Electronic supplementary information

Gap maximum of graphene nano-flakes: a first-principles study combined with the Monte-Carlo tree search

Zhipeng Cao,[a] Yujun Zhao,[a] Jihai Liao[a] and Xiaobao Yang[a]

[a.]Department of Physics, South China University of Technology, Guangzhou 510640, P. R. China

The distributions of bond lengths in GNFs

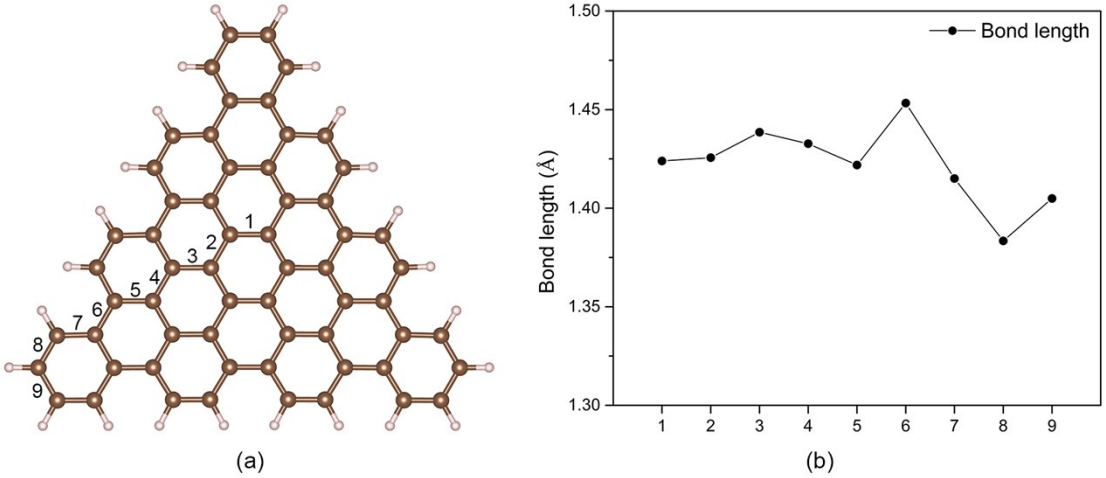


Figure S1. (a) A triangle armchair GNF structure and the number from 1 to 9 represent different C-C bonds from center to edge. (b) The corresponding bond length distribution which reflects the bonds near edges have more change than that near center when comparing to 1.42Å C-C bond in graphene.

The congruence check of GNFs based on the triangle lattice

s	d^2	m	n
1	0	0	0
2	1	-1	0
3	1	-1	1
4	1	0	-1
5	1	0	1
6	1	1	-1
7	1	1	0
8	3	-2	1
9	3	-1	-1
10	3	-1	2
11	3	1	-2
12	3	1	1
13	3	2	-1
...	...	...	...

(a)

(b)

Figure S2. (a) The list of the name rule, where *s* represents the 'name' of every triangle lattice site,

d^2 is the square of distance from one site to origin in rectangular coordinates, m and n represent corresponding triangle coordinate. Sorting d^2, m and n in turn to acquire this list. (b) The result after naming triangle lattice.

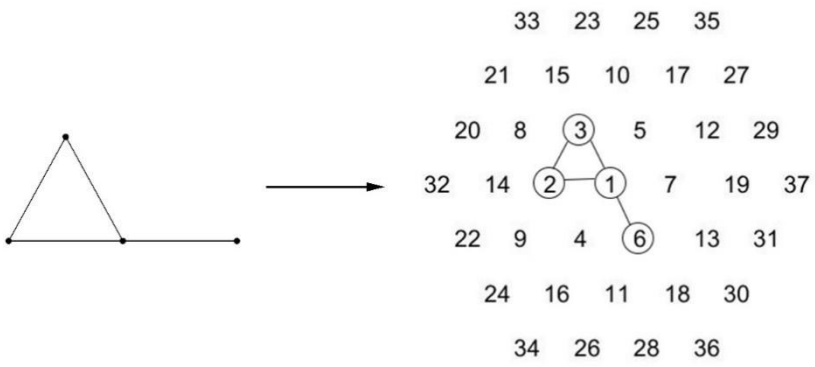


Figure S3. Considering all 12 types of symmetry operation on the triangle lattice for a structure and choose the situation which has the minimum summation. After sorting these number, we get this structure's name: 1 2 3 6.

