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Electronic Supplementary Information for "Generalized structural motif model for studying the thermodynamic stability of fullerenes: from C_{60} to graphene passing through giant fullerenes"

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Contents

1 Derivation of eqn (3) of the manuscript

According to the definition of excess energy, the total energy of a given fullerene C_{2n} is

$$E_{\mathrm{tot}}(C_{2n}) = E(C_{2n}) + 2n\,E_{\mathrm{at}}(\mathrm{Gr}) \tag{S1}$$

where $E(C_{2n})$ is the excess energy[2,3] of fullerene C_{2n} and $E_{\mathrm{at}}(\mathrm{Gr})$ is the total energy per atom of graphene. The latter can be calculated using periodic boundary conditions.[2]

Substituting eqn (S1) to eqn (2) of the manuscript, we obtain eqn (3) of the manuscript:

$$\begin{aligned}\Delta H_{\mathrm{f}}^{\mathrm{o}}(C_{2n}) &= \Big[E(C_{2n}) + 2n\,E_{\mathrm{at}}(\mathrm{Gr})\Big] - \frac{2n}{60}\Big[E(C_{60}) + 60\,E_{\mathrm{at}}(\mathrm{Gr})\Big] + \frac{2n}{60}\Delta H_{\mathrm{f}}^{\mathrm{o}}(C_{60}) \\ &= E(C_{2n}) + \frac{2n}{60}\Big[\Delta H_{\mathrm{f}}^{\mathrm{o}}(C_{60}) - E(C_{60})\Big]\end{aligned}$$

2 The constraint for correct convergence to the graphene limit

For the sake of simplicity, let's consider the icosahedral leapfrog[4] fullerene C_{2n} approaching the graphene limit ($2n \to \infty$). For giant icosahedral fullerenes, $N_1 = n - 130$, $N_2 = N_{14} = 60$ and $N_m = 0$ for all other motifs. According to eqn (4) in the manuscript, its excess energy is

$$E(2n) = (n - 130)E_1 + 60E_2 + 60E_{14} + F(2n) \tag{S2}$$

Then, when $2n \to \infty$, the excess energy per atom is:

$$\left.\frac{E(2n)}{2n}\right|_{2n\to\infty} = \left[\frac{(n - 130)E_1 + 60(E_2 + E_{14})}{2n} + \frac{F(2n)}{2n}\right]_{2n\to\infty} = \frac{E_1}{2} \tag{S3}$$

Note that the global curvature term $F(2n)/2n$ vanishes as $2n$ goes to infinity. Since the the excess energy per atom is zero for graphene (by definition[2,3]), the right side of eqn (S3) is zero, which leads to:

$$E_1 = 0 \tag{S4}$$

3 Elimination of linear dependence using the relationships among motif contributions $\{E_m\}$

Using the five relationships given in the manuscript, namely, $E_1 = 0$, $E_2 = E_{14}$, $E_3 = E_{24}$, $E_{15} = E_{27}$, $E_{17} = E_{25}$, eqn (4) in the manuscript can be reduced to:

$$E(C_{2n}) = \left(\sum_{m\in\mathcal{M}} E_m N_m\right) + E_2(N_2 + N_{14}) + E_3(N_3 + N_{24}) + E_{15}(N_{15} + N_{27}) + E_{17}(N_{17} + N_{25}) + F(2n) \tag{S5}$$

where set $\mathcal{M}$ includes all motifs except motifs 1, 2, 3, 14, 15, 17, 24, 25 and 27. Hence, there are 25 parameters $\{E_m\}$ in the fitting equation (S5) without linear dependence.

4 Least-squares fit using the SVD method

We have also carried out a least-squares fit, based on eqn (15) in the manuscript, using the singular value decomposition (SVD)[5] technique. As motif 1 has no contribution to the total excess energy, we have excluded this motif in the fitting equation, as given in the following:

$$E(\mathrm{C}_{2n}) = \sum_{m=2}^{30} C_m N_m + \quad J \ln \frac{2n+L}{60}. \tag{S6}$$

The fitted parameters are listed in Table S1. We have checked that the excess energies reproduced by eqn (S6) (with SVD-optimized parameters) are exactly the same as those reproduced by eqn (15) in the manuscript, for both fitting procedures yield mathematically equivalent results.

