

# Theoretical investigations on diamondoids ( $C_nH_m$ , $n = 10-41$ ): Nomenclature, structural stabilities, and gap distributions

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Combining the congruence check and the first-principles calculations, we have systematically investigated the structural stabilities and gap distributions of possible diamondoids ( $C_nH_m$ ) with the carbon numbers ( $n$ ) from 10 to 41. A simple method for the nomenclature is proposed, which can be used to distinguish and screen the candidates with high efficiency. Different from previous theoretical studies, the possible diamondoids can be enumerated according to our nomenclature, without any pre-determination from experiments. The structural stabilities and electronic properties have been studied by density functional based tight binding and first-principles methods, where a nearly linear correlation is found between the energy gaps obtained by these two methods. According to the formation energy of structures, we have determined the stable configurations as a function of chemical potential. The maximum and minimum energy gaps are found to be dominated by the shape of diamondoids for clusters with a given number of carbon atoms, while the gap decreases in general as the size increases due to the quantum confinement. Published by AIP Publishing. <https://doi.org/10.1063/1.5004437>

## I. INTRODUCTION

Diamondoids, isolated from petroleum,<sup>1</sup> can be regarded as a fragment of diamond with hydrogen surface passivation, with their optical properties intensively investigated by the theorists and experimentalists.<sup>2-9</sup> Its equilibrium atomic arrangement is similar to bulk diamond, making diamondoids a good building block of functional nanostructures.<sup>10,11</sup> Richter *et al.* have presented a deep demonstration<sup>3</sup> about the photoluminescence properties of diamondoids, indicating that free diamondoids can induce laser fluorescence.<sup>2</sup> The modified diamondoids with other elements or functional groups can tune the absorption region to the infrared spectral region, making diamondoids a promising candidate for nanophotodevices.<sup>7,12-17</sup> Voros *et al.* showed that the C=S double bonds would play an important role in tuning the optical gap of sulfur modified diamondoids, where the absorption onset will vary from visible light to the infrared spectral region.<sup>16</sup> Rander *et al.*<sup>13</sup> pointed out that different functional groups (thiol, hydroxy, and amina) would have distinct influence on the electronic properties of system since all the HOMOs of the modified system will be localized on the functional group, and the electronegativity of system is dominated by the electronegativity of the functional group. In addition, it has a potential application in biomedicine such as sensing and sequencing DNA,<sup>18,19</sup> which is widely regarded as a critical aspect in the development of human beings. Furthermore, passivating the surface of adamantane, diamantane, triamantane, and tetramantane with halides and alcohols will be extended to the application in therapeutic and metal catalysis.<sup>20</sup>

In general, the properties of diamondoids are size and shape dependent. When the size is smaller than 1 nm, the gaps will decrease as the size increases.<sup>21-24</sup> By combining first-principles calculations and important sampling Monte Carlo methods, the simulated optical adsorption spectrum is in quantitative agreement with the experimental observation for diamondoids.<sup>25</sup> Using time-dependent density functional theory, Gali *et al.*<sup>14,16</sup> demonstrated that the sulfur modification on the diamondoids' surface will reduce the optical gaps of system from the ultraviolet region to the infrared region, while the fluorination will enlarge the optical gaps by lowering HOMO energies.

The structures of diamondoids<sup>26,27</sup> were often pre-determined which were proposed in experimental observations<sup>1,28</sup> because it is difficult to screen the isomers for the diamondoids with given number ( $n > 22$ ) of carbon atoms due to numerous possible candidates. In our previous studies,<sup>29,30</sup> we proposed an effective bond energy model to search the possible stable diamondoids under various hydrogen chemical potential, which fails to distinguish the  $C_nH_m$  isomers because the model shows that the total energies only depend on  $m$  and  $n$ . Based on the systematic nomenclature proposed by Balaban and Schleyer, diamondoids can be regarded as the superposition of adamantane, where other polymantane (such as diamantane, triamantane, tetramantane, pentamantane, and hexamantane) can be formed by increasing the number of adamantanes. However, it is often very time-consuming to determine the main and side chains for a given structure with the corresponding coordinates.

