

Endohedral Silicon Fullerenes  $\text{Si}_N$  ( $27 \leq N \leq 39$ )Soohaeng Yoo,<sup>†</sup> Jijun Zhao,<sup>‡</sup> Jinlan Wang,<sup>§</sup> and Xiao Cheng Zeng<sup>\*†</sup>

Contribution from the Department of Chemistry and Center for Materials Research & Analysis, University of Nebraska, Lincoln, Nebraska 68588, Department of Physics and Astronomy, University of North Carolina, Chapel Hill, North Carolina 27599, and Department of Physics, Nanjing University, Nanjing, 210093, China

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**Abstract:** We have performed an unbiased search for the lowest-energy geometric structures of medium-sized silicon clusters  $\text{Si}_N$  ( $27 \leq N \leq 39$ ) using a genetic algorithm and nonorthogonal-tight-binding method, followed by a refining and biased search using basin-hopping method coupled with density-functional theory. We show that the carbon fullerene cages are most likely generic cage motifs (“magic cages”) to form low-lying stuffed-cage silicon clusters (beyond the size  $N > 27$ ). An empirical rule that provides optimal “stuffing/cage” combinations for constructing low-energy endohedral silicon fullerenes is suggested, with a hope that it can provide guidance to future synthesis of “bucky” silicon.

## Introduction

Among the group IV atomic clusters, fullerene-cage structures are only found in the carbon clusters<sup>1</sup> in which the closed cage consists of only pentagonal and hexagonal rings, and all carbon atoms are 3-fold coordinated. For silicon, a nearest neighbor of carbon in group IV, both experimental measurements and ab initio calculations have shown that silicon atoms in small- to medium-sized clusters can exhibit higher than 4-fold coordination.<sup>2–6</sup> To date, silicon fullerenes have not yet been observed in nature nor synthesized in the laboratory. Nevertheless, for medium-sized silicon clusters, high-resolution ion mobility measurements<sup>7,8</sup> have revealed a structural transition from prolate shapes to more spherically like ones for both anions  $\text{Si}_N^-$  and cations  $\text{Si}_N^+$  beyond the size  $N = 27$ . However, detailed geometric structures of the more spherically like medium-sized silicon clusters still cannot be fully determined from measurements. In this aspect, structural determination relies heavily on quantum-mechanical calculations of the potential energy surface of the clusters.

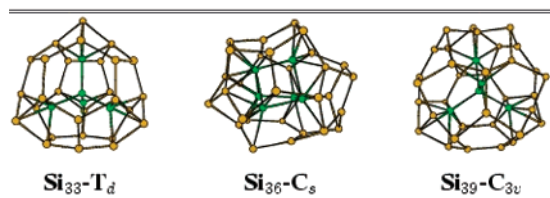
Despite the lack of evidences of “bucky” silicon in nature, geometric structures of medium-sized silicon clusters have attracted considerable interests over the past 20 years, both experimentally<sup>2–5,7–17</sup> and theoretically,<sup>6,18–31</sup> with the hope that

more light can be brought onto the long-standing question: Are there any generic structural features for the medium- to large-sized silicon clusters? Thus far, much understanding has been achieved on the structures of small-sized silicon clusters, such as  $\text{Si}_6$ ,  $\text{Si}_7$ , and  $\text{Si}_{10}$ , which are known to be the *magic-number clusters* due to their high stability and abundance.<sup>2–5</sup> However, for silicon clusters  $\text{Si}_N$  beyond the size  $N = 10$ , detailed structural information about the arrangement of atoms in the low-lying forms cannot be directly inferred from today’s experiments. Ion mobility measurements performed by Jarrold

<sup>†</sup> University of Nebraska.<sup>‡</sup> University of North Carolina.<sup>§</sup> Nanjing University.

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**Figure 1.** Geometries of three previously reported “handmade” endohedral silicon fullerene models, optimized at the B3LYP/6-31G(d) level of DFT: Si<sub>33</sub> [Si<sub>5</sub>@Si<sub>28</sub> cage],<sup>19,20</sup> Si<sub>36</sub> [Si<sub>6</sub>@Si<sub>30</sub> cage],<sup>30</sup> and Si<sub>39</sub> [Si<sub>5</sub>@Si<sub>34</sub> cage].<sup>22</sup> The core-filling atoms are highlighted in green.

