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Search for Lowest-Energy Fullerenes: C<sub>98</sub> to C<sub>110</sub>

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By combining the semiempirical density-functional based tight-binding optimization with density-functional theory single-point energy calculation at the PBE1PBE/6-311G\* level, we propose an efficient computational approach to determine lowest-energy structures of large-sized carbon fullerenes. Our studies show that C<sub>92</sub> (*D*<sub>3</sub>: 28) and C<sub>94</sub> (*C*<sub>2</sub>: 43) are the new leading candidates for the lowest-energy structures of C<sub>92</sub> and C<sub>94</sub>. Moreover, for the first time, the lowest-energy structures of C<sub>98</sub>–C<sub>110</sub> are identified on the basis of the density-functional theory calculation. The lowest-energy isomers C<sub>102</sub> (*C*<sub>1</sub>: 603) and C<sub>108</sub> (*D*<sub>2</sub>: 1771) are readily isolated experimentally because they are much lower in energy than their other low-lying IPR isomers.

## I. Introduction

Exploration of the formation mechanism of large-sized multishell fullerenes (e.g., buckyonion C<sub>60</sub>@C<sub>240</sub>)<sup>1</sup> as well as large-sized endohedral metallofullerenes (e.g., recently isolated Dy<sub>2</sub>@C<sub>100</sub>)<sup>2</sup> calls for a better understanding of the lowest-energy structures of large-sized (empty) fullerenes beyond the size of C<sub>100</sub>. To date, the largest (empty) fullerene cage isolated and characterized in the laboratory is C<sub>96</sub>, although some larger fullerenes (e.g., C<sub>176</sub>) have been detected.<sup>3</sup> On the other hand, previous ab initio theoretical studies have corroborated nearly all the low-lying fullerene structures of C<sub>80</sub> to C<sub>96</sub>.<sup>4–12</sup> Additionally, low-lying structures of several larger fullerenes, such as C<sub>98</sub>, C<sub>100</sub> and C<sub>116</sub>, have also been explored on the basis of semiempirical methods.<sup>13–16a</sup> However, few global searches for low-energy fullerenes beyond the size of C<sub>96</sub> have involved ab initio or density-functional theory (DFT) calculations.<sup>16b</sup>

The theoretical challenge associated with the global search of low-energy structures of large-sized fullerenes stems mainly from the rapid increase of the number of isomers with the fullerene size. For example, the total number of fullerene isomers ranges from 39 718 for C<sub>82</sub> to 713 319 for C<sub>110</sub>.<sup>17</sup> In principle, one could determine the lowest-energy isomer by using ab initio electronic structure methods to compute energies of all fullerene isomers.<sup>5–9</sup> However, such an approach becomes increasingly impractical for large-sized fullerenes such as C<sub>110</sub>. To alleviate this “million-isomer” problem, two theoretical strategies have been commonly adopted: (1) to apply the isolated-pentagon-rule (IPR) as a filter, and (2) to utilize a highly efficient prescreening tool<sup>10–12,16</sup> such as empirical force fields (e.g., Brenner potential) or semiempirical methods (e.g., AM1, PM3 and SAM1) to further reduce the number of candidate isomers for the last-stage ab initio calculation. Indeed, the IPR conjecture can dramatically reduce the number of candidate isomers. For example, the number of IPR isomers of C<sub>110</sub> is only 2355 as opposed to 713 319 fullerene isomers of C<sub>110</sub>. However, full geometry optimization of thousands of large-sized fullerene isomers using ab initio methods can still be laborious. It is desirable to further cut down the number of candidate isomers to a few tens for the last-stage ab initio electronic energy

calculation. Toward this end, a highly efficient prescreening tool is required. Generally, such a pre-screening tool has to meet three prerequisites: (1) fast geometry optimization, (2) reasonably accurate optimized structures, and (3) modest error bar in the relative energies between isomers. Semiempirical methods, which have been used the most as the prescreening tool to obtain low-lying isomers of C<sub>92</sub>–C<sub>96</sub>,<sup>10–12</sup> meet the three prerequisites reasonably well. For C<sub>96</sub>, a complete calculation of the IPR isomer energies by Zhao et al.<sup>12</sup> shows that the error bar in relative energies with the SAM1 method can amount to ~15 kcal/mol, when compared with the DFT calculation at the B3LYP/6-31G level. As such, at least 10% of total IPR isomers should be subjected to the last-stage ab initio calculation to sort out the energy ranking of low-lying isomers (For C<sub>110</sub>, this means that more than 200 IPR isomers are subjected to ab initio geometry optimization). In this paper, we demonstrate a highly efficient prescreening tool in conjunction with DFT single-point energy calculation to find out top candidates of the lowest-energy IPR cluster of C<sub>98</sub>–C<sub>110</sub>.

