# Electronic Supplementary Information (ESI)

## Theoretically Modelling Graphene-Like Carbon Matryoshka with Strong Stability and Particular Three-Center Two-Electron $\pi$ Bonds

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**Table of Contents**

## 1. Optimal conformations of $C_nH_2$ ($2 \le n \le 8$)

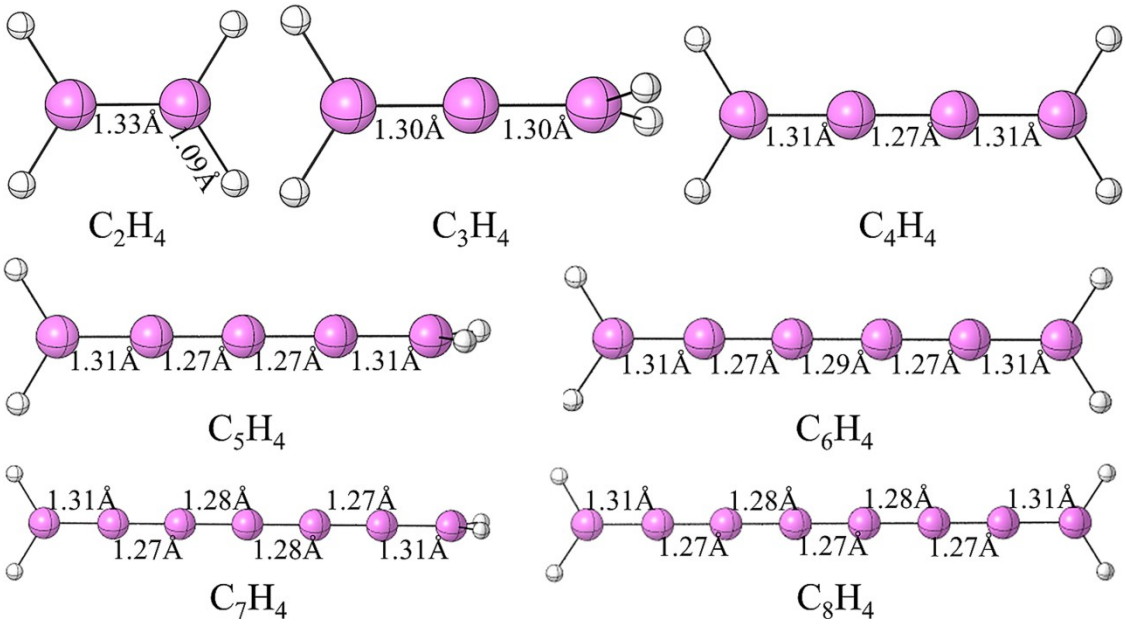


**Figure S1** Optimal conformations of $C_nH_2$ ($2 \le n \le 8$) based on the B3LYP/6-311G(d,p).

## 2. Stiffness tensor matrixes for L-2Gy and L-3Gy

**Table S1** Stiffness tensor $C_{ij}$ in GPa matrixes for L-2Gy and L-3Gy.

| **L-2Gy** | | | | | | |
|---|---|---|---|---|---|---|
| | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ |
| $C_1$ | 25.029 | 23.359 | 0.445 | 0.000 | 0.000 | 0.000 |
| $C_2$ | 23.359 | 25.029 | 0.445 | 0.000 | 0.000 | 0.000 |
| $C_3$ | 0.445 | 0.445 | 1.557 | 0.000 | 0.000 | 0.000 |
| $C_4$ | 0.000 | 0.000 | 0.000 | 0.835 | 0.000 | 0.000 |
| $C_5$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.523 | 0.000 |
| $C_6$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.523 |
| **L-3Gy** | | | | | | |
| | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ |
| $C_1$ | 18.615 | 18.209 | 0.336 | 0.000 | 0.000 | 0.000 |
| $C_2$ | 18.209 | 18.615 | 0.336 | 0.000 | 0.000 | 0.000 |
| $C_3$ | 0.336 | 0.336 | 1.161 | 0.000 | 0.000 | 0.000 |
| $C_4$ | 0.000 | 0.000 | 0.000 | 0.203 | 0.000 | 0.000 |
| $C_5$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.331 | 0.000 |
| $C_6$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.331 |

