

# Supplementary Information to: TAO-DFT Study on the Electronic Properties of Diamond-Shaped Graphene Nanoflakes

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TABLE S1. Singlet-triplet energy gap  $E_{\text{ST}}$  (in kcal/mol) of  $n$ -pyrene, calculated by spin-unrestricted TAO-LDA.

| $n$ | $E_{\text{ST}}$ |
|-----|-----------------|
| 2   | 50.07           |
| 3   | 23.50           |
| 4   | 10.15           |
| 5   | 4.71            |
| 6   | 2.67            |
| 7   | 1.80            |
| 8   | 1.36            |
| 9   | 1.09            |
| 10  | 0.91            |
| 11  | 0.78            |
| 12  | 0.69            |
| 13  | 0.62            |
| 14  | 0.55            |
| 15  | 0.51            |

TABLE S2. Vertical ionization potential  $\text{IP}_v$  (in eV), vertical electron affinity  $\text{EA}_v$  (in eV), fundamental gap  $E_g$  (in eV), and symmetrized von Neumann entropy  $S_{\text{vN}}$  of ground-state  $n$ -pyrene, calculated by spin-unrestricted TAO-LDA.

| $n$ | $\text{IP}_v$ | $\text{EA}_v$ | $E_g$ | $S_{\text{vN}}$ |
|-----|---------------|---------------|-------|-----------------|
| 2   | 7.01          | 0.25          | 6.76  | 0.02            |
| 3   | 5.99          | 1.43          | 4.55  | 0.28            |
| 4   | 5.43          | 2.11          | 3.32  | 1.03            |
| 5   | 5.14          | 2.49          | 2.65  | 1.92            |
| 6   | 4.97          | 2.73          | 2.24  | 2.86            |

|    |      |      |      |       |
|----|------|------|------|-------|
| 7  | 4.86 | 2.90 | 1.96 | 3.81  |
| 8  | 4.77 | 3.03 | 1.74 | 4.78  |
| 9  | 4.70 | 3.13 | 1.57 | 5.77  |
| 10 | 4.65 | 3.21 | 1.43 | 6.77  |
| 11 | 4.61 | 3.29 | 1.32 | 7.79  |
| 12 | 4.57 | 3.35 | 1.22 | 8.83  |
| 13 | 4.54 | 3.40 | 1.14 | 9.88  |
| 14 | 4.51 | 3.45 | 1.06 | 10.96 |
| 15 | 4.49 | 3.49 | 1.00 | 12.06 |

TABLE S3. Active orbital occupation numbers (HOMO−9, HOMO−8, ..., HOMO, LUMO, ..., LUMO+8, and LUMO+9) of ground-state *n*-pyrene, calculated by spin-restricted TAO-LDA. For brevity, HOMO/LUMO is denoted as H/L.

| <i>n</i> | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9     | 10    | 11    | 12    | 13    | 14    | 15    |
|----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| H−9      | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 1.999 | 1.995 | 1.987 | 1.982 | 1.977 | 1.951 |
| H−8      | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 1.999 | 1.994 | 1.991 | 1.987 | 1.981 | 1.927 | 1.805 |
| H−7      | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 1.998 | 1.997 | 1.994 | 1.991 | 1.970 | 1.891 | 1.731 | 1.521 |
| H−6      | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 1.999 | 1.998 | 1.997 | 1.991 | 1.952 | 1.837 | 1.638 | 1.420 | 1.252 |
| H−5      | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 1.999 | 1.998 | 1.985 | 1.921 | 1.760 | 1.530 | 1.324 | 1.189 | 1.123 |
| H−4      | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 1.997 | 1.973 | 1.870 | 1.657 | 1.417 | 1.241 | 1.145 | 1.108 | 1.096 |
| H−3      | 2.000 | 2.000 | 2.000 | 2.000 | 1.995 | 1.950 | 1.789 | 1.533 | 1.310 | 1.176 | 1.112 | 1.086 | 1.086 | 1.091 |
| H−2      | 2.000 | 2.000 | 2.000 | 1.990 | 1.905 | 1.673 | 1.404 | 1.223 | 1.133 | 1.095 | 1.077 | 1.080 | 1.075 | 1.083 |
| H−1      | 2.000 | 1.999 | 1.976 | 1.821 | 1.524 | 1.280 | 1.141 | 1.073 | 1.040 | 1.058 | 1.071 | 1.066 | 1.072 | 1.055 |
| H        | 1.998 | 1.938 | 1.669 | 1.351 | 1.161 | 1.071 | 1.028 | 1.019 | 1.038 | 1.035 | 1.052 | 1.061 | 1.040 | 1.022 |
| L        | 0.002 | 0.062 | 0.334 | 0.660 | 0.852 | 0.946 | 0.992 | 1.002 | 1.011 | 1.016 | 0.995 | 0.977 | 0.982 | 1.001 |
| L+1      | 0.000 | 0.001 | 0.021 | 0.170 | 0.478 | 0.744 | 0.895 | 0.971 | 0.981 | 0.963 | 0.949 | 0.961 | 0.964 | 0.980 |
| L+2      | 0.000 | 0.000 | 0.000 | 0.008 | 0.080 | 0.299 | 0.576 | 0.771 | 0.872 | 0.918 | 0.942 | 0.940 | 0.961 | 0.955 |
| L+3      | 0.000 | 0.000 | 0.000 | 0.000 | 0.004 | 0.040 | 0.181 | 0.434 | 0.670 | 0.820 | 0.899 | 0.938 | 0.932 | 0.925 |
| L+4      | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.002 | 0.021 | 0.107 | 0.306 | 0.550 | 0.738 | 0.845 | 0.892 | 0.912 |
| L+5      | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.001 | 0.012 | 0.064 | 0.207 | 0.431 | 0.645 | 0.792 | 0.872 |

|     |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|-----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| L+6 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.001 | 0.003 | 0.007 | 0.038 | 0.137 | 0.323 | 0.542 | 0.719 |
| L+7 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.003 | 0.005 | 0.007 | 0.024 | 0.090 | 0.234 | 0.438 |
| L+8 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.005 | 0.007 | 0.011 | 0.015 | 0.059 | 0.166 |
| L+9 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.004 | 0.011 | 0.015 | 0.020 | 0.040 |

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