## II. Computational Details

We employed the semiempirical self-consistent charge density-functional based tight-binding (DFTB) method<sup>18a,b</sup> as the prescreening tool.<sup>18c,d</sup> All the IPR fullerene isomers were fully optimized using the DFTB method. We first used the IPR isomers C<sub>82</sub>–C<sub>96</sub> as a testing database to evaluate the typical error bar with the DFTB method in calculating relative energies among the isomers. Guided by the error bar, an energy cutoff criterion is suggested. Next, all isomers that are within the energy cutoff are viewed as top candidates and are subject to the single-point energy calculation using the PBE1PBE hybrid functional<sup>19</sup> with a midsize basis set 6-311G\*. Here, we chose the hybrid exchange-correlation functional PBE1PBE, rather than the B3LYP or B3PW91 functional, because we previously showed that the PBE1PBE functional predicts the same energy ranking as that from the high-level coupled-cluster calculation for the top-three lowest-energy isomers of C<sub>20</sub> (bowl, cage, and ring isomers).<sup>19b</sup> All PBE1PBE/6-311G\* single-point energy calculations were performed using GAUSSIAN03 package.<sup>20</sup>

## III. Results and Discussions

**A. C<sub>82</sub>–C<sub>96</sub> as Test Database.** Geometries of all 540 IPR isomers of C<sub>82</sub>–C<sub>96</sub> were fully optimized using the DFTB

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**TABLE 1: Relative Energies  $\Delta E$  (kcal/mol) and HOMO–LUMO Gap  $E_{\text{gap}}$  (eV) of the Low-Lying Isomers of  $\text{C}_{82}$ – $\text{C}_{96}$ <sup>a</sup>**