and co-workers<sup>7,8,12,16</sup> have revealed much of what is known today about the overall structural information of the medium-sized clusters. Specifically, the high-resolution ion mobility measurements<sup>8,16</sup> have shown that a structural transition from prolate shapes to *more sphericallylike* ones can occur for silicon cluster anions Si<sub>N</sub><sup>−</sup> in the size range 27 ≤ N ≤ 29 and for cations Si<sub>N</sub><sup>+</sup> in the size range 25 ≤ N ≤ 27. Photoelectron spectra measurements<sup>15</sup> also provided indirect evidence of the structural transition for anions between the size N = 27 and N = 30. All these measurements suggest that medium-sized cluster ions, both negative and positive, favor more spherical shapes at least beyond the size N = 27. Presumably, the structural transition may also occur for neutral silicon clusters at a certain size, possibly between 25 and 30.<sup>12,16</sup>

For N < 27, structural information about relatively small-sized silicon clusters has been mainly obtained on the basis of unbiased search of the global-minimum clusters by use of the genetic algorithm coupled with semiempirical tight-binding (TB) method and density functional theory (DFT).<sup>12,26</sup> For example, Ho et al.<sup>12</sup> have reported that a low-lying class of prolate-shaped neutral silicon clusters Si<sub>N</sub> (12 ≤ N ≤ 26) can be built up with the motif of the tricapped trigonal prism (TTP) Si<sub>9</sub>.

On the other hand, little is known about the structural information of the medium-sized clusters (N > 27) except that they are compact and more sphericallylike in shape. To the best of our knowledge, an unbiased search for the global-minimum clusters by either TB or DFT methods has not yet been reported for N > 27. Several “handmade” structural models<sup>19–23,30</sup> have been proposed, and among them, the endohedral or “stuffed” fullerene model appears to be the most promising candidate as a low-lying form of sphericallylike clusters.<sup>30</sup> In Figure 1 we display several representative stuffed-fullerene models for Si<sub>33</sub>,<sup>19,20</sup> Si<sub>36</sub>,<sup>30</sup> and Si<sub>39</sub>.<sup>22</sup> The initial configuration of these stuffed-fullerene clusters was generally built based upon high-symmetry fullerene cages containing various preconstructed core-filling units. However, it can be shown that most of these handmade clusters show quite high energy (see Table 1). For example, their binding energies per atom are all smaller than that of a smaller cluster, Si<sub>25</sub> [a low-lying endohedral fullerene cluster shown in ref 31] (see Table 1 and also Table 1 in Supporting Information).

## Computation Procedures

To seek low-lying geometric models for the medium-sized clusters, we adopt a two-step approach with two global optimization techniques: the genetic algorithm (GA)<sup>12,32,33</sup> and the basin-hopping (BH) method.<sup>34</sup> The first step is an unbiased search of the global minimum

**Table 1.** Optimal Stuffing/Cage Combinations for Low-Lying Endohedral Silicon Fullerenes<sup>a</sup> and the Binding Energy per Atom<sup>b</sup>

stuffed fullerene Si <sub>N</sub>	optimal stuffing/cage combinations	binding energy (eV/atom)
Si <sub>27</sub>	Si <sub>3</sub> @Si <sub>24</sub> cage	3.274
Si <sub>27a</sub>	Si <sub>1</sub> @Si <sub>26</sub> cage	3.269
Si <sub>28</sub>	Si <sub>2</sub> @Si <sub>26</sub> cage	3.292
Si <sub>29a</sub>	Si <sub>3</sub> @Si <sub>26</sub> cage	3.278
Si <sub>29</sub>	Si <sub>1</sub> @Si <sub>28</sub> cage	3.287
Si <sub>30</sub>	Si <sub>2</sub> @Si <sub>28</sub> cage	3.286
Si <sub>31</sub>	Si <sub>3</sub> @Si <sub>28</sub> cage	3.306
Si <sub>32</sub>	Si <sub>4</sub> @Si <sub>28</sub> cage	3.299
Si <sub>32a</sub>	Si <sub>2</sub> @Si <sub>30</sub> cage	3.294
Si <sub>33</sub>	Si <sub>3</sub> @Si <sub>30</sub> cage	3.313
Si <sub>34</sub>	Si <sub>4</sub> @Si <sub>30</sub> cage	3.301
Si <sub>35</sub>	Si <sub>3</sub> @Si <sub>32</sub> cage	3.308
Si <sub>36</sub>	Si <sub>4</sub> @Si <sub>32</sub> cage	3.318
Si <sub>37</sub>	Si <sub>3</sub> @Si <sub>34</sub> cage	3.306
Si <sub>38</sub>	Si <sub>4</sub> @Si <sub>34</sub> cage	3.315
Si <sub>39</sub>	Si <sub>5</sub> @Si <sub>34</sub> cage	3.320
Si <sub>25</sub> <sup>c</sup>	Si <sub>1</sub> @Si <sub>24</sub> cage	3.277
Si <sub>33</sub> -T <sub>d</sub> <sup>c</sup>	Si <sub>5</sub> @Si <sub>28</sub> cage	3.211
Si <sub>36</sub> -C <sub>s</sub> <sup>c</sup>	Si <sub>6</sub> @Si <sub>30</sub> cage	3.267
Si <sub>39</sub> -C <sub>3v</sub> <sup>c</sup>	Si <sub>5</sub> @Si <sub>34</sub> cage	3.241

