Supplemental material of

A thorough theoretical exploration of the intriguing characteristics of cyclo[18]carbon: Geometry, bonding nature, aromaticity, weak interaction, reactivity, excited states, vibrations, molecular dynamics and various molecular properties

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1. Reproduction of experimental AFM observation

Based on the ωB97XD/def2-TZVP geometry and wavefunction, we plotted electron density map above 1 Å of the cyclo[18]carbon plane, see Fig. S1. It can be seen that the electron density above the two kinds of C-C bonds in this system is detectably different, the short C-C bonds correspond to brighter white due to higher electron density over the bonding regions, while the long C-C bonds look relatively darker. The basic feature of this map is fully in line with the atomic force microscopy (AFM) image presented in Fig. 3(s) of Ref. [1].

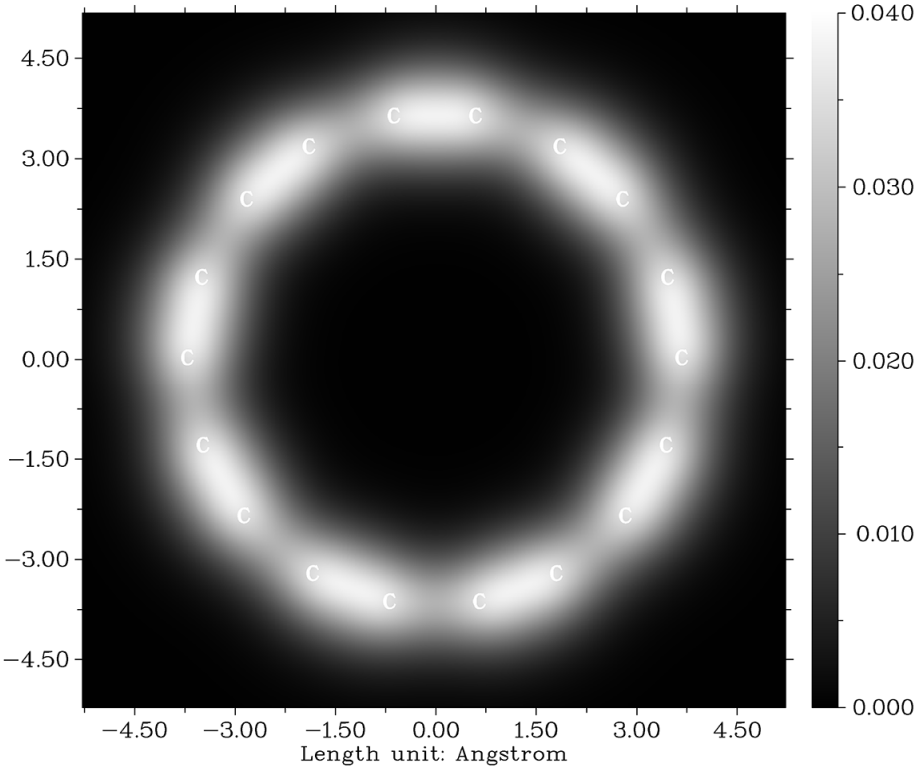

Fig. S1 Electron density map above 1 Å of the cyclo[18]carbon plane.