After translating hexagonal lattice to triangle lattice, we want to represent a structure through its atom coordinates naturally. But we can't easily judge if any two structures with same number of atoms are equivalent when concerning their symmetry operations, sequence of atom coordinates and so on. For this reason, we number the planar triangular lattice according to the certain rule (Fig. S2) so that every structure on lattice points in a position can be represented by a sequence of number (Fig. S3). To judge equivalent structures of a structure, we perform all symmetry operations of planar triangular lattice for a giving structure and get some sequences of number. Then we only choose the sequence who has the minimum summation and sort it from small to large to name this structure so that we exclude the equivalent structures naturally (i.e. one unique structure corresponds to one unique sequence). Therefore, we only need to save the name data of

every structure we have found and exclude equivalent structures naturally.

The excluded structures

In the growth of GNFs, some special structures will appear. As an example in Fig. S4a. We can find that there are two hydrogen atoms extremely close to each other (0.57Å) and even less than the bond length of hydrogen molecule (0.74Å). Its structure after optimizing changed a lot (Fig. S4b, the bond length between these two hydrogen atoms adds to 1.52Å and other carbon rings are out of shape) which would cause a large change of electronic properties and it's usually difficult to be acquired in experiments. Therefore, we ruled out this circumstance in the whole enumeration calculations and Monte-Carlo tree search method (i.e. we directly deleted the growing points which will generate these unstable structures to any structures, an example has been shown in Fig. S4c).