<sup>a</sup> Shown in Figure 2a. <sup>b</sup> Calculated at B3LYP/6-311G(2d) level of DFT,<sup>39</sup> including the zero-point-energy correction calculated at B3LYP/6-31G(d) level. <sup>c</sup> The binding energies per atom for the endohedral fullerenes Si<sub>25</sub>,<sup>31</sup> as well as Si<sub>33</sub>-T<sub>d</sub>,<sup>19,20</sup> Si<sub>36</sub>-C<sub>s</sub>,<sup>30</sup> and Si<sub>39</sub>-C<sub>3v</sub>,<sup>22</sup> (Figure 1), are also given.

of the potential energy surface by use of the GA coupled with the nonorthogonal tight-binding (NTB) method.<sup>35</sup> Note that the NTB method proposed by Menon and Subbaswamy<sup>23</sup> successfully reproduces the structures and binding energies of small silicon clusters (N ≤ 10) from density functional theory calculations and has been applied to a medium-sized Si<sub>45</sub> cluster. The genetic algorithm (GA) simulation employed in this work is essentially the same as in Deaven and Ho’s work,<sup>32</sup> and the details of it has been reviewed recently by one of us.<sup>33</sup> Briefly, the essential idea of GA optimization strategy is to mimic the Darwinian biological evolution process during which only the fittest candidate can survive. At beginning, we generate a number (128 in the present simulation) of initial configurations by random. Any two candidates in this population can be chosen as parents to generate a child cluster through a mating process. At the end of the mating procedure, a mutation operation is allowed to apply on the configuration of child cluster with 30% possibility. The child cluster from each GA generation can be relaxed by highly efficient BFGS numerical minimization.<sup>36</sup> Thus the locally minimized child is selected to replace its parent in the population if it has lower energy. In this study, 40 000 GA iterations are performed to guarantee the global minimum in the NTB configuration space. The resulting lowest-energy isomeric structures are thereafter called the NTB global minima. Guided by the NTB global minima, the second step is a refining step via a biased search of the potential energy hypersurface by means of the BH method<sup>34</sup> combined with the density-functional theory (DFT) within the general-gradient approximation (GGA).<sup>37</sup> In essence the BH method is Monte Carlo minimization, which removes relatively low barriers separating local minima of the potential energy hypersurface and thus effectively converts portions of the potential energy surface into a multidimensional staircase. Each accepted Monte Carlo move is associated with an energy minimization. Here we calculated the potential energy and energy gradient using subroutines of CPMD source code<sup>37</sup> (freely available to academic researchers).