In this paper, we have proposed a simple method for the diamondoids' nomenclature to distinguish the candidates with high efficiency. Combined with the first-principles

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calculations, we have screened all the possible diamondoids ( $C_nH_m$ ,  $n = 10\text{--}36$ ) and determined the structural stabilities as a function of hydrogen chemical potential. With the pre-screening of density functional based tight binding (DFTB), we have determined the energy gap maximum and minimum of clusters with the same number of C atoms ( $n = 37\text{--}41$ ). Our finding might generate experimental interest and explore the possible application in nano-devices with diamondoids of proper energy gaps.

## II. METHODOLOGY

The nomenclature can be used to distinguish the candidates, which should be concise and easily available. The centers of each adamantane unit in the diamondoids can form a cluster, which can be regarded as a fragment of the diamond lattice. We propose a simple method for the nomenclature as follows: (i) we first generate a diamond lattice and choose an arbitrary atom as the origin point of coordinates (labeled with 1), where the other atoms are labeled with the order depending on the distance to the origin atom and the components of coordinates as shown in Fig. 1(a); (ii) for a given structure, we consider the possible translations and rotations and map the structure with the numbered lattice, where possible arrays are obtained for the nomenclature; and (iii) we will find a smallest array by comparing the components successively, which is the unique name for the given structure.

To enumerate the possible diamondoids, we increase the centers by adding the extra atom on the nearest neighboring positions, where the congruence check is done according to the nomenclature. Starting from the origin atom, 2, 3, 4, and 5 can be added as the second center and we can transform the structures of [1,3], [1,4], and [1,5] into [1,2], making [1,2] the unique structure with two centers. Starting from the structure of [1,2], 3, 4, 5, 6, 8, and 11 can be added as the third center and we repeat the procedures of nomenclature, which indicates that all these six structures have the same characters

with the array of [1,2,3]. Similarly, 4, 5, 6, 7, 8, 9, 11, and 12 can be added as the fourth center and the corresponding arrays are [1,2,3,11], [1,2,3,6], and [1,2,3,4], respectively. As shown in Figs. 1(b)–1(d), we obtain the three isomers with four centers, where the corresponding diamondoids can be constructed with the surfaces of the candidates passivated by hydrogen atoms to maintain the  $sp^3$  hybridization as shown in Figs. 1(e)–1(g). With this nomenclature, we achieve the congruence check by comparing arrays and screen all the possible candidates of diamondoids with the carbon number from 10 to 41.

It is often difficult to determine the main chain in the conventional nomenclature of organic molecules, while the nomenclature for diamondoids in our paper is feasible for the computer, with higher efficiency for structure screening. Despite most investigations in the literature focusing on the symmetrical diamondoids, we have enumerated the possible diamondoids with various sizes and shapes, including the candidates without symmetry. In addition, possible diamondoids found by our nomenclature are the same with those proposed by Balaban and Von Schleyer, which indicates a practical avenue to screen the diamondoids automatically and it will not conflict with the chemical classification.

We performed the calculations of diamondoids with various sizes by the first-principles method, as implemented in the Vienna *ab initio* simulation package (VASP).<sup>31–34</sup> The projector augmented wave (PAW) method was adopted, and the exchange-correlation functional was in the form of Perdew-Burke-Ernzerhof (PBE) within the generalized gradient approximation (GGA). The energy cutoff was set to be 550 eV with a  $k$ -point mesh of  $1 \times 1 \times 1$ , and the vacuum distance was 10 Å, ensuring the convergence of the forces on each atom was less than 0.01 eV/Å. Due to the underestimation of the GGA calculation, we have also performed the Heyd-Scuseria-Ernzerhof (HSE06)<sup>35–38</sup> calculation for the comparison with experiment. Considering the efficiency and accuracy, we screened the energy gap maximum and minimum of diamondoids by the self-consistent-charge density functional-tight-binding (SCC-DFTB) method<sup>39,40</sup> in conjunction with mio-1-1 parameter set, which was implemented in the DFTB+ code.<sup>41</sup> The structures of configurations were optimized until the atomic forces were less than 5.14 meV/Å, with the SCC tolerance of  $10^{-5}$  for charge consistence.