### 3. Crystal structures and Localized orbital locator (LOL) maps for graphene and αGy (L-1Gy)

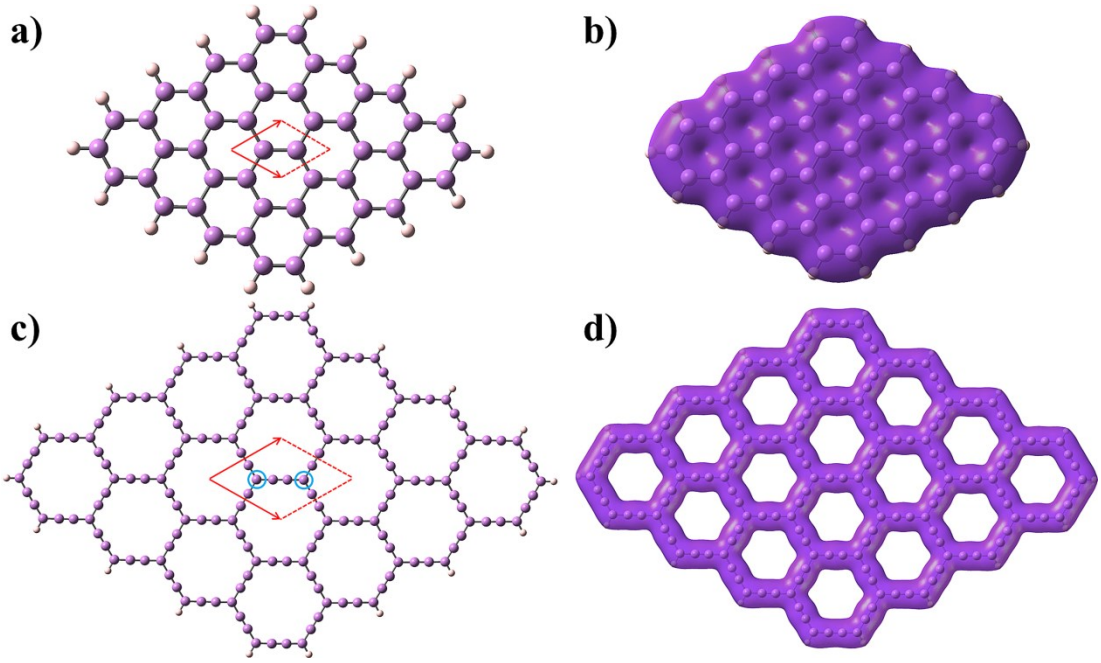


**Figure S2** Crystal structures of a) graphene and c) αGy (L-1Gy). The marginal threefold carbon atoms are saturated by hydrogen atoms and their primitive cells are marked by a red box. Localized orbital locator (LOL) maps for b) graphene and d) αGy (L-1Gy) with isovalue of 0.05.