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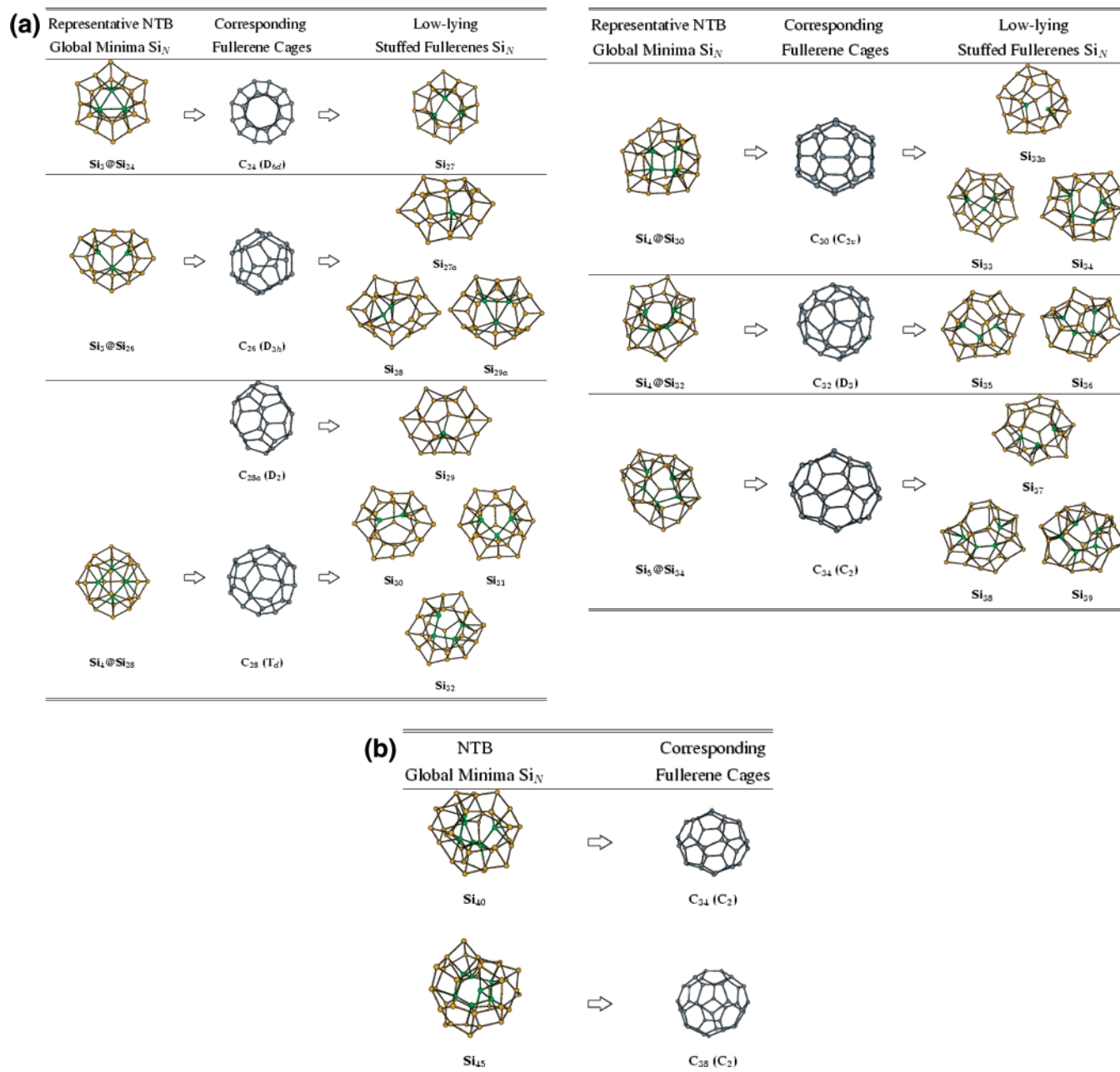
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**Figure 2.** (a) Geometries of low-energy stuffed-fullerene clusters  $\text{Si}_{27}$ – $\text{Si}_{39}$ . Each set of structures displays a representative NTB global minimum, the corresponding homologue carbon fullerene cages, and the endohedral fullerene family, obtained from the refining biased search based on a combined BH/DFT method. The corresponding fullerene cages (except  $\text{C}_{28a}$ ) can be achieved by removing the core-filling atoms (green spheres) from the corresponding NTB global-minimum isomers, followed by replacing all cage atoms (yellow spheres) by the carbon atoms (gray spheres) along with rescaling the bond distance by a factor of 0.7, and then reoptimizing the carbon cages. Almost all these carbon fullerene cages have been proven to be the global minima of carbon clusters.<sup>38</sup> (b) Geometries of the NTB global-minimum structures  $\text{Si}_{40}$  and  $\text{Si}_{45}$  and the corresponding homologue carbon fullerene cages.