## III. RESULTS AND DISCUSSIONS

With the congruence check based on the nomenclature, we have screened the possible configurations of the center atoms and constructed the corresponding diamondoids. The stable structures of  $C_nH_m$  ( $n \leq 36$ ) as a function of chemical potential are determined by the first-principles calculation with the enumeration as shown in Sec. III A. In Sec. III B, the gap distributions of  $C_nH_m$  ( $n = 37\text{--}41$ ) are pre-screened by the DFTB method, which is further confirmed by the first-principles calculations.

### A. Enumeration of $C_nH_m$ ( $n = 10\text{--}36$ )

In the diamondoids, the centers of each adamantane unit form a cluster of the diamond lattice, which can be enumerated

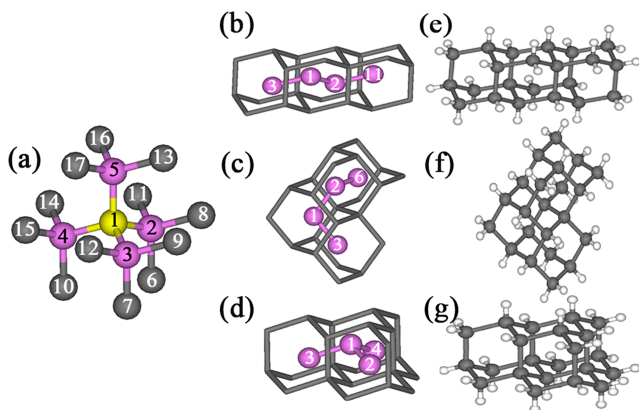


FIG. 1. The nomenclature of diamondoids. (a) A diamond lattice with labeled numbers, where the yellow atom represents the original atom and magenta and gray atoms are its first and second adjacent atoms, respectively. (b)–(d) are cage-like diamond clusters and their corresponding center atoms. (e)–(g) are the shapes of tetramantane, and gray and white atoms are carbon and hydrogen atoms, respectively.

with the nomenclature. The corresponding structures of diamondoids can be further constructed, and we have obtained 1973 candidates with the carbon number ( $n$ ) from 10 to 41. Considering the time cost, we first studied the 188 diamondoids with small size ( $n = 10\text{--}36$ ) in detail by the first-principles calculations. To study the structural stabilities of diamondoids,<sup>29,42,43</sup> the formation energy of  $C_nH_m$  can be expressed as

$$E_f = (E_{tot} - n * \mu_{C0} - m * \mu_{H0} - m * \mu_H)/n,$$

where  $E_{tot}$  is total energy of  $C_nH_m$ ,  $n$  and  $m$  are the number of carbon and hydrogen atoms, respectively.  $\mu_{C0}/\mu_{H0}$  represents the isolated energy of C/H atoms, and  $\mu_H$  is the chemical potential of the hydrogen atom. The hydrogen chemical potential of  $H_2$  is calculated to be  $-4.56$  eV. Considering the temperature and pressure in the environment, the chemical potential should be less than that in hydrogen molecules, e.g.,  $\mu_H \leq 0.5\mu_{H_2}$ .<sup>44</sup> In our previous study,<sup>29</sup> there is a critical point (about  $-2.6$  eV) of the chemical potential. The structures with less hydrogen atoms will be more stable with  $\mu_H \leq -2.6$  eV, while these structures will be less stable with  $\mu_H \geq -2.6$  eV. Thus, we select the typical values of ( $-2.5$  eV and  $-4.0$  eV) to demonstrate the structural stabilities of diamondoids from  $C_{22}$  to  $C_{41}$  as a function of the number of carbon atoms.

When  $\mu_H = -2.5$  eV, all the diamondoids from  $C_{22}$  to  $C_{36}$  considered are shown in Fig. 2(a). Here, the magic structures are  $C_{22}H_{28}$ ,  $C_{26}H_{32}$ ,  $C_{30}H_{36}$ , and  $C_{34}H_{40}$ , which can be expressed as [1,2,3,4], [1,2,3,4,5], [1,2,3,11,12,40], and [1,2,3,11,12,40,41]. All the arrays can be determined from the labeled lattice in our nomenclature, where the corresponding structures can be constructed further. According to the nomenclature proposed by Balaban and Schleyer,<sup>45</sup> these structures are expressed as tetramantane ([1(2)3]), pentamantane ([1(2,3)4]), hexamantane ([12121]), and heptamantane ([121212]), respectively. Note that  $C_{26}H_{32}$  and  $C_{22}H_{28}$  are three-dimensional structures with  $T_d$  and  $C_{3v}$  symmetry. Furthermore, the asymmetric stable configurations are two-dimensional ( $C_{25}H_{30}$ ,  $C_{29}H_{34}$ , and  $C_{33}H_{38}$ ) or three-dimensional ( $C_{32}H_{36}$  and  $C_{36}H_{40}$ ), where the shapes of  $C_{32}H_{36}$  and  $C_{36}H_{40}$  are close to octahedron. Thus, diamondoids with the shapes of two dimensions or similar to octahedron are less stable, while those with one dimension and tetrahedron-like shapes are more stable when  $\mu_H = -2.5$  eV.