**4. Molecular AdNDP orbitals for the optimized benzene ($C_6H_6$)**

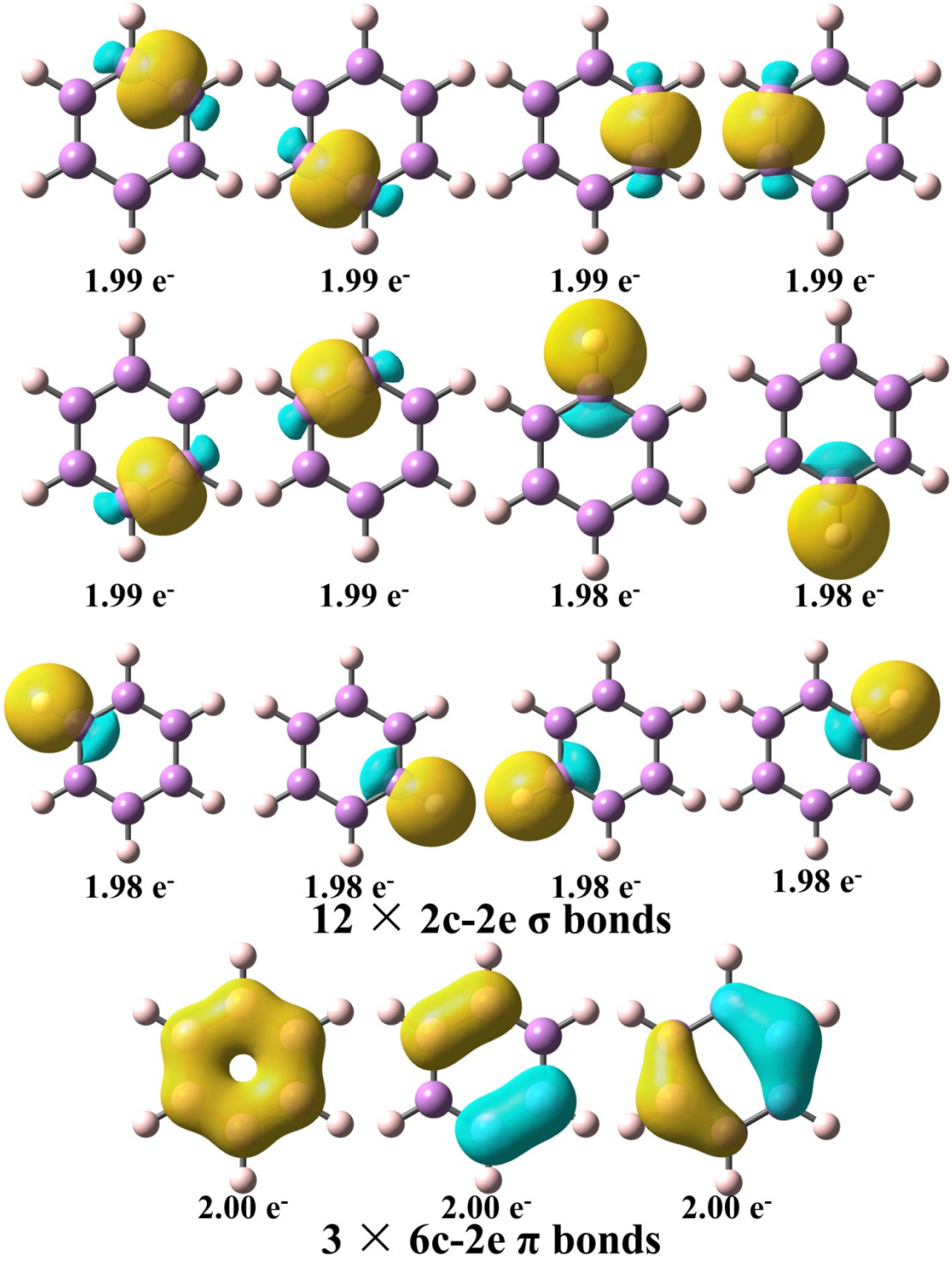


**Figure S3** Molecular orbitals for the optimized benzene ($C_6H_6$) based on the AdNDP method.

## 5. Molecular AdNDP orbitals for the optimized $C_{18}H_6$

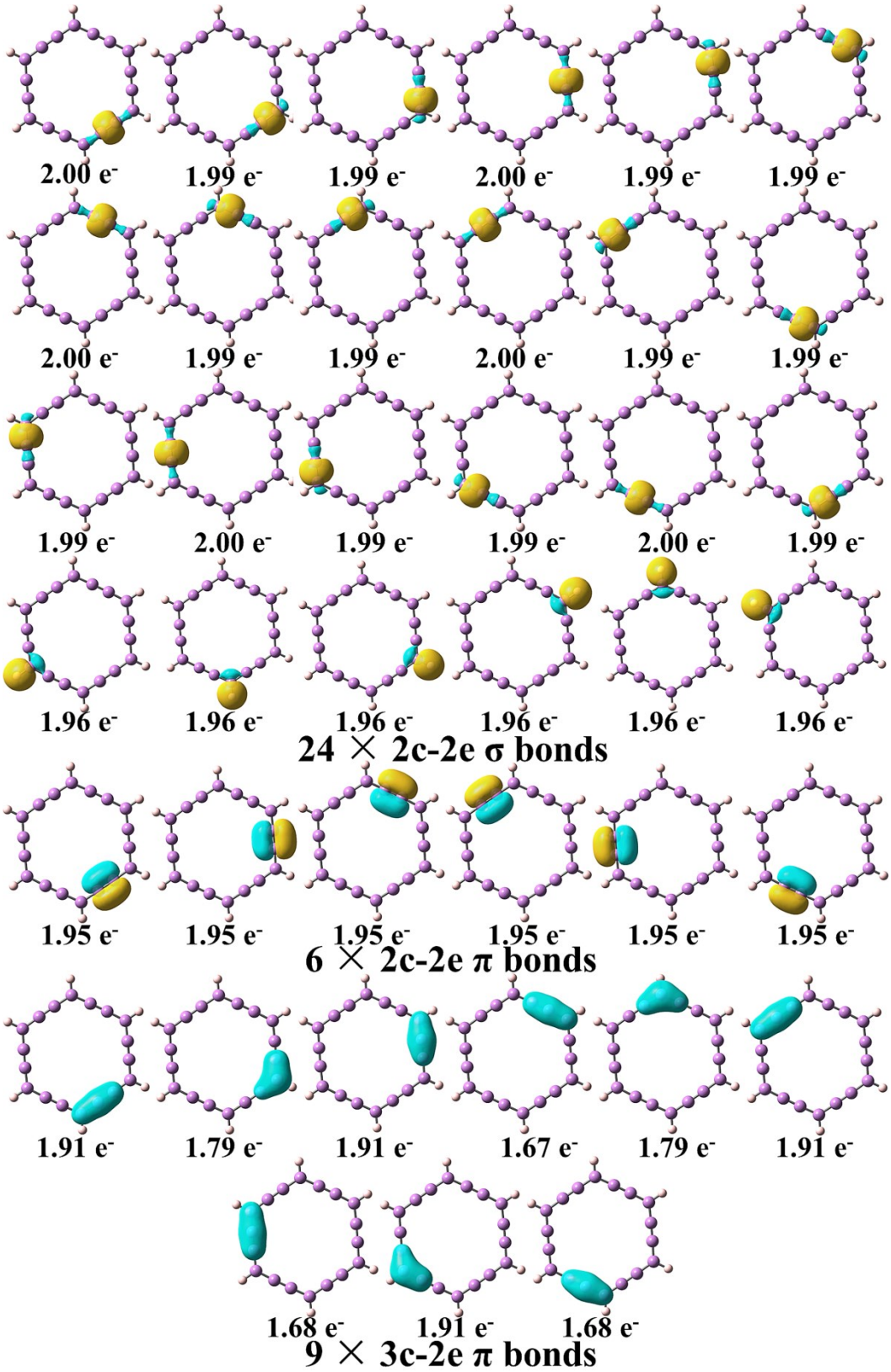