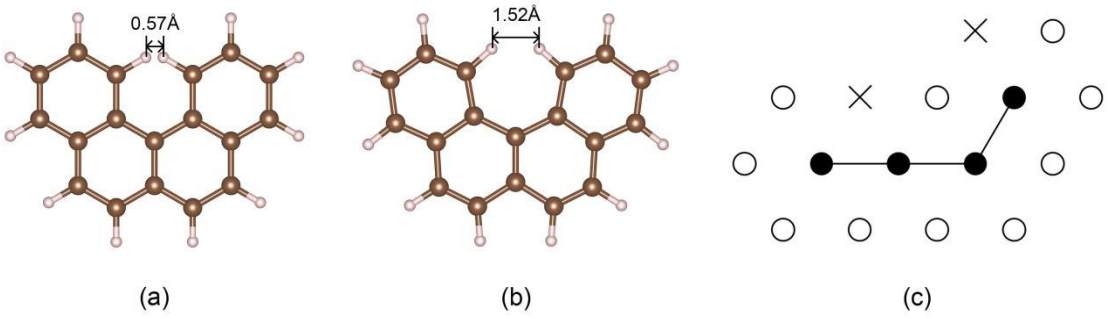
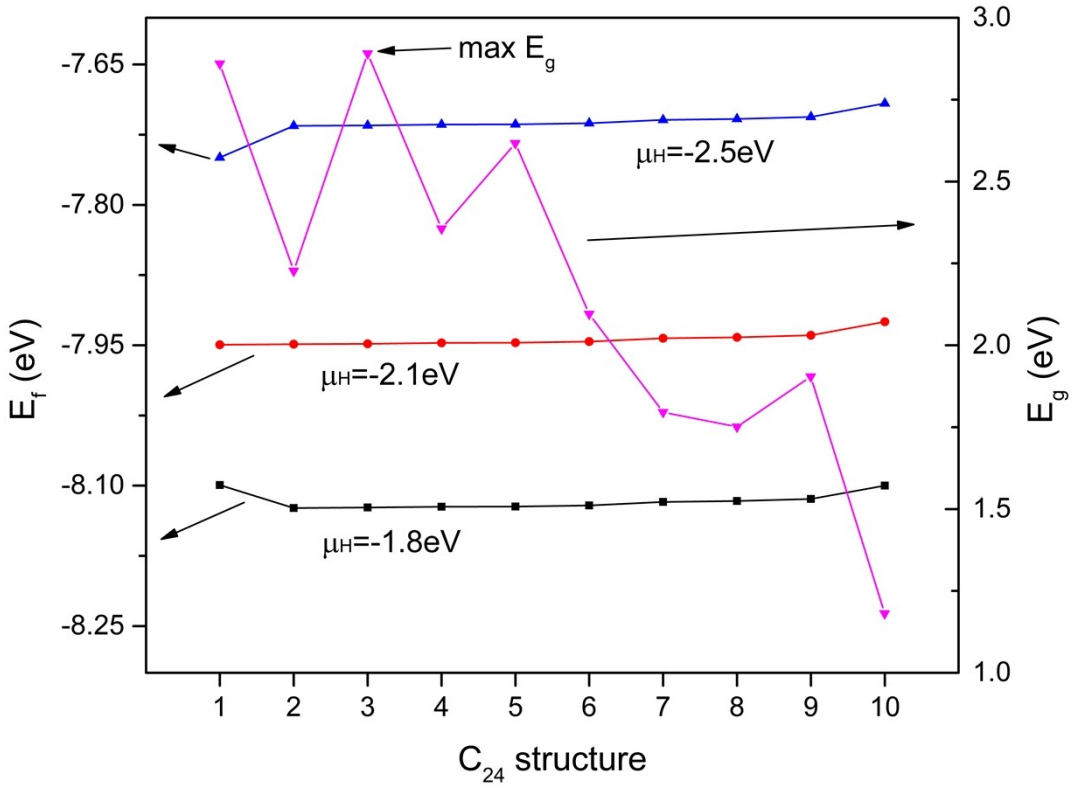
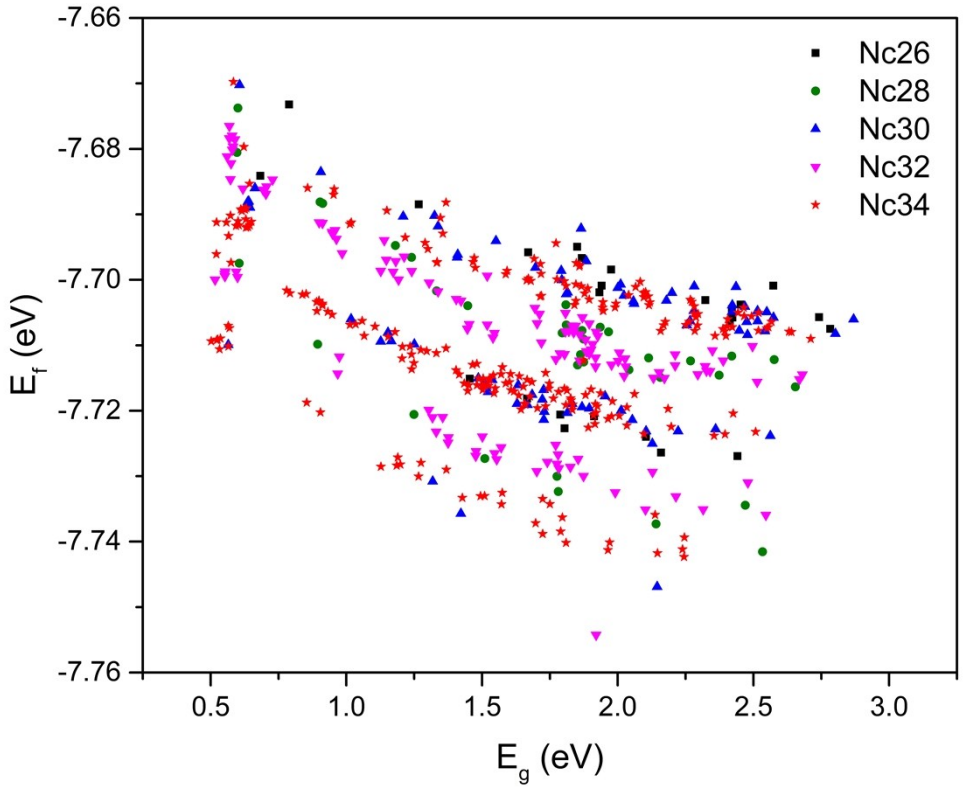