When  $\mu_H = -4$  eV, the structures with lower H/C ratio will be more stable as shown in Fig. 2(b). For example, the formation energies of  $C_{26}H_{30}$ ,  $C_{30}H_{34}$ ,  $C_{33}H_{36}$ , and  $C_{34}H_{36}$  are lower than those of  $C_{26}H_{32}$ ,  $C_{30}H_{36}$ ,  $C_{33}H_{38}$ , and  $C_{34}H_{40}$ . In our nomenclature, the magic number of  $C_{26}H_{30}$ ,  $C_{30}H_{34}$ , and  $C_{35}H_{36}$  are [1,2,3,6,7,18], [1,2,3,4,8,9,17], and [1,2,3,6,7,8,9,18,30], corresponding to hexamantane ([12312]), heptamantane ([121321]), and decamantane ([1231241(2)3]). In addition, the formation energy of  $C_{35}H_{36}$  with the octahedron shape is lowest among all the diamondoids with  $n \leq 36$ . Note that the minimum number of H atoms is 36 for the diamondoids with  $n = 32\text{--}34$ , and the corresponding configurations would gradually approach the shape of octahedron. It is demonstrated that the hydrogen chemical potential will have great

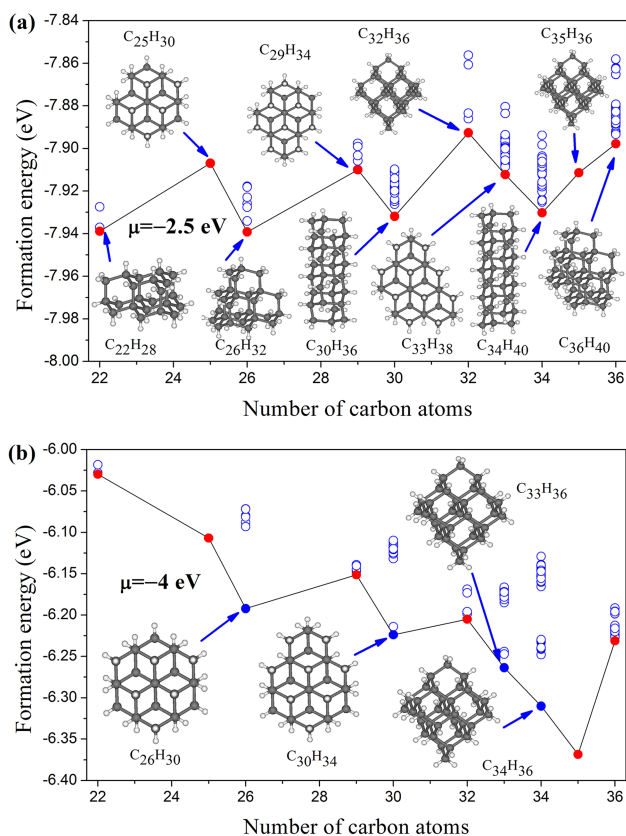


FIG. 2. The formation energies of diamondoids as a function of carbon atoms under different chemical potentials of hydrogen atom. (a)  $\mu_H = -2.5$  eV, the inset pictures are the most stable structures. (b)  $\mu_H = -4$  eV, the inset pictures are the shapes of the most stable structures which changed compared with the situation of  $\mu_H = -2.5$  eV, showed by blue points. The values of the most stable structures are presented by red points, and the blue circles are their isomers.

effect on the structural stabilities of the diamondoids: two-dimensional and octahedron-like configurations with less hydrogen atoms will be more stable under lower  $\mu_H$ , whereas one-dimensional and tetrahedron-like structures with more hydrogen atoms will be energetically preferable as  $\mu_H$  increases.