**Figure S4** Molecular orbitals for the optimized $C_{18}H_6$ based on the AdNDP method.

## 6. Partial Molecular AdNDP orbitals for the optimized $C_{30}H_6$

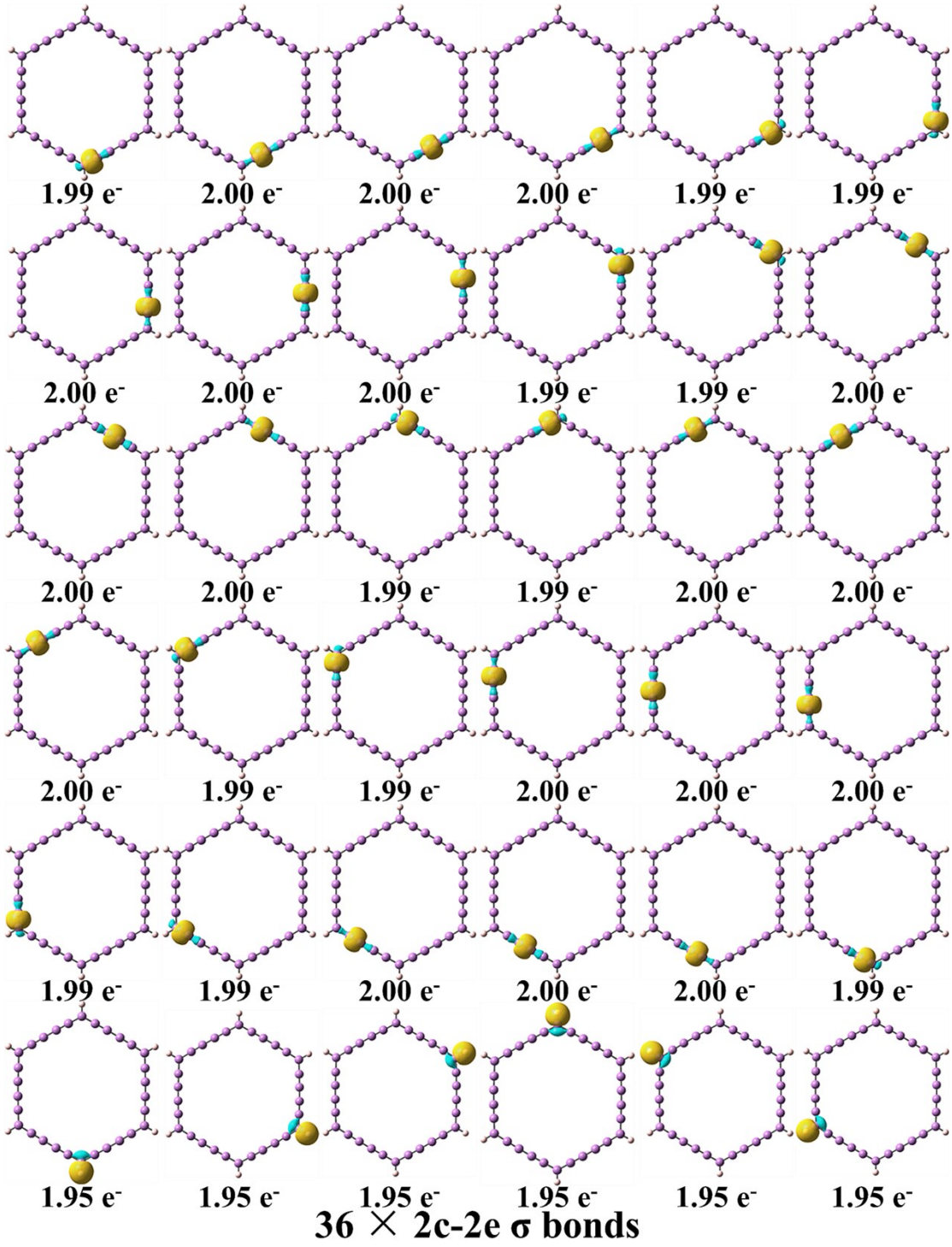


**Figure S5** Molecular orbitals of 2c-2e σ bonds for the optimized $C_{30}H_6$ based on the AdNDP method.

## 7. Band structure of L-2Gy based on the HSE06

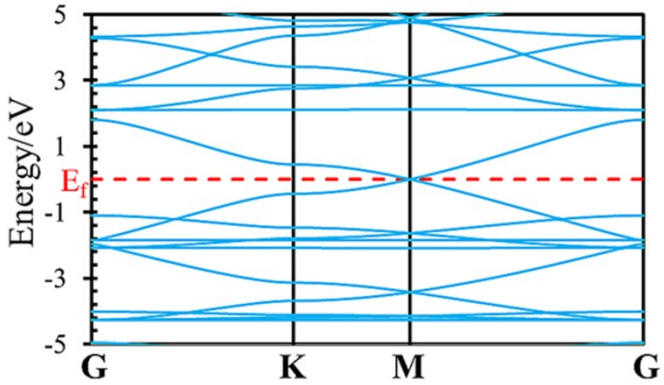


**Figure S6** Band structure of L-2Gy based on the HSE06 level.

## 8. Stiffness tensor matrixes for graphene and αGy (L-1Gy)

Table S2 Stiffness tensor $C_{ij}$ in GPa matrixes for graphene and αGy (L-1Gy).