$C_N$ <sup>b</sup>	label <sup>c</sup>	symmetry	PBE1PBE/6-311G*/DFTB		DFTB	$C_N$	label	symmetry	PBE1PBE/6-311G*/DFTB		DFTB
			$\Delta E$	$E_{\text{gap}}$	$\Delta E$				$\Delta E$	$E_{\text{gap}}$	$\Delta E$
$\text{C}_{82}$ (9)	<b>3</b>	$C_2$	<b>0.000</b>	<b>1.687</b>	<b>0.000</b>	82	$D_2$		5.760	1.759	5.437
	4	$C_s$	4.245	1.633	1.977		$C_1$		5.315	1.888	5.505
	5	$C_2$	9.255	1.333	4.426		$D_3$		11.352	1.440	7.099
	6	$C_s$	13.628	1.143	6.563		$C_1$		10.175	1.350	7.345
	1	$C_2$	7.937	1.279	6.966		$C_2$		10.076	1.315	7.736
	2	$C_s$	6.524	1.687	6.980		$D_2$		9.669	1.614	9.438
	9	$C_{2v}$	19.871	0.830	9.027		$C_2$		<b>0.000</b>	<b>1.905</b>	<b>0.000</b>
	<b>22</b>	$D_2$	<b>0.589</b>	<b>2.068</b>	<b>0.000</b>		$C_s$		1.988	1.986	2.130
	<b>23</b>	$D_{2d}$	<b>0.000</b>	<b>2.150</b>	<b>0.355</b>		$C_2$		7.018	1.660	6.593
$\text{C}_{84}$ (24)	11	$C_2$	8.704	1.702	7.935	133	$C_s$		6.032	1.742	6.659
	16	$C_s$	8.254	1.959	8.749		$C_1$		8.369	1.551	7.322
	15	$C_s$	12.090	1.604	9.118		$C_1$		8.074	1.712	7.421
	24	$D_{6h}$	7.244	2.457	9.140		$C_1$		10.676	1.497	7.426
	<b>17</b>	$C_2$	<b>0.000</b>	<b>1.578</b>	<b>0.000</b>		$C_2$		7.981	1.633	7.475
	11	$C_1$	10.959	1.170	6.891		$C_1$		10.416	1.438	8.519
$\text{C}_{86}$ (19)	16	$C_s$	5.650	1.970	7.430	$\text{C}_{96}$ (187)	<b>181</b>	$C_2$	<b>0.249</b>	<b>1.605</b>	<b>0.000</b>
	18	$c3$	11.158	1.269	7.648		<b>183</b>	$D_2$	<b>0.000</b>	<b>1.714</b>	<b>0.616</b>
	12	$C_1$	10.394	1.242	8.548		144	$C_1$	1.660	1.769	2.558
	<b>17</b>	$C_s$	<b>0.000</b>	<b>1.597</b>	<b>0.000</b>		145	$C_1$	2.666	1.578	3.238
$\text{C}_{88}$ (35)	7	$C_2$	1.212	1.633	1.313		182	$C_2$	3.930	1.551	3.647
	33	$C_2$	2.132	1.796	2.030		114	$C_1$	5.544	1.524	3.651
	15	$C_1$	13.065	1.058	8.977		94	$C_1$	6.124	1.524	5.624
	20	$C_2$	10.832	1.401	9.109		146	$C_s$	4.738	1.751	6.619
	<b>45</b>	$C_2$	<b>0.000</b>	<b>1.736</b>	<b>0.000</b>		142	$C_2$	6.572	1.675	6.869
$\text{C}_{90}$ (46)	35	$C_s$	2.877	1.905	3.431		164	$C_1$	8.638	1.397	7.143
	46	$C_{2v}$	3.062	1.865	4.736		130	$C_1$	7.976	1.605	7.940
	30	$C_1$	6.473	1.807	5.857		176	$C_2$	7.291	1.633	7.975
	28	$C_2$	7.734	1.748	6.659		47	$C_1$	8.796	1.666	8.084
	40	$C_2$	9.468	1.450	6.910		180	$C_s$	7.907	1.299	8.367
	18	$C_2$	10.430	1.524	9.071		116	$C_1$	9.130	1.453	8.658
$\text{C}_{92}$ (86)	<b>28</b>	$D_3$	<b>0.000</b>	<b>2.204</b>	<b>0.000</b>		179	$C_2$	9.545	1.361	8.794
	26	$C_2$	5.315	1.732	4.567		90	$C_1$	9.978	1.310	9.013
	84	$D_2$	4.891	1.984	4.922		165	$C_2$	12.674	1.216	9.317

<sup>a</sup> An arbitrary energy cut-off value of 0.015 au (9.4 kcal/mol) was adopted to collect all the leading candidates for the lowest-energy isomers. The boldface marks the top candidates for the lowest-energy isomer. <sup>b</sup> The number of IPR isomers is given in parentheses. <sup>c</sup> The labels are according to Fowler and Manolopoulos.<sup>21</sup>

**TABLE 2: Total Electronic Energies  $E$  (au), Relative Energies  $\Delta E$  (kcal/mol) and HOMO–LUMO Gap  $E_{\text{gap}}$  (eV) of the Lowest-Energy Structures of  $\text{C}_{92}$  ( $D_3$ : 28) and  $\text{C}_{94}$  ( $C_2$ : 43) (in Boldface), Compared with Those of  $\text{C}_{92}$  ( $D_2$ : 84)<sup>10</sup> and  $\text{C}_{94}$  ( $C_2$ : 133)<sup>11,16a</sup>**

$C_N$	label	symmetry	PBE1PBE/6-311G*			B3LYP/6-311G*		
			$E$	$\Delta E$	$E_{\text{gap}}$	$E$	$\Delta E$	$E_{\text{gap}}$
$\text{C}_{92}$	<b>28</b>	$D_3$	<b>−3502.572737</b>	<b>0.000</b>	<b>2.204</b>	<b>−3506.403673</b>	<b>0.000</b>	<b>2.007</b>
	84	$D_2$	−3502.564828	4.963	2.106	−3506.396750	4.344	1.872
$\text{C}_{94}$	<b>43</b>	$C_2$	<b>−3578.733040</b>	<b>0.000</b>	<b>1.948</b>	<b>−3582.648302</b>	<b>0.000</b>	<b>1.755</b>
	133	$C_2$	−3578.722665	6.511	1.793	−3582.637759	6.616	1.578