Table S1. Fitted parameters C_m (in kcal/mol), J (in kcal/mol) and L using eqn (S6)

Parameter	Value	Parameter	Value
C_2	0.4052	C_{18}	10.2538
C_3	0.0042	C_{19}	8.8784
C_4	0.6818	C_{20}	9.8512
C_5	−0.2094	C_{21}	6.2757
C_6	5.2524	C_{22}	7.2417
C_7	−0.9405	C_{23}	2.4958
C_8	0.5538	C_{24}	23.9560
C_9	2.9614	C_{25}	26.6463
C_{10}	−0.0230	C_{26}	22.6462
C_{11}	−3.1987	C_{27}	23.7450
C_{12}	2.4847	C_{28}	25.5246
C_{13}	−2.6070	C_{29}	25.0960
C_{14}	9.0144	C_{30}	39.2357
C_{15}	10.2464	J	283.4915
C_{16}	10.1851	L	−31.5064
C_{17}	8.1373		

5 Tube- and disk-shaped isomers considered in this work

For testing the performance of the models, we have considered the following tube-[6,7] and disk-shaped fullerene isomers.

The tubular isomers are C_{114}-D_{3h}(2), C_{120}-D_{5d}(1), C_{120}-D_2(2), C_{130}-D_{5h}(1), C_{132}-D_3(3), C_{150}-D_{5h}(1) and C_{180}-D_{5d}(1).

The disk-like isomers are C_{96}-D_{3h}(33), C_{108}-D_2(210), C_{110}-C_2(155), C_{112}-C_s(134), C_{114}-C_2(229), C_{116}-C_{2v}(149), C_{118}-C_2(738), C_{120}-C_s(3340), C_{120}-D_{2h}(3342), C_{150}-D_{5h}(335568) and C_{180}-D_{6h}(4071774).

6 Prediction performance of other models

6.1 Models using a combined form of the curvature term

We have also used a combined form of the curvature term, namely, $F(2n) = A/(2n+B)+J\ln(2n/60)$ or $F(2n) = A/(2n + B) + J\ln[(2n + L)/60]$. The prediction results are shown in Fig. S1 and S2, respectively. As we can see, These models still give significant errors for giant fullerenes.

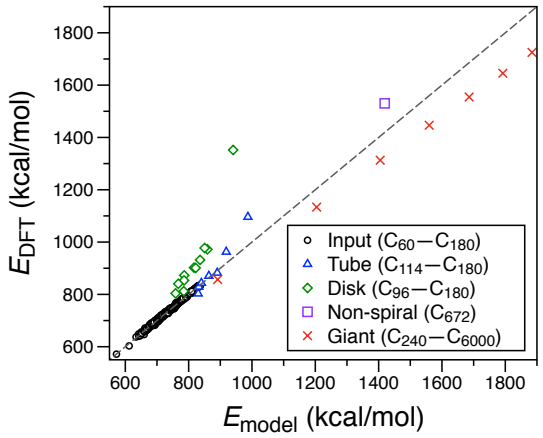

Figure S1. Predicted excess energies (E_{model}) by the model using the global curvature term, $F(2n) = A/(2n + B) + J\ln(2n/60)$, compared with those ($E_{\mathrm{DFT}}$) obtained from DFT calculations. The fitting parameters have been optimized based on 426 structures from C_{60} to C_{180} as input (black circles). The fitted models are then applied to some tube-shaped (blue triangles), disk-shaped (green diamonds), non-spiral (purple square) and giant icosahedral (red crosses) fullerenes.

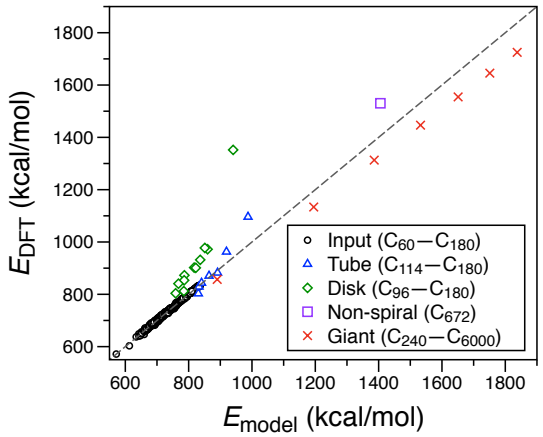

Figure S2. Idem Fig. S1 for the model using the global curvature term, $F(2n) = A/(2n + B) + J\ln[(2n + L)/60]$.

6.2 Reparameterized Cioslowski's model by Cai et al.[1]

The original Cioslowski's model was reparameterized by Cai *et al.*,[1] based on the DFT energies of 536 isomers of C_{60}–C_{90}, C_{116}–C_{120} and C_{130}–C_{160}. Here, using the 426 fullerenes (C_{60} to C_{180}) in the training set in the present work, we have checked the prediction performance of this reparameterized model. The results are shown in Fig. S3 and S4.

