  from barium and  $2s$  from lithium) are bonded together into 3 groups of orbitals, which are also shown in Fig. 4.

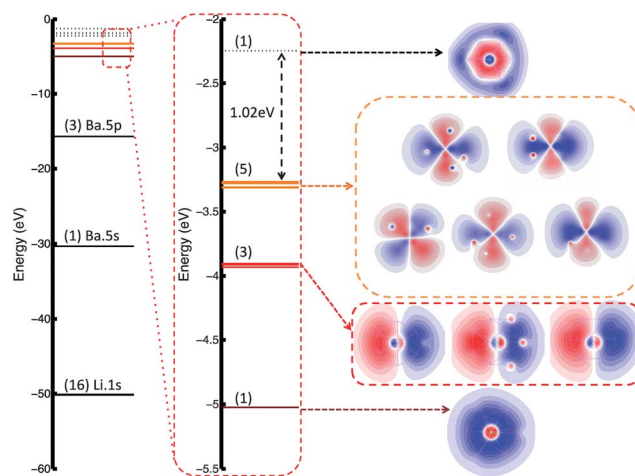
One interesting thing to notice is that the clusters size of M@Li<sub>16</sub> ( $M = \text{Ca, Sr, Ba, Ti, Zr and Hf}$ ) are very similar regardless of the huge difference of the radius of the corresponding cations. Fig. 5 shows energy levels for the binary metal clusters of M@Li<sub>16</sub>, ( $M = \text{Ca, Sr, Ba, Ti, Zr and Hf}$ ). If we recall our earlier results,  $s$  orbitals in the spherical shell model would be pushed up when the shell radius increases.<sup>30</sup> When molecular orbitals are pushed outwards due to the denser electronic distribution from the core levels of heavier inner core atom, the  $S$  orbitals are pushed up most significantly. This leads to a larger HOMO–LUMO gap since the LUMO of M@Li<sub>16</sub> ( $M = \text{Ca, Sr and Ba}$ ) are the  $s$  orbitals.

As we know, gold fullerenes are stabilized by the shorter bond lengths on the surface due to the relativistic effect. To investigate the possibility of the similar shorter-bonds mechanism, we have also calculated the M@Be<sub>16</sub> ( $M = \text{Mg, Ca, Sr and Ba}$ ) clusters, since the ionic radius of beryllium is much smaller than lithium. In this series of clusters, they fulfil the 34-electron rules since beryllium has two valence electrons. As a matter of fact, most of the isomers have considerable HOMO–LUMO gaps (listed in Table 2). Unfortunately, the heterogeneous core–shell structure isn’t found to be the global minimum: it is easy to find other compact disordered structures with lower energies. Nevertheless, the spherical clusters with high symmetry possess superatomic molecular orbitals as well, as shown in Fig. 6.

To explore whether there is substantial covalent bonding in the systems, we apply the well-known Mulliken’s population<sup>31</sup> and Mayer’s covalent bond order analysis<sup>32</sup> to a typical case of Ba@Li<sub>16</sub>, where the free atomic  $5d$  orbitals of Ba are very close to the  $6s$  orbital in energy and hence covalent bonding characters might be expected.

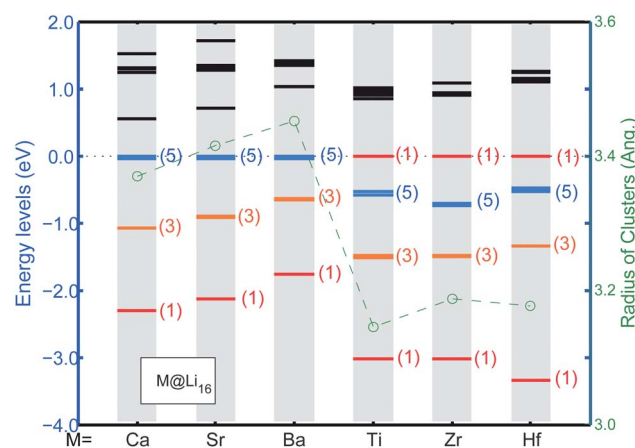
**Table 2** Calculated HOMO–LUMO gaps,  $E_g$  (eV), for the M@Li<sub>16</sub> and M@Be<sub>16</sub> clusters

| M                  | Ba   | Sr   | Ca   | Hf   | Zr   | Ti   |
|--------------------|------|------|------|------|------|------|
| M@Li <sub>16</sub> | 1.02 | 0.72 | 0.56 | 1.10 | 0.90 | 0.84 |
| M                  | Ba   | Sr   | Ca   | Mg   | Be   |      |
| M@Be <sub>16</sub> | 1.10 | 1.54 | 1.39 | 0.50 | 0.08 |      |