2. Isosurface map of molecular orbitals of cyclo[18]carbon

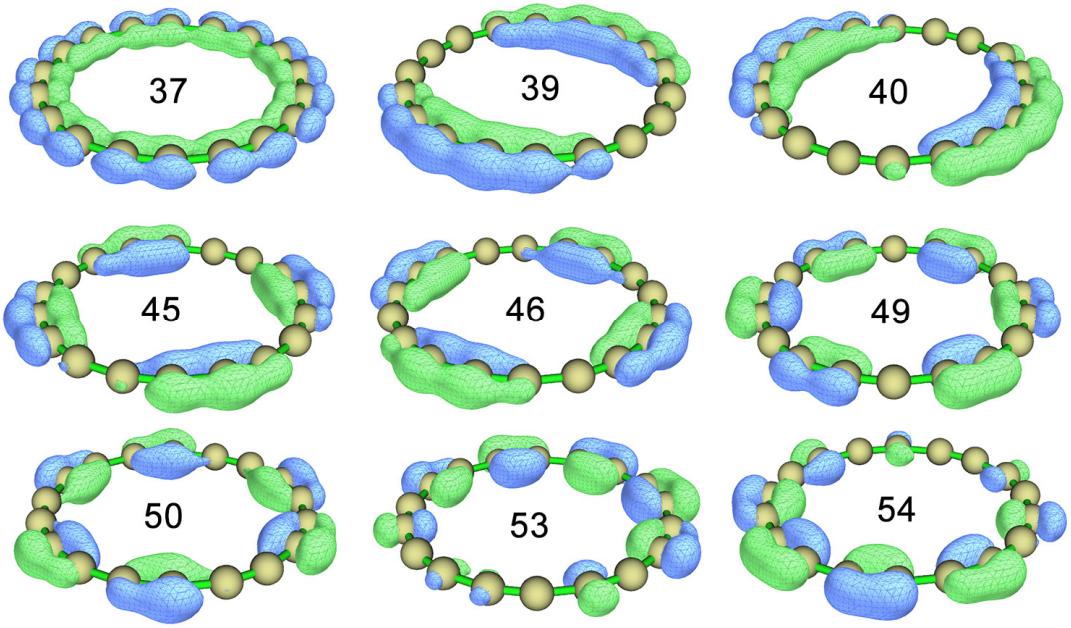

Fig. S2 Isosurface map of in-plane π type of occupied MOs with isovalue of 0.05. The numbers indicate indices of the orbitals.

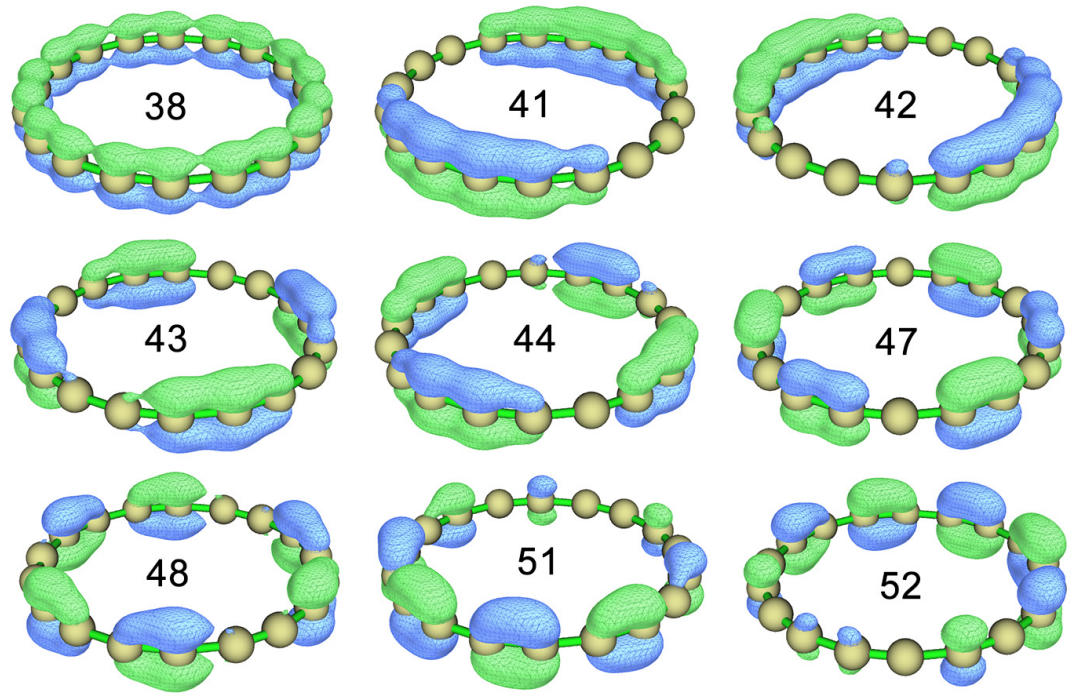

Fig. S3 Isosurface map of out-plane π type of occupied MOs with isovalue of 0.05. The numbers indicate indices of the orbitals.