<sup>a</sup> Two hybrid density functionals are used for geometry optimization and energy calculation.

method. Relative energies of low-lying isomers (those with energy within 0.015 au or 9.4 kcal/mol from the lowest-lying DFTB isomer) are listed in the Table 1, together with the PBE1PBE/6-311G\* relative energies and HOMO–LUMO gaps. All isomers are labeled according to the Fowler and Manolopoulos scheme,<sup>21</sup> along with their point-group symmetries. First, we found that the lowest-energy isomers (based on the PBE1PBE/6-311G\* calculation) are mostly consistent with the literature results (see below for  $\text{C}_{92}$  and  $\text{C}_{94}$ ).<sup>5–12</sup> Second, many lowest-lying DFTB isomers are also the lowest-energy isomers according to the PBE1PBE/6-311G\* calculation. Third, with exception of two isomers of  $\text{C}_{82}$ , the error bar in relative energies using the DFTB method is less than 4.9 kcal/mol, compared with the PBE1PBE/6-311G\* calculation. We therefore adopted 0.01 au (6.3 kcal/mol) as an energy cutoff criterion. Namely, those isomers within 0.01 au from the lowest-lying DFTB isomer are considered to be a candidate for the true lowest-energy isomer. A noteworthy byproduct from this preliminary

test is that new lowest-energy IPR isomers of  $\text{C}_{92}$  ( $D_3$ : 28) and  $\text{C}_{94}$  ( $C_2$ : 43) are identified. To further ensure that both isomers are true global minima, we performed full geometry optimization of the two isomers using two hybrid DFT functionals, PBE1PBE/6-311G\* and B3LYP/6-311G\*. As shown in Table 2, the two newly identified lowest-energy isomers are about 4–7 kcal/mol lower in energy than those previously reported lowest-energy isomers,<sup>10,11,16a</sup> indicating that our newly proposed energy-ranking determination scheme is quite robust.

In Table 1, we also list the HOMO–LUMO gaps for all the leading IPR isomers, which were calculated at the PBE1PBE/6-311G\* level of theory. It can be seen that the HOMO–LUMO gaps span a large range from 0.83 to 2.46 eV. Except for  $\text{C}_{82}$  and  $\text{C}_{92}$ , all lowest energy isomers of  $\text{C}_{82}$ – $\text{C}_{96}$  do not possess the largest HOMO–LUMO gap. Although the HOMO–LUMO gaps of the low-lying isomers do not show special correlation with the relative energies, the HOMO–LUMO gaps of all the

**TABLE 3: Relative Electronic Energies  $\Delta E$  (kcal/mol) and HOMO–LUMO Gap  $E_{\text{gap}}$  (eV) of the Top-Six Lowest-Energy  $C_{98}$  Isomers, for Which One Set of Data Are Based on the Optimized Geometry at the PBE1PBE/6-311G\* Level and the Other Set Are Based on the DFTB Optimized Structure<sup>a</sup>**

$C_N$	label	symmetry	PBE1PBE/6-311G*/DFTB		PBE1PBE/6-311G*	
			$\Delta E$	$E_{\text{gap}}$	$\Delta E$	$E_{\text{gap}}$
$C_{98}$	<b>248</b>	$C_2$	<b>0.000</b>	<b>1.837</b>	<b>0.000</b>	<b>1.971</b>
	120	$C_s$	1.166	1.690	1.162	1.791
	253	$C_3$	3.044	1.517	2.998	1.549
	254	$C_2$	3.207	1.415	3.217	1.459
	148	$C_3$	2.930	1.388	3.273	1.430
	244	$C_1$	4.079	1.252	4.140	1.301

<sup>a</sup> The boldface marks the lowest-energy isomer.

lowest-energy isomer are greater than 1.5 eV, indicating that these isomers are all chemically stable.