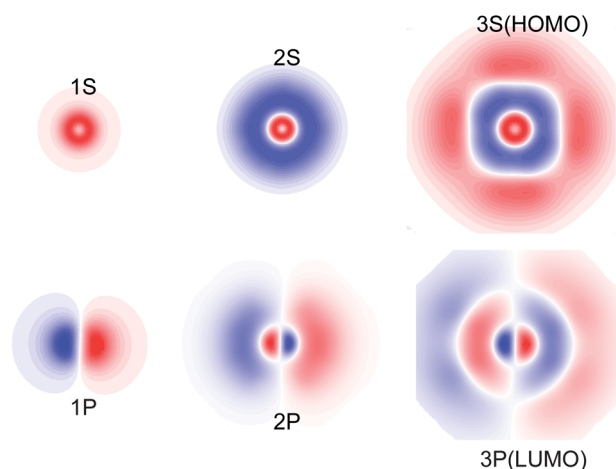
**Fig. 4** Molecular orbitals of Ba@Li<sub>16</sub>. Degeneracies of orbitals are shown as the numbers in brackets. Solid lines represent the occupied orbitals; dotted lines represent the unoccupied orbitals. The left panel is the energy levels for the molecular orbitals. The right panel shows sections for each orbital. The distortion from the perfect sphere has split the  $D$  orbitals; however, they are still very close to each other.

The occupied states, which contains the bonding information, are down-folded from large planewave basis to the representation of the quasi-atomic minimal basis-set orbitals (QUAMBO),<sup>33–36</sup> including Ba  $5s, 5p, 6s, 5d$  and Li  $2s$  orbitals. The sharing Mulliken charge is evaluated to be 0.11 between Ba and Li1 and 0.12 between Ba and Li2, which indicates weak covalent bonding character by reference to the typical nearest neighbour sharing Mulliken charge of 0.378 for semiconductor Si and 0.069 for simple FCC Al metal.<sup>33</sup> Similarly, the Mayer’s covalent bond order index is found to be 0.28(0.32) for the pair of Ba–Li1(Li2). By comparing the typical nearest neighbour bond order of 0.87 for semiconductor Si and 0.21 for simple FCC Al metal,<sup>33</sup> we can consistently infer that the system is essentially metallic. The Li  $2s$  and Ba  $5d$  orbitals contribute 80% to the weak covalent bonding character. We also find that the sharing Mulliken charge (bond order) between neighbouring Li atoms is 0.06 (0.111),



**Fig. 5** Energy levels for Li<sub>16</sub>M, ( $M = \text{Ca, Sr, Ba, Ti, Zr and Hf}$ ). All the levels are relative to  $E_F$ , which is shifted to zero. The degeneracy of orbitals are shown on the levels, the numbers are in the brackets. The size of the clusters are shown as open circles.





**Fig. 6** Molecular orbitals of Sr@Be<sub>16</sub>. The color map is shown in blue, white and red, where white is zero. The semi-core orbitals (4s and 4p of Sr atom) are noted as 1S and 1P.

which is very small and hence shows almost no covalent bonding character.

## Conclusions

In conclusion, we have shown a 16-coordinate tetrahedral structure of M@Li<sub>16</sub> (M = Ca, Sr, Ba, Ti, Zr and Hf). Superatomic molecular orbitals are predicted in these high symmetrical clusters. The central atom provides both size-suitable inner core for the Li<sub>16</sub> cage and certain number of valence electrons to match the magic number. When the Li<sub>16</sub> shell is combined with transition elements, such as Ti, Zr and Hf, this series expands. Other M@Li<sub>16</sub> clusters would be worth further exploration.

## Acknowledgements

This work was partially supported by the Special Funds for Major State Basic Research, National Science Foundation of China, Ministry of education and Shanghai municipality. The computation was performed in the Supercomputer Center of Shanghai and the Supercomputer Center of Fudan University.