3. Character of electron localization function of different kinds of bonds

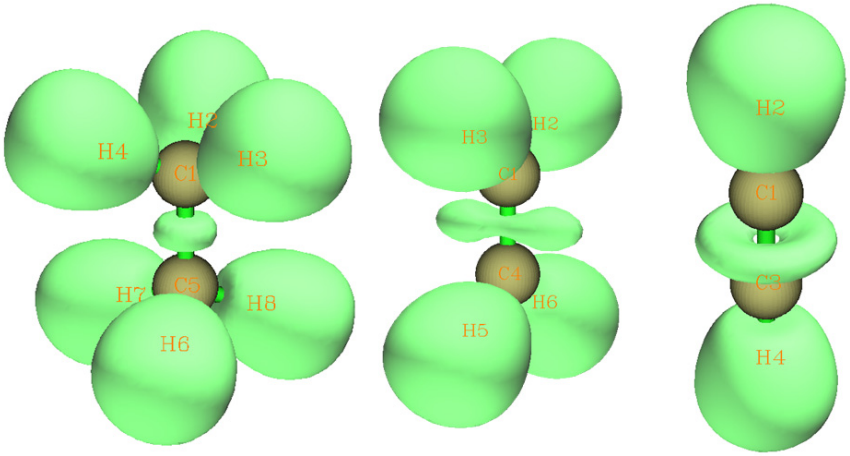

Fig. S4 Electron localization function (isovalue=0.85) of ethane, ethene and acetylene, which contains prototype single, double and triple C-C bonds, respectively.

4. Temperature control of molecular dynamics simulation

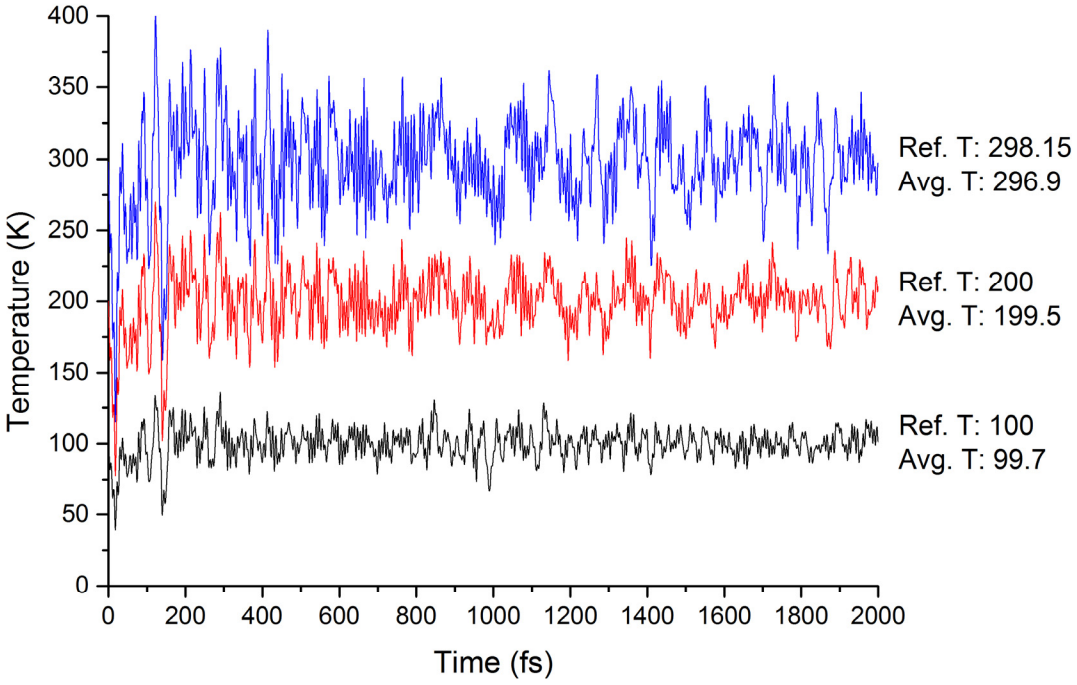

Fig. S5 Temperature fluctuation of three *ab-initio* molecular dynamics trajectories of cyclo[18]carbon simulated at different temperatures. Ref. T and Avg. T denote reference temperature of thermostat and actual average temperature, respectively.