Figure S4. (a) The structure we firstly obtained. (b) The corresponding structure after optimizing. (c) To a structure represented by solid circle, the hollow circle represents the sites which can be used as growing sites and cross represents the sites we will delete

The enumerated results of structural stabilities and electronic properties



(a)



(b)

Figure S5. (a) The curves about E_f for different given μ_H and E_g of all ten structures when N_C=24 respectively. First structure has 12 H atoms and the other structures have 14 H atoms. The corresponding meaning of every curve has been pointed in this figure. (b) The relation between stability (E_f) and electronic properties (E_g) of all structures in for N_C from 26 to 34. The points with different shapes and colors represent different N_C structures and μ_H is set to -2.5eV.

All E_g results with their extreme structures have been shown in Fig. S6. We can clearly find a great difference between these structures and those structures in Fig. 2a, which indicates that a structure with the largest E_g would not be the most stable one.

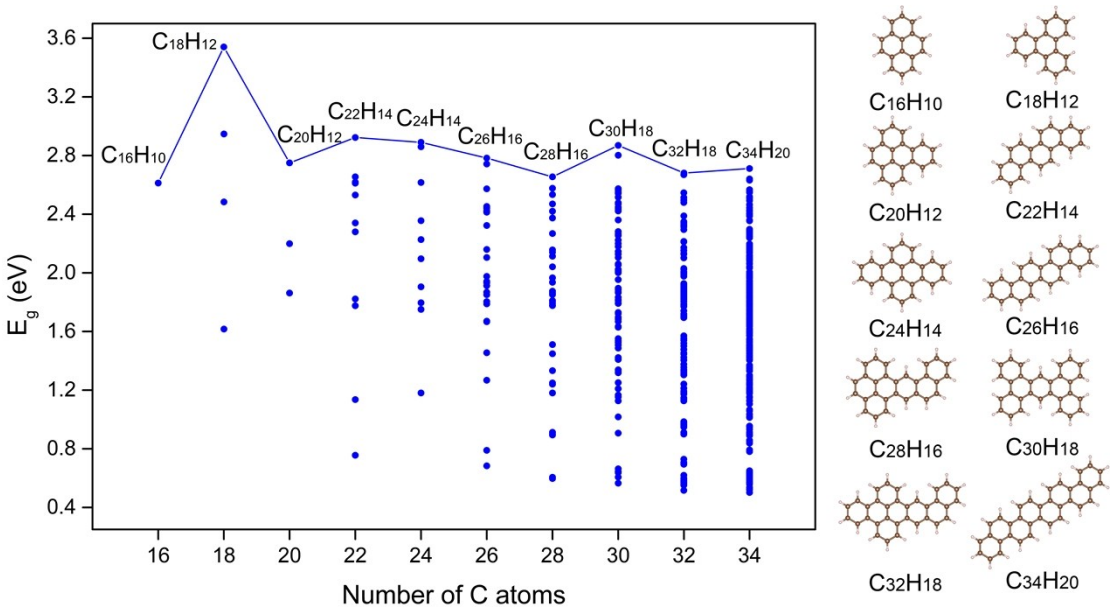


Figure S6. The curve about the largest E_g of structures for N_C from 16 to 34. The corresponding structures and molecular formulas have also been shown. Blue points represent all structures we have calculated.