By calculating the vibrational mode of diamondoids, Han and Bester<sup>46</sup> have made a correction for the energy gaps of the systems. However, the calculations of vibration spectrums are often expensive, especially for the high-throughput screening with numerous candidates. Alternatively, we have performed the Heyd-Scuseria-Ernzerhof (HSE06) calculation and made comparisons with experiment (shown in Table I). Note that the energy gaps from HSE06 are in agreement with the values obtained experimentally, which are about 1 eV higher than those from the traditional DFT(GGA-PBE) method. On the other hand, the energy gaps of diamondoids ( $n = 10\text{--}33$ ) calculated by HSE06 and GGA-PBE are shown in the inset of Fig. 3(a), in which there is a linear dependence of the HSE06 results on those of GGA-PBE. Despite underestimating the energy gaps, the GGA-PBE method is practical to predict the electronic properties of diamondoids qualitatively.

Figure 3(a) shows the gap variance and formation energies of diamondoids with  $n \leq 36$  when  $\mu_H = -2.5$  eV. From

TABLE I. Optical gaps (in eV) of some diamondoids calculated by HSE06 and GGA approaches, and numbers in bracket are named diamondoids with Balaban and Schleyer nomenclature.

| Diamondoid            | Formula                         | HSE06 | GGA  | Exp. (Ref. 16) |
|-----------------------|---------------------------------|-------|------|----------------|
| Adamantane            | C <sub>10</sub> H <sub>16</sub> | 6.79  | 5.71 | 6.49           |
| Diamantane            | C <sub>14</sub> H <sub>20</sub> | 6.41  | 5.36 | 6.40           |
| Triamantane           | C <sub>18</sub> H <sub>24</sub> | 6.16  | 5.19 | 6.06           |
| [1(2)3]Tetramantane   | C <sub>22</sub> H <sub>28</sub> | 6.06  | 5.07 | 5.94           |
| [123]Tetramantane     | C <sub>22</sub> H <sub>28</sub> | 6.03  | 5.03 | 5.95           |
| [121]Tetramantane     | C <sub>22</sub> H <sub>28</sub> | 6.00  | 5.00 | 6.10           |
| [1(2,3)4]Pentamantane | C <sub>26</sub> H <sub>32</sub> | 5.97  | 4.98 | 5.81           |
| [12312]Hexamantane    | C <sub>26</sub> H <sub>30</sub> | 5.83  | 4.84 | 5.88           |
| [1212]Pentamantane    | C <sub>26</sub> H <sub>32</sub> | 5.87  | 4.90 | 5.85           |

C<sub>22</sub> to C<sub>36</sub>, the energy gap will vary from 4.56 eV to 5.02 eV, according to our first-principles calculations. The gap difference of isomers is largest (about 0.30 eV) for C<sub>30</sub>, while it is smallest (only 0.032 eV) for C<sub>32</sub>. Moreover, most of the structures with larger gaps will be more stable, according to the formation energies shown in Fig. 3(a).

As the carbon atoms increase, their allotropes will increase largely [cf. Fig. 3(b)]. We studied the relationship between the energy gaps and the structural stabilities of C<sub>30</sub>H<sub>36</sub>, C<sub>33</sub>H<sub>38</sub>,