5. Geometry of cationic and anionic states of cyclo[18]carbon

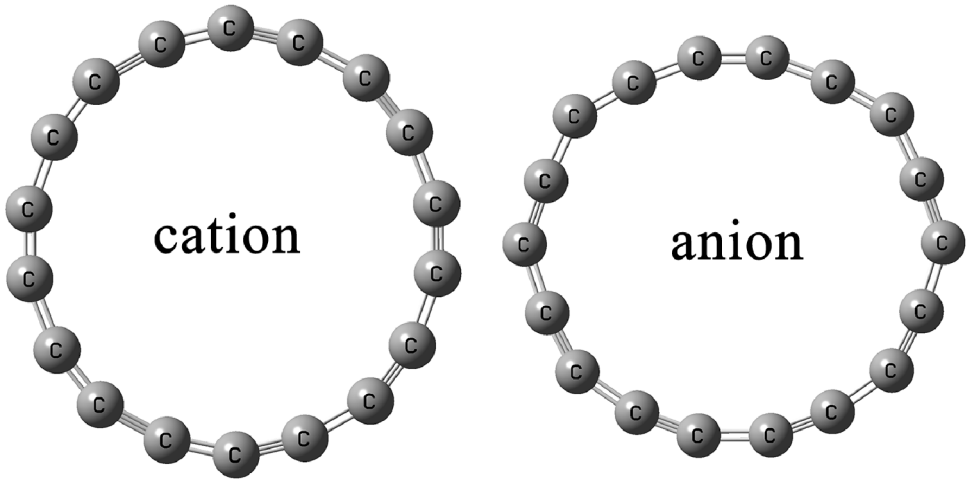

Fig. S6 Geometry of cationic and anionic states of cyclo[18]carbon

6. HOMO and LUMO maps

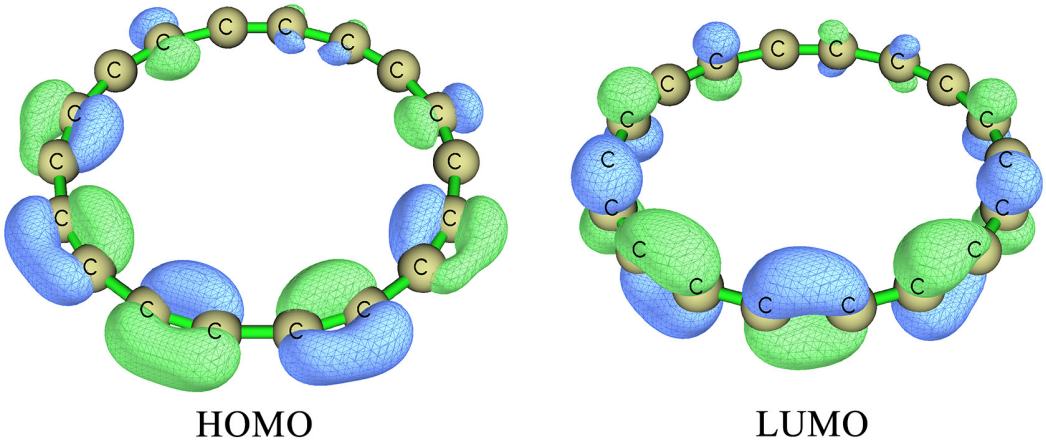

Fig. S7 Isosurface map of the HOMO and LUMO of cyclo[18]carbon calculated at ωB97XD/aug-cc-pVTZ level based on the geometry of neutral state optimized at ωB97XD/def2-TZVP level. Isovalue is set to 0.05.

7. Relationship between Laplacian bond order and bond dissociation energy