The results of the Monte-Carlo tree search

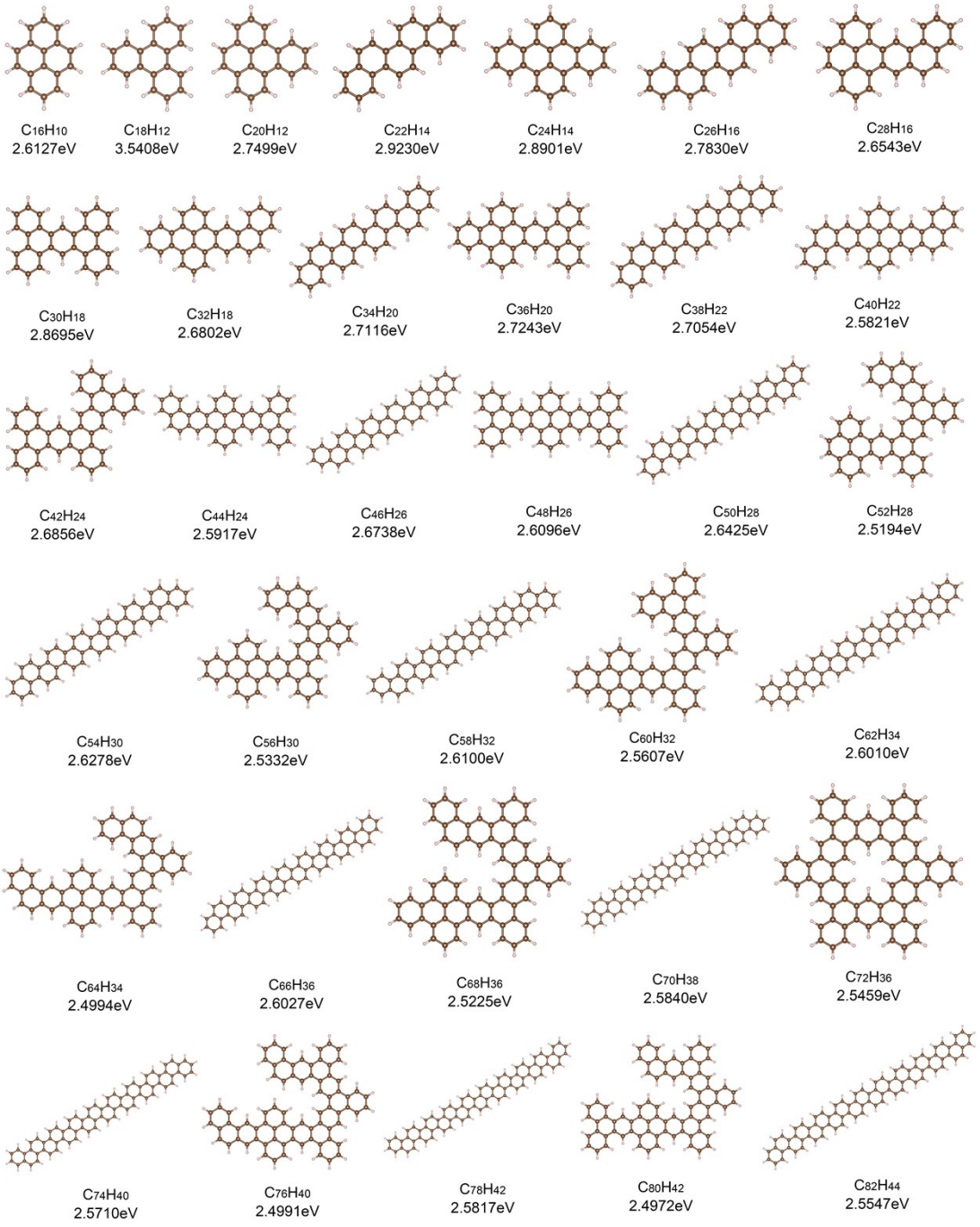


Figure S7. All GNF structures with the maximum E_g we have acquired after confirming by DFT method. N_C is from 16 to 82 and even. The corresponding molecular formulas and E_g results have also been shown.