## Notes and references

- 1 V. Kumar and Y. Kawazoe, *Phys. Rev. Lett.*, 2001, **87**, 045503.
- 2 K. Koyasu, M. Akutsu, M. Mitsui and A. Nakajima, *J. Am. Chem. Soc.*, 2005, **127**, 4998.
- 3 J.-P. Dognon, C. Clavaguera and P. Pykkö, *J. Am. Chem. Soc.*, 2009, **131**, 238.
- 4 J. Raab, R. H. Lindh, X. Wang, L. Andrews and L. Gagliardi, *J. Phys. Chem. A*, 2007, **111**, 6383.
- 5 S. R. Daly, P. M. B. Piccoli, A. J. Schultz, T. K. Todorova, L. Gagliardi and G. S. Girolami, *Angew. Chem., Int. Ed.*, 2010, **49**, 3379.
- 6 A. Hermann, M. Lein and P. Schwerdtfeger, *Angew. Chem., Int. Ed.*, 2007, **46**, 2444.
- 7 D. E. Bergeron, P. J. Roach, A. W. Castleman, N. Jones and S. N. Khanna, *Science*, 2005, **307**, 231.

- 8 D. E. Bergeron, A. W. Castleman, T. Morisato and S. N. Khanna, *Science*, 2004, **304**, 84.
- 9 X. G. Gong and V. Kumar, *Phys. Rev. Lett.*, 1993, **70**, 2078.
- 10 P. Pykkö and N. Runeberg, *Angew. Chem., Int. Ed.*, 2002, **41**, 2174.
- 11 J. P. Dognon, C. Clavaguera and P. Pykkö, *Angew. Chem., Int. Ed.*, 2007, **46**, 1427.
- 12 H. J. Zhai, J. Li and L. S. Wang, *J. Chem. Phys.*, 2004, **121**, 8369.
- 13 X. Li, B. Kiran, J. Li, H. J. Zhai and L. S. Wang, *Angew. Chem., Int. Ed.*, 2002, **41**, 4786.
- 14 S. Bulusu, X. Li, L.-S. Wang and X. C. Zeng, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 8326.
- 15 L. M. Wang, S. Bulusu, H. J. Zhai, X. C. Zeng and L. S. Wang, *Angew. Chem., Int. Ed.*, 2007, **46**, 2915.
- 16 L. M. Wang, S. Bulusu, W. Huang, R. Pal, L. S. Wang and X. C. Zeng, *J. Am. Chem. Soc.*, 2007, **129**, 15136.
- 17 J. Li, X. Li, H. J. Zhai and L. S. Wang, *Science*, 2003, **299**, 864.
- 18 X. Gu, M. Ji, S. H. Wei and X. G. Gong, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2004, **70**, 205401.
- 19 J. T. Lau, K. Hirsch, P. Klar, A. Langenberg, F. Lofink, R. Richter, J. Rittmann, M. Vogel, V. Zamudio-Bayer, T. Moller and B. von Issendorff, *Phys. Rev. A: At., Mol., Opt. Phys.*, 2009, **79**, 053201.
- 20 J. P. Perdew and Y. Wang, *Phys. Rev. B: Condens. Matter*, 1992, **45**, 13244.
- 21 J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B: Condens. Matter*, 1992, **46**, 6671.
- 22 G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter*, 1996, **54**, 11169.
- 23 M. Ji, C. Z. Wang and K. M. Ho, *Phys. Chem. Chem. Phys.*, 2010, **12**, 11617.
- 24 D. M. Deaven and K. M. Ho, *Phys. Rev. Lett.*, 1995, **75**, 288.
- 25 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *GAUSSIAN 09 (Revision A.01)*, Gaussian, Inc., Wallingford, CT, 2009.
- 26 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
- 27 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
- 28 P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.
- 29 A. Hirsch, Z. Chen and H. Jiao, *Angew. Chem., Int. Ed.*, 2000, **39**, 3915.
- 30 W. J. Yin, X. Gu and X. G. Gong, *Solid State Commun.*, 2008, **147**, 323.
- 31 R. S. Mulliken, *J. Chem. Phys.*, 1955, **23**, 1833.
- 32 I. Mayer, *Chem. Phys. Lett.*, 1983, **97**, 270.
- 33 W. C. Lu, C. Z. Wang, T. L. Chan, K. Ruedenberg and K. M. Ho, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2004, **70**, 041101.
- 34 T. L. Chan, Y. X. Yao, C. Z. Wang, W. C. Lu, J. Li, X. F. Qian, S. Yip and K. M. Ho, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, **76**, 205119.
- 35 X. Qian, J. Li, L. Qi, C. Z. Wang, T. L. Chan, Y. X. Yao, K. M. Ho and S. Yip, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 245112.
- 36 G. P. Zhang, X. W. Fang, Y. X. Yao, C. Z. Wang, Z. J. Ding and K. M. Ho, *J. Phys.: Condens. Matter*, 2011, **23**, 025302.