| **Graphene** | | | | | | |
|---|---|---|---|---|---|---|
| | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ |
| $C_1$ | 145.979 | 27.143 | 1.287 | 0.000 | 0.000 | 0.000 |
| $C_2$ | 27.143 | 145.979 | 1.287 | 0.000 | 0.000 | 0.000 |
| $C_3$ | 1.287 | 1.287 | 4.467 | 0.000 | 0.000 | 0.000 |
| $C_4$ | 0.000 | 0.000 | 0.000 | 59.418 | 0.000 | 0.000 |
| $C_5$ | 0.000 | 0.000 | 0.000 | 0.000 | 1.327 | 0.000 |
| $C_6$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 1.327 |
| **αGy** | | | | | | |
| | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ |
| $C_1$ | 40.194 | 34.574 | 0.685 | 0.000 | 0.000 | 0.000 |
| $C_2$ | 34.574 | 40.194 | 0.685 | 0.000 | 0.000 | 0.000 |
| $C_3$ | 0.685 | 0.685 | 2.380 | 0.000 | 0.000 | 0.000 |
| $C_4$ | 0.000 | 0.000 | 0.000 | 2.810 | 0.000 | 0.000 |
| $C_5$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.754 | 0.000 |
| $C_6$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.754 |

## 9. Possible absorbed configurations of H atom on L-2Gy

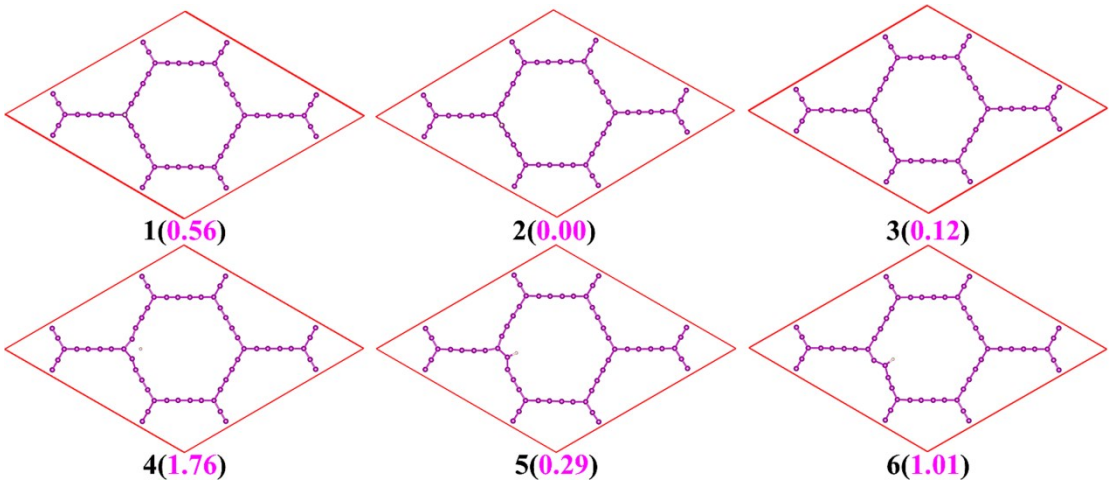


**Figure S7** Possible absorbed configurations of H atom on L-2Gy including their relative energies marked in pink shown in brackets. H atoms are on the top of corresponding carbon atoms for configurations in **1**, **2**, and **3**. The configurations of **4**, **5**, and **6** are that H atoms in the plane of L-2Gy.

## 10 Calculational Details

The hydrogen evolution reaction (HER) performance is evaluated with the free energy of absorbed hydrogen atom under equilibrium conditions, which is defined as[1-4]

$$\Delta G_H = E_{ads} + \Delta ZPE - T\Delta S$$

where $E_{ads}$ is the adsorption energy of the hydrogen atom, ΔZPE is the change of zero-point energy of absorbed H and that of free $H_2$(g), $T\Delta S$ is the difference of entropy of absorbed H and that of $H_2$(g). We employ the ZPE and TS of free $H_2$ gas molecule from previous work, while for the adsorbed H, the free energy corrections were calculated using the corresponding formula including ZPE and S obtained from T. Vegge's work using vibrational frequency based on the harmonic approximation. The $E_{ads}$, ΔZPE, and TΔS are calculated with the following equations[5]