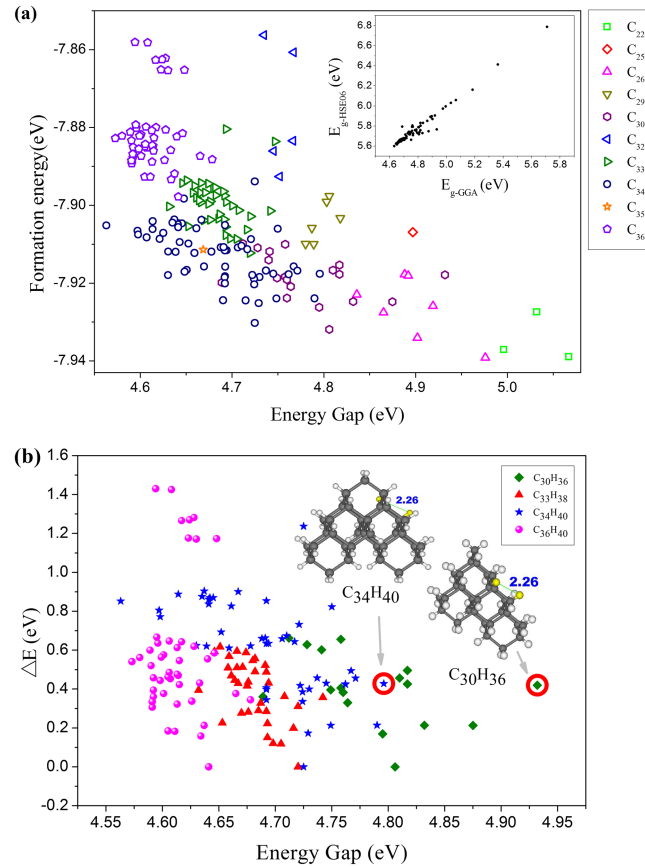


FIG. 3. (a) Formation energies as a function of energy gaps with  $\mu_H = -2.5$  eV. The inset is the relationship of the energy gaps calculated by HSE06 and GGA-PBE. (b) Relative energies ( $\Delta E = E_{tot}^i - E_{tot}^{min}$ ) as a function of energy gaps, the inset pictures are the shapes of C<sub>30</sub>H<sub>36</sub> and C<sub>34</sub>H<sub>40</sub> with maximum energy gap. Different symbols present the isomers of different diamondoids.

C<sub>34</sub>H<sub>40</sub>, and C<sub>36</sub>H<sub>40</sub> due to their large number of candidates. Note that the number of isomers for C<sub>32</sub>H<sub>36</sub> and C<sub>35</sub>H<sub>36</sub> are four and one, respectively. There is an approximate trend that the diamondoids with larger gaps are more stable. Note that there are some candidates (C<sub>30</sub>H<sub>36</sub> and C<sub>34</sub>H<sub>40</sub>) with larger gaps that are less stable. In such structures, there are hydrogen atom pairs with the distance of 2.26 Å (which will be enlarged to be 2.50 Å after the relaxation). Hence, the systems are destabilized due to the impulsion of hydrogen atoms.

## B. Gap distributions of C<sub>n</sub>H<sub>m</sub> (n = 37–41)

As is known, the energy gaps are dominant to the optical properties of diamondoids, where surface modifications have been applied to tune the gaps.<sup>14,16</sup> In our work, we focus on the gap distributions of the intrinsic diamondoids, as a function of the shape and size. Combining the enumeration and the first-principles calculations, we obtained the gap distributions of C<sub>n</sub>H<sub>m</sub> (n ≤ 36) as shown in Fig. 4(a). As shown in the inset of Fig. 4(a), there is a nearly linear correlation of gaps from DFTB and DFT calculations, which indicates that the DFTB method is efficient to screen the electronic properties of diamondoids.

For larger C<sub>n</sub>H<sub>m</sub> (n = 37–41, the number of candidates are 198, 203, 25, 385, and 974 respectively), we pre-screened