## Results and Discussion

**Unbiased Search with Genetic Algorithm.** We have performed an unbiased search for the global minima of neutral silicon clusters  $\text{Si}_N$  in the size range  $27 \leq N \leq 39$ . Some representative NTB global minima are shown in Figure 2 (Figure 1 in the Supporting Information displays all NTB global minima obtained in this work). Overall, the shapes of the NTB global-minimum structures for the medium-sized clusters are spherically-like. More interestingly, we find that most of the global minima exhibit fullerene-like cages, namely, the cages contain only pentagonal and hexagonal rings. When we removed the core-filling atoms (green spheres in Figure 2a), followed by

replacing all cage atoms by carbon along with rescaling the bond distance by a factor of 0.7, and then reoptimizing the carbon cages, the more ideal carbon fullerene cages were recovered. It turns out that most of these carbon fullerene cages are those proven to be the global-minimum carbon cages by Wang et al.<sup>38</sup> To our knowledge, this is the first direct computational evidence through unbiased search that establishes a relationship between carbon fullerene cages and the homologue cages for low-lying silicon clusters over quite broad size range. Note, however, that several NTB global minima also show imperfect fullerene cages;

(38) Wang, C. Z.; Zhang, B. L.; Ho, K. M. In *Computational Studies of New Materials*; World Scientific: Singapore, 1999; p 74.

namely, the cages contain, in addition to five- and six-membered rings, four- or seven-membered rings (see Figure 1 in the Supporting Information). These include  $\text{Si}_{28}$ ,  $\text{Si}_{30}$ ,  $\text{Si}_{33}$ ,  $\text{Si}_{35}$ , and  $\text{Si}_{38}$ . It is possible that the selection of these nonfullerene cages is also a general feature for certain medium-sized clusters. It is also possible that the selection of these imperfect fullerene cages is due to the inaccuracy of the NTB description of the configuration space.

**Biased Search with Basin-Hopping DFT Method.** To test the second possibility, we carried out the (second-step) biased search of low-lying silicon clusters using the BH Monte Carlo method<sup>34</sup> combined with DFT within the GGA. Here, the biased search was limited to stuffed-cage clusters, where the cages can be either fullerene cages or the imperfect fullerene cages of several NTB global minima. The number of core-filling atoms can be adjusted from one to six, and the initial configurations of the core-filling atoms are based on those of the NTB global minima. For a given silicon cluster size, there are multiple ways to construct the stuffed-cage clusters. For example, for the smallest cluster considered here,  $\text{Si}_{27}$ , the initial isomeric structures can be either  $\text{Si}_3@ \text{Si}_{24}$  fullerene cage or  $\text{Si}_1@ \text{Si}_{26}$  fullerene cage. Our local search by a combined BH–DFT method indicates that isomers based on the fullerene cages consistently achieve lower energies than those based on the imperfect fullerene cages (see Tables 1 and 2 in the Supporting Information). In general, all NTB global minima can be slightly improved (having a lower energy) after the refining search in the DFT configuration space, indicating some subtle differences between the NTB and DFT configuration space. For  $\text{Si}_{29}$ , in particular, we find another isomeric fullerene cage  $\text{C}_{28a}(\text{D}_2)$  yields slightly lower energy than the isomer based on the  $\text{C}_{28}(\text{T}_d)$  cage, even though the latter cage is selected by the NTB global minimum  $\text{Si}_{32}$ . In Figure 2a, the resulting low-lying stuffed-fullerene silicon clusters are displayed, where the green atoms denote core-filling atoms (“stuffing”).

**All-Electron High-Level DFT Calculations.** To further affirm the relative stability of all stuffed-cage clusters and to compare binding energies with those of other medium-sized silicon clusters, we also performed geometric optimization at the B3LYP/6-31G(d) level of theory implemented in the Gaussian 03 software package<sup>39</sup> with no symmetry constraint. Harmonic vibrational analysis at the same level of theory was then taken to ensure that the clusters are local minima with no imaginary frequency. Finally, an all-electron single-point energy calculation at the B3LYP/6-311G(2d) level of theory was carried out to obtain the binding energies per atom (see Table 1 as well as Tables 1 and 2 in the Supporting Information). The use of the larger basis sets [6-311G(2d)] allows more accurate dif-

ferentiation of the energy order for isomers with very close binding energies (e.g., within 5 meV) at the lower level of theory [B3LYP/6-31G(d)]. As shown in Table 1, except for  $\text{Si}_{27}$ , all endohedral fullerene clusters derived from the local search show greater binding energy per atom than that of the low-lying endohedral fullerene cluster  $\text{Si}_{25}$  previously reported in ref 31. Overall, the binding energy per atom increases gradually with increasing cluster size,<sup>6</sup> an essential requirement for identifying low-lying medium-sized clusters. For comparison, the binding energies of those previously reported stuffed-fullerene clusters are notably smaller than that of the  $\text{Si}_{25}$  (see Table 1 and Supporting Information Table 1).