$$E_{ads} = E_{*H} - E_S - 1/2E_{H_2}$$

$$\Delta ZPE = ZPE_{*H} - 1/2ZPE_{H_2}$$

$$T\Delta S = TS_{vi-*H} - 1/2TS_{H_2}$$

where $E_{*H}$ and $E_S$ represent the total energy of L-2Gy with and without adsorbed H, respectively, and $E_{H_2}$ is the energy of the hydrogen molecule in the gas phase. $ZPE_{*H}$ and $ZPE_{H_2}$ are on behalf of the zero-point energy of absorbed H and that of free $H_2$(g), respectively. $TS_{vi-*H}$ is the vibrational entropy of absorbed H while $TS_{H_2}$ is the entropy of $H_2$(g) of 0.41 eV. The previous report shows that the vibrational entropy in the absorbed state is small meaning that the entropy of adsorption of $1/2H_2$ is $\Delta S_H \cong -1/2S_{H_2}$.[6] Thus, the TΔS here is calculated to be -0.205 eV.

**11 Fractional coordinates for 14 and 20 independent carbon atoms for optimized primitive cell of L-2Gy and L-3Gy, respectively.**

| L-2Gy | | |
|---|---|---|
| 0.6666666666666643 | 0.3333333333333357 | 0.5000000000000000 |
| 0.3333333333333357 | 0.6666666666666643 | 0.5000000000000000 |
| 0.5961842373225368 | 0.4038157626774633 | 0.5000000000000000 |
| 0.4038157626774633 | 0.5961842373225368 | 0.5000000000000000 |
| 0.5961842373225368 | 0.1923684746450664 | 0.5000000000000000 |
| 0.4038157626774633 | 0.8076315253549337 | 0.5000000000000000 |
| 0.8076315253549337 | 0.4038157626774633 | 0.5000000000000000 |
| 0.1923684746450664 | 0.5961842373225368 | 0.5000000000000000 |
| 0.5336413338968912 | 0.4663586661031087 | 0.5000000000000000 |
| 0.4663586661031087 | 0.5336413338968912 | 0.5000000000000000 |
| 0.5336413338968912 | 0.0672826677937754 | 0.5000000000000000 |
| 0.4663586661031087 | 0.9327173322062244 | 0.5000000000000000 |
| 0.9327173322062244 | 0.4663586661031087 | 0.5000000000000000 |
| 0.0672826677937754 | 0.5336413338968912 | 0.5000000000000000 |
| L-3Gy | | |
| 0.6666667000000004 | 0.3333333380000028 | 0.5000000000000000 |
| 0.3333333030000034 | 0.6666666050000032 | 0.5000000000000000 |
| 0.6159786295070929 | 0.3840212944929078 | 0.5000000000000000 |
| 0.3840213474929087 | 0.6159787205070898 | 0.5000000000000000 |
| 0.6159786905070944 | 0.2319573190141839 | 0.5000000000000000 |
| 0.3840212984929082 | 0.7680426599858180 | 0.5000000000000000 |
| 0.7680426829858163 | 0.3840213294929072 | 0.5000000000000000 |
| 0.2319573380141819 | 0.6159786495070946 | 0.5000000000000000 |
| 0.4773309774685701 | 0.5226689635314288 | 0.5000000000000000 |
| 0.5226690125314292 | 0.4773310154685661 | 0.5000000000000000 |
| 0.4773310154685661 | 0.9546620319371358 | 0.5000000000000000 |
| 0.5226689895314309 | 0.0453379790628617 | 0.5000000000000000 |
| 0.0453379550628668 | 0.5226689635314288 | 0.5000000000000000 |
| 0.9546620339371360 | 0.4773310154685661 | 0.5000000000000000 |
| 0.5708670658543540 | 0.4291329401456463 | 0.5000000000000000 |
| 0.4291329061456436 | 0.5708670038543561 | 0.5000000000000000 |
| 0.5708669838543544 | 0.1417341537087101 | 0.5000000000000000 |
| 0.4291329351456495 | 0.8582658082912938 | 0.5000000000000000 |

| |
|---|
| 0.8582657942912928 0.4291329041456434 0.5000000000000000<br>0.1417341647087075 0.5708670748543513 0.5000000000000000 |

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