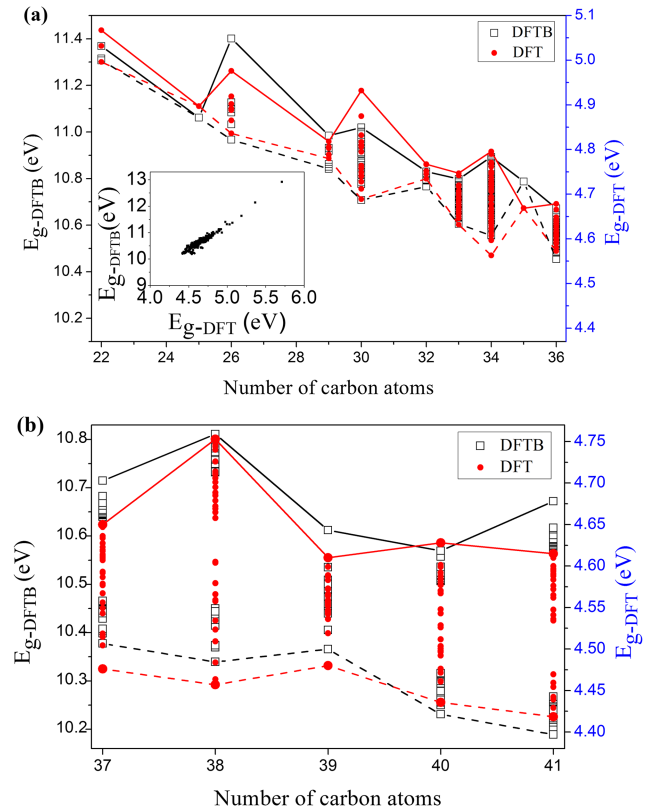
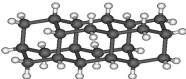
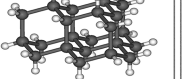
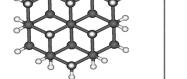
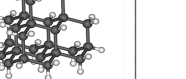
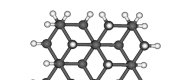
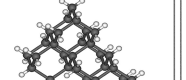
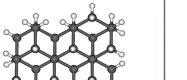
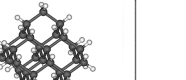
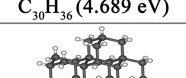
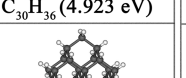
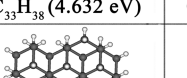
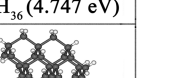


FIG. 4. Energy gaps calculated by DFT and DFTB methods as a function of carbon atoms (C<sub>n</sub>H<sub>m</sub>, n = 22–41), the left of Y axis presents the DFTB value and the right presents the DFT value. (a) C<sub>n</sub>H<sub>m</sub> (n = 22–36), the inset is relationship of the energy gaps calculated by these two methods. (b) C<sub>n</sub>H<sub>m</sub> (n = 37–41), red solid circles and black open squares present the results of DFT and DFTB methods, respectively. Solid and dashed lines link the maximum and minimum values of DFT and DFTB methods, respectively.

| (a) $E_{g \min}$                                                                                               | $E_{g \max}$                                                                                                   | $E_{g \min}$                                                                                                   | $E_{g \max}$                                                                                                   |
|----------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|
| <br>$C_{22}H_{28}$ (4.996 eV) | <br>$C_{22}H_{28}$ (5.067 eV) | <br>$C_{26}H_{30}$ (4.836 eV) | <br>$C_{26}H_{32}$ (4.926 eV) |
| <br>$C_{30}H_{36}$ (4.689 eV) | <br>$C_{30}H_{36}$ (4.923 eV) | <br>$C_{33}H_{38}$ (4.632 eV) | <br>$C_{33}H_{36}$ (4.747 eV) |
| <br>$C_{34}H_{40}$ (4.563 eV) | <br>$C_{34}H_{40}$ (4.800 eV) | <br>$C_{36}H_{40}$ (4.573 eV) | <br>$C_{36}H_{40}$ (4.678 eV) |

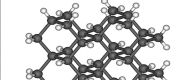
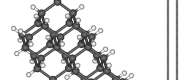
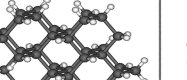
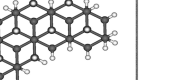
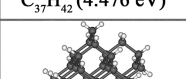
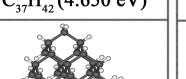
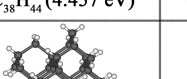
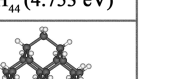
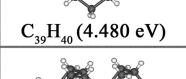
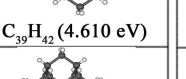
| (b) $E_{g \min}$                                                                                               | $E_{g \max}$                                                                                                   | $E_{g \min}$                                                                                                   | $E_{g \max}$                                                                                                   |
|----------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|
| <br>$C_{37}H_{42}$ (4.476 eV) | <br>$C_{37}H_{42}$ (4.650 eV) | <br>$C_{38}H_{44}$ (4.457 eV) | <br>$C_{38}H_{44}$ (4.753 eV) |
| <br>$C_{39}H_{40}$ (4.480 eV) | <br>$C_{39}H_{42}$ (4.610 eV) | <br>$C_{40}H_{44}$ (4.436 eV) | <br>$C_{40}H_{44}$ (4.628 eV) |
| <br>$C_{41}H_{46}$ (4.418 eV) | <br>$C_{41}H_{46}$ (4.615 eV) |                                                                                                                |                                                                                                                |