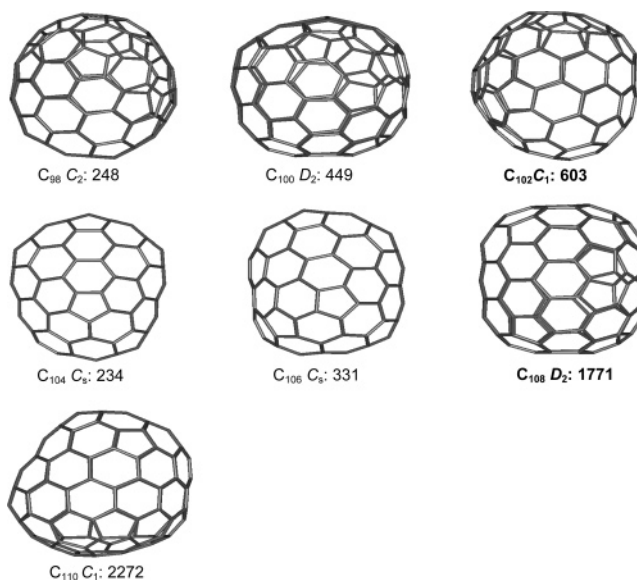
**B.  $C_{98}$  as a Testing Case.** An advantage of the DFTB method as a prescreening tool is that the optimized geometries are very close to those based on DFT optimization. This is because the DFTB method is designed to reproduce the results of DFT calculations at the outset. Because few ab initio studies have been reported for fullerenes beyond the size  $C_{96}$ , we used  $C_{98}$  as a testing case, for which full geometry optimization at PBE1PBE/6-311G\* level was carried out for leading lowest-energy isomers. In Table 3, we show the relative energies and HOMO–LUMO gaps of top-six lowest-energy isomers of  $C_{98}$ , where one set of data were based on the DFTB optimized geometries whereas the other set were based on the full geometry optimization at the PBE1PBE/6-311G\* level. It can be seen that the differences in the relative energies are only a few tenths of a kcal/mol, which proves the robustness of the energy ranking determined solely on the basis of the DFTB geometries.

**C. Lowest-Energy IPR Isomers of  $C_{98}$ – $C_{110}$ .** First, all 7535 IPR isomers of  $C_{98}$ – $C_{110}$  were geometrically optimized using

**TABLE 4: Relative Electronic Energies  $\Delta E$  (kcal/mol), Symmetries, Ring Spiral Codes, and HOMO–LUMO Gaps (eV) of the Low-Lying Isomers of  $C_{98}$ – $C_{110}$ <sup>a</sup>**