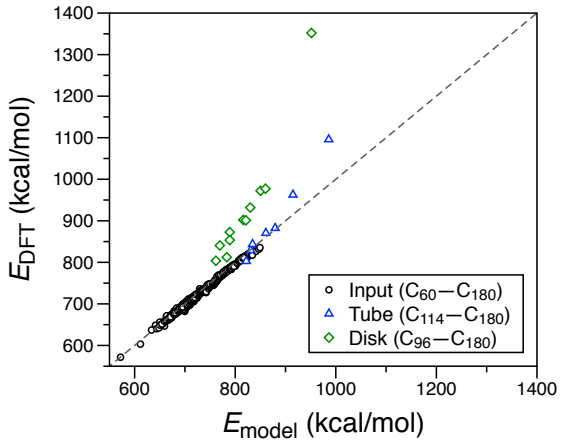

Figure S3. Predicted excess energies (E_{model}) by the reparameterized Cioslowski's model by Cai et al.,[1] compared with those (E_{DFT}) obtained from DFT calculations. The results are shown for the 426 structures in the training set in the present work (black circles) and for some tube-shaped (blue triangles) and disk-shaped (green diamonds) fullerenes.

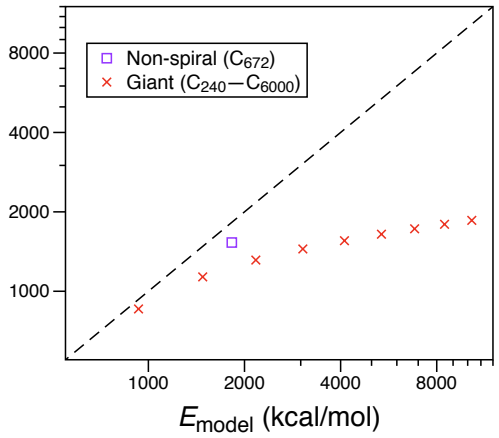

Figure S4. Idem Fig. S3 for non-spiral (purple square) and giant icosahedral (red crosses) fullerenes. Note that a logarithmic scale is used.

7 Correction for largely aspherical fullerenes based on cage asphericity

As we have shown in the manuscript, for largely aspherical fullerenes, the deviation by our new model roughly correlates with the cage asphericity f, defined by eqn (19) of the manuscript. By making a linear least-squares fit with the data presented in Fig. 7 of the manuscript, we obtain the following empirical formula for the deviation ΔE_{dev} (in kcal/mol) by the model:

$$\Delta E_{\mathrm{dev}} \approx 638.0492 f - 163.8770 \tag{S7}$$

Then, the model including this correction can be formulated as

$$E(\mathrm{C}_{2n}) = \sum_{m=1}^{30} E_m N_m + \quad J \ln \frac{2n + L}{60} \; + \Delta E_{\mathrm{dev}}. \tag{S8}$$

Applying this formula to the tubular, disk-shaped and non-spiral fullerenes, we have corrected the excess energies predicted by our model, as shown in Fig. S5. As we can see, the prediction accuracy of the model has been substantially improved, compared with the uncorrected results shown in Fig. 5b of the manuscript.

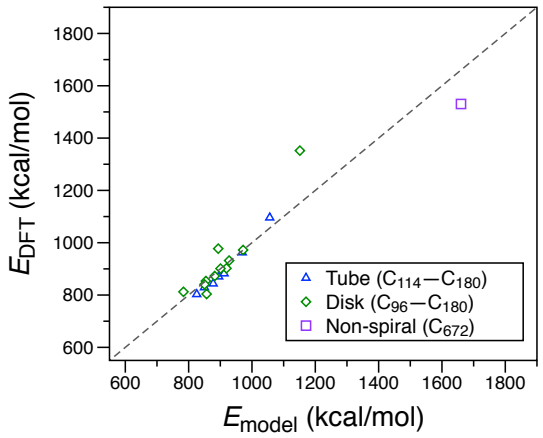

Figure S5. Predicted excess energies (E_{model}) by the logarithmic model (using eqn (18) of the manuscript) after the correction based on the cage asphericity f, compared with those (E_{DFT}) obtained from DFT calculations. The results are shown for the tube-shaped (blue triangles), disk-shaped (green diamonds) and non-spiral (purple square) fullerenes.

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