FIG. 5. The structures with maximum ( $E_{g \max}$ ) and minimum ( $E_{g \min}$ ) energy gaps under different carbon number (a)  $C_nH_m$  ( $n \leq 36$ ) and (b)  $C_nH_m$  ( $n \geq 37$ ). The numbers in the parentheses are energy gaps; gray and white balls are carbon and hydrogen atoms, respectively.

the candidates with the DFTB method to obtain the gap distributions. The top 15 structures for the gap maximum and minimum were further confirmed by the DFT method as shown in Fig. 4(b). As the carbon number increases, both the maximum and minimum energy gaps will decrease gradually attributed to the quantum confinement effect. Note that the energy gaps of diamondoids with given number of carbon atoms can be tuned by the shape, and the gap minimum and maximum of  $C_{37}$ ,  $C_{38}$ ,  $C_{39}$ ,  $C_{40}$ , and  $C_{41}$  are (4.476 eV, 4.650 eV), (4.457 eV, 4.753 eV), (4.480 eV, 4.610 eV), (4.436 eV, 4.628 eV), and (4.418 eV, 4.615 eV), respectively; the largest difference of which is 0.296 eV from  $C_{38}$ .

Following the distributions of energy gaps, we presented the structures with maximum ( $E_{g \max}$ ) and minimum ( $E_{g \min}$ ) energy gaps as shown in Fig. 5. In agreement with the experiments, we have found that all the isomers for  $C_{22}$ , among which the structures of  $C_{22}H_{28}$ -minimum is one-dimensional with  $C_{2h}$  symmetry and the ones of  $C_{22}H_{28}$ -maximum is three-dimensional with  $C_{3v}$  symmetry [shown in Fig. 5(a)]. For  $C_{26}$ ,  $C_{26}H_{30}$ -minimum is a two-dimensional structure with  $D_{3d}$  symmetry, while  $C_{26}H_{32}$ -maximum is three-dimensional with  $T_d$  symmetry. Note that the numbers of isomers for  $C_{25}$ ,  $C_{29}$ ,  $C_{32}$ , and  $C_{35}$  are less than 7, which is the reason why the differences between  $E_{g \max}$  and  $E_{g \min}$  are

small for these structures. For  $C_{30}$ ,  $C_{33}$ ,  $C_{34}$ , and  $C_{36}$ , the structures with minimum energy gaps are two-dimensional (e.g.,  $C_{30}H_{36}$ -minimum with  $C_{2h}$  symmetry,  $C_{33}H_{38}$ -minimum, and  $C_{36}H_{40}$ -minimum), while the one of  $C_{34}H_{40}$ -minimum is three-dimensional. The structures with maximum energy gaps are three-dimensional, including  $C_{34}H_{40}$ -maximum with  $C_2$  symmetry, tetrahedron-like  $C_{22}H_{28}$  and  $C_{26}H_{32}$  with  $C_{3v}$  and  $T_d$  symmetry, and the octahedron-like  $C_{33}H_{36}$ . For larger diamondoids ( $C_nH_m$ ,  $n \geq 37$ ) shown in Fig. 5(b), despite two-dimensional  $C_{38}H_{44}$ -maximum with  $C_2$  symmetry, most structures with minimum/maximum gaps are three-dimensional without typical symmetry. With the increasing of carbon atom, the structures with maximum gaps tend to be the shape of an octahedron.

#### IV. SUMMARY

In summary, we have proposed a diamondoids' nomenclature to identify the candidates, with enhanced efficiency of searching stable structures. With the DFTB method, we pre-screen the gap distributions of diamondoids and confirm the gap maximum/minimum by the first-principles calculations. The shapes of stable diamondoids could be modulated by the hydrogen chemical potential, which will further tune the gaps of intrinsic diamondoids. Possible diamondoids

can be enumerated based on the nomenclature without any pre-determination from experiments, which is an important complement to the first-principles calculations. Our finding will provide theoretical foundations to generate experimental interest of diamondoids, which might further explore the potential applications in nano-devices with these diamondoids.

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