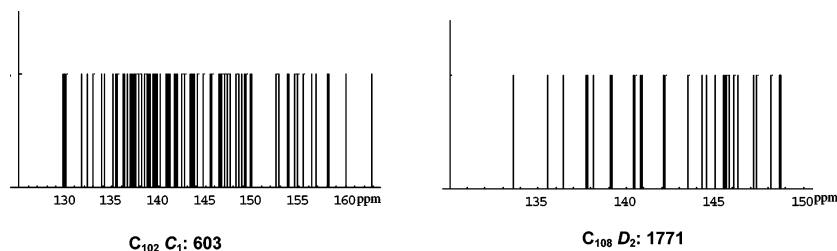
$C_N^b$	label <sup>c</sup>	ring spiral code	symmetry	PBE1PBE/6-311G*/DFTB		
				$\Delta E$	$E_{\text{gap}}$	DFTB $\Delta E$
$C_{98}$ (259)	<b>248</b>	<b>1 7 9 11 13 27 33 36 41 46 48 51</b>	$C_2$	<b>0.000</b>	<b>1.837</b>	<b>1.285</b>
	120	1 7 9 11 13 27 33 36 41 44 48 50	$C_s$	1.166	1.690	2.247
	148	1 7 9 11 26 30 32 34 36 38 40 50	$C_3$	2.930	1.388	0.000
	253	1 7 9 14 18 22 34 36 38 40 43 49	$C_3$	3.001	1.524	2.557
	<b>449</b>	<b>1 7 9 18 23 25 27 33 40 43 46 48</b>	$D_2$	<b>0.000</b>	<b>1.225</b>	<b>0.000</b>
$C_{100}$ (450)	<b>425</b>	<b>1 7 9 11 13 15 33 35 39 43 47 50</b>	$C_1$	<b>0.009</b>	<b>1.420</b>	<b>1.194</b>
	<b>442</b>	<b>1 7 9 11 13 27 34 38 41 44 47 51</b>	$C_2$	<b>0.260</b>	<b>1.282</b>	<b>1.379</b>
	173	1 7 9 11 13 15 38 33 40 43 46 52	$C_1$	1.204	1.180	1.088
	440	1 7 9 11 13 15 34 39 41 44 47 51	$C_2$	2.152	1.273	2.584
	<b>603</b>	<b>1 7 9 14 18 23 31 36 39 44 49 52</b>	$C_1$	<b>0.000</b>	<b>1.373</b>	<b>0.000</b>
$C_{102}$ (616)	<b>234</b>	<b>1 7 9 11 13 18 34 45 44 46 51 54</b>	$C_s$	<b>0.000</b>	<b>1.605</b>	<b>0.000</b>
	<b>812</b>	<b>1 7 9 11 13 18 29 31 37 45 49 53</b>	$D_2$	<b>0.046</b>	<b>2.041</b>	<b>5.080</b>
	443	1 7 9 11 13 18 34 37 40 44 46 49	$C_2$	1.532	1.197	1.310
	766	1 7 9 11 26 28 31 35 45 48 51 53	$C_2$	2.074	1.170	3.414
	106	1 7 9 11 13 18 37 40 43 45 51 53	$C_1$	2.478	1.361	6.113
$C_{106}$ (1233)	<b>331</b>	<b>1 7 9 11 13 24 29 46 49 47 50 53</b>	$C_s$	<b>0.000</b>	<b>1.769</b>	<b>3.215</b>
	534	1 7 9 11 13 24 29 46 49 46 52 55	$C_1$	1.339	1.170	0.269
	1194	1 7 9 11 13 30 32 37 40 46 49 52	$C_2$	1.715	1.061	1.024
	318	1 7 9 11 13 24 29 46 46 49 51 53	$C_1$	2.776	1.878	6.113
	314	1 7 9 11 13 24 30 38 43 46 49 55	$C_1$	2.838	1.633	4.658
$C_{108}$ (1799)	<b>1771</b>	<b>1 7 9 11 13 18 43 45 48 44 51 55</b>	$D_2$	<b>0.000</b>	<b>1.660</b>	<b>0.036</b>
	<b>2272</b>	<b>1 7 9 11 13 15 47 49 44 46 52 56</b>	$C_1$	<b>0.000</b>	<b>1.388</b>	<b>2.115</b>
	<b>1262</b>	<b>1 7 9 11 13 15 47 39 42 46 48 54</b>	$C_{2v}$	<b>0.355</b>	<b>0.980</b>	<b>0.776</b>
	<b>2293</b>	<b>1 7 9 11 13 15 47 49 41 49 52 54</b>	$C_1$	<b>0.404</b>	<b>1.442</b>	<b>1.422</b>
	2232	1 7 9 11 13 15 47 49 41 46 50 57	$C_1$	1.793	1.442	3.166
$C_{110}$ (2355)	1946	1 7 9 11 13 15 47 49 43 45 51 56	$C_1$	2.364	1.252	3.200
	2070	1 7 9 11 13 15 34 36 41 44 49 57	$C_1$	2.768	1.225	2.792

<sup>a</sup> The energies are calculated at the PBE1PBE/6-311G\* level of theory and based on DFTB optimized geometries. The boldface marks the top candidates for the lowest-energy isomer. <sup>b</sup> The number of IPR isomers is given in parentheses. <sup>c</sup> The labels are according to Fowler and Manolopoulos.<sup>21</sup>

**Figure 1.** Top candidate for the lowest-energy isomer of large-sized fullerenes  $C_{98}$ – $C_{110}$ .

the DFTB method. Again, those isomers whose relative energies with respect to the lowest-energy DFTB isomer are within the energy cutoff value (6.3 kcal/mol) were collected. Next, single-point energy calculation at the PBE1PBE/6-311G\* level was carried out to obtain the energy ranking and the top candidates for the lowest-energy isomer (highlighted in boldface in Table S1). It can be seen from Table S1 that all the lowest-energy isomers identified on the basis of the PBE1PBE/6-311G\* calculation have corresponding (DFTB) energies within 5.1 kcal/mol from the lowest-lying DFTB isomer, which justifies the use of 6.3 kcal/mol as the energy cutoff criterion.





**Figure 2.** Calculated  $^{13}\text{C}$  NMR spectra of  $\text{C}_{102}$  ( $C_1$ : 603) and  $\text{C}_{108}$  ( $D_2$ : 1771). The two isomers are predicted to be more easily isolated by the experiment than other large-sized fullerenes.