In Table 1, we also give a list of suggested optimal “stuffing/cage” combinations to construct stuffed-fullerene clusters. This list offers an explanation for why most previously reported stuffed-fullerene clusters are energetically less favorable. As an example, for  $\text{Si}_{33}$ , the previously “handmade” model was based on the  $\text{C}_{28}(\text{T}_d)$  cage (Figure 1) with addition of five core-filling atoms [hereafter, this model is denoted as  $\text{Si}_5@ \text{Si}_{28}$  cage]. As shown in Table 1, five core-filling atoms may be viewed as “over-stuffing” for the  $\text{C}_{28}(\text{T}_d)$  cage. In fact, the  $\text{C}_{30}(\text{C}_{2v})$  cage is a better one for constructing low-energy stuffed-fullerene clusters for  $\text{Si}_{33}$ . Similarly, six core-filling atoms are “over-stuffing” for the  $\text{C}_{30}(\text{C}_{2v})$  cage for constructing low-energy  $\text{Si}_{36}$ . For  $\text{Si}_{39}$ , the five core-filling atoms are optimal for the  $\text{C}_{34}(\text{C}_{3v})$  cage. However, the tetrahedral core-filling unit is not an optimal structure, which can give rise to a relatively higher energy isomer. In turn, these total-energy calculations reassure the necessity of the unbiased search for finding optimal stuffing/cage combinations as well as optimal geometries for the core-filling units.

The stuffing/cage combination list in Table 1 also provides a simple recipe to build, “by hand”, low-energy configuration of larger stuffed-fullerene clusters ( $N > 39$ ), which may have good possibility to become low-lying large-sized clusters (up to a certain size). A tentative “rule of thumb” that can be derived from the list in Table 1 is that the “stuffing”  $\text{Si}_{3+m}$  and  $\text{Si}_m$  ( $m = 1, 2, \dots$ ) appear to be upper and lower limits, respectively, for the core-filling atoms in the  $\text{Si}_{26+2m}$  fullerene cage. Note that one should be cautious when extrapolating the empirical rule to larger clusters as this rule has not been tested for  $N > 39$ . At the least, however, we expect the upper limit would work well since strong steric interaction due to “overstuffing” is unlikely to produce low-lying clusters. As an example, to build a low-energy stuffed-fullerene cluster  $\text{Si}_{40}$ , the stuffing/cage combination  $\text{Si}_6@ \text{Si}_{34}$  is likely a good choice, whereas  $\text{Si}_8@ \text{Si}_{32}$  cage may be “overstuffing”. For  $\text{Si}_{45}$ , the stuffing/cage combination  $\text{Si}_7@ \text{Si}_{38}$  cage appears to be a sensible choice, whereas a  $\text{Si}_9@ \text{Si}_{36}$  cage may not be. We have confirmed both cases through the NTB unbiased search. Indeed, we find that the NTB global minimum  $\text{Si}_{40}$  selects the  $\text{C}_{34}$ -homologue cage while that of  $\text{Si}_{45}$  selects the  $\text{C}_{38}$ -homologue cage (Figure 2b). For even larger clusters such as  $\text{Si}_{60}$ , the empirical rule would suggest that the stuffing/cage combination  $\text{Si}_{12}@ \text{Si}_{48}$  cage is possibly a good choice, but the borderline cases,  $\text{Si}_{14}@ \text{Si}_{46}$  cage,  $\text{Si}_{10}@ \text{Si}_{50}$  cage, and  $\text{Si}_8@ \text{Si}_{52}$  cage, should be also examined. A more thorough global search for  $N \geq 40$  is underway.

## Conclusions

Our study supports the previously suggested notion<sup>20–23</sup> that carbon fullerene cages are promising general cage motifs

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(“magic cages”) for building low-lying sphericallylike clusters. In particular, we show that the fullerene cages can form low-lying stuffed-cage silicon clusters beyond the size  $N > 27$ . The present study also demonstrates a close structural relationship between the lowest-energy carbon fullerene and their group IV counterpart: the low-lying sphericallylike silicon clusters over quite broad medium-size range. An empirical rule that provides optimal “stuffing/cage” combinations for constructing low-energy endohedral silicon fullerenes is suggested, with a hope that it can provide guidance to future synthesis of “bucky” silicon.

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**Supporting Information Available:** Tables of B3LYP/6-311G(2d) energies, zero-point corrections, and binding energies per atom and figure of NTB global-minimum clusters (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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