In Table 4, we summarize the main results of this work, including the identified top candidates for the lowest-energy isomers of  $\text{C}_{98}$ – $\text{C}_{110}$  (see Figure 1), the relative energies, ring spiral codes, and the HOMO–LUMO gaps. In light of the intrinsic error bar for the DFT electronic-energy calculation<sup>18b</sup> and possible temperature effects on the relative stability, those low-lying isomers within 3.0 kcal/mol from the top candidate are also listed in Table 4. For  $\text{C}_{98}$  and  $\text{C}_{100}$ , ( $C_2$ : 248) and ( $D_2$ : 449) are the leading candidate for the lowest-energy isomer, the same as those identified on the basis of semiempirical methods.<sup>13,14,16a</sup> However, the second lowest isomers differ from those determined from previous semiempirical calculation. Note that for the third and fourth lowest-energy isomers of  $\text{C}_{98}$ , ( $C_3$ : 148) and ( $C_3$ : 253), previous semiempirical (SAM1) calculation predicted that they are ranked 36th and 71st, respectively.<sup>13</sup> For  $\text{C}_{100}$ , the second and third lowest-energy isomers ( $C_1$ : 425) and ( $C_2$ : 442) are only 0.009 and 0.26 kcal/mol higher in energy than the leading candidate ( $D_2$ : 449). We therefore view the three  $\text{C}_{100}$  isomers iso-energetic.

Particular noteworthy are the lowest-energy isomers of  $\text{C}_{102}$  and  $\text{C}_{108}$  ( $C_1$ : 603 and  $D_2$ : 1771). Being 5.1 and 3.2 kcal/mol more stable than their second lowest-energy isomer (Table S1), these two isomers are more likely to be isolated experimentally among the large-sized fullerenes. For this reason, we calculated the  $^{13}\text{C}$  NMR chemical shift of the two isomers at the PBE1PBE/6-311G\* level of theory (Table S2). The simulated NMR spectra are plotted in Figure 2, which are readily compared with experimental spectra. On the other hand, our calculation indicates that there exist at least three nearly iso-energetic isomers for  $\text{C}_{100}$  and  $\text{C}_{110}$ . As a result, these isomers are likely to coexist in the soot and hard to separate experimentally. Of course, confirmation of the predicted lowest-energy isomers must await future experiments.

As in the case of  $\text{C}_{82}$ – $\text{C}_{96}$ , the HOMO–LUMO gaps of fullerene  $\text{C}_{98}$ – $\text{C}_{110}$  do not show strong correlation with the relative energy. In Table 4 and Table S1, it can be seen that  $\text{C}_{98}$  ( $C_2$ : 248) is the only isomer that has both the lowest energy and the largest HOMO–LUMO gap. Among all the large fullerene considered in this study, it appears that  $\text{C}_{104}$  ( $D_2$ : 812) has the largest HOMO–LUMO gap of 2.04 eV. Finally, comparing Table 1 with Table S1, it seems that the HOMO–LUMO gaps tend to decrease with increasing the size of fullerene.

#### IV. Conclusions

We have shown that the semiempirical DFTB method can be a highly efficient pre-screening tool, when combined with the DFT single-point energy calculation, to determine the best candidates for the lowest-energy isomer of large fullerenes. Our studies reveal new candidate isomers  $\text{C}_{92}$  ( $D_3$ : 28) and  $\text{C}_{94}$  ( $C_2$ : 43) to be the lowest-energy isomer of  $\text{C}_{92}$  and  $\text{C}_{94}$ . Moreover, for the first time, the lowest-energy structures of  $\text{C}_{98}$ –

$\text{C}_{110}$  (as well as new low-lying structures) are identified on the basis of DFT calculation. In particular, the predicted lowest-energy isomers of  $\text{C}_{102}$  ( $C_1$ : 603) and  $\text{C}_{108}$  ( $D_2$ : 1771) are notably lower in energy than their corresponding low-lying IPR isomers, suggesting that the two isomers are more readily isolated experimentally than other large-sized fullerenes in the size range  $\text{C}_{98}$ – $\text{C}_{110}$ .

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**Supporting Information Available:** Data of electronic energies for  $\text{C}_{98}$ – $\text{C}_{110}$ ,  $^{13}\text{C}$  NMR chemical shifts for  $\text{C}_{102}$  ( $C_1$ : 603) and  $\text{C}_{108}$  ( $D_2$ : 1771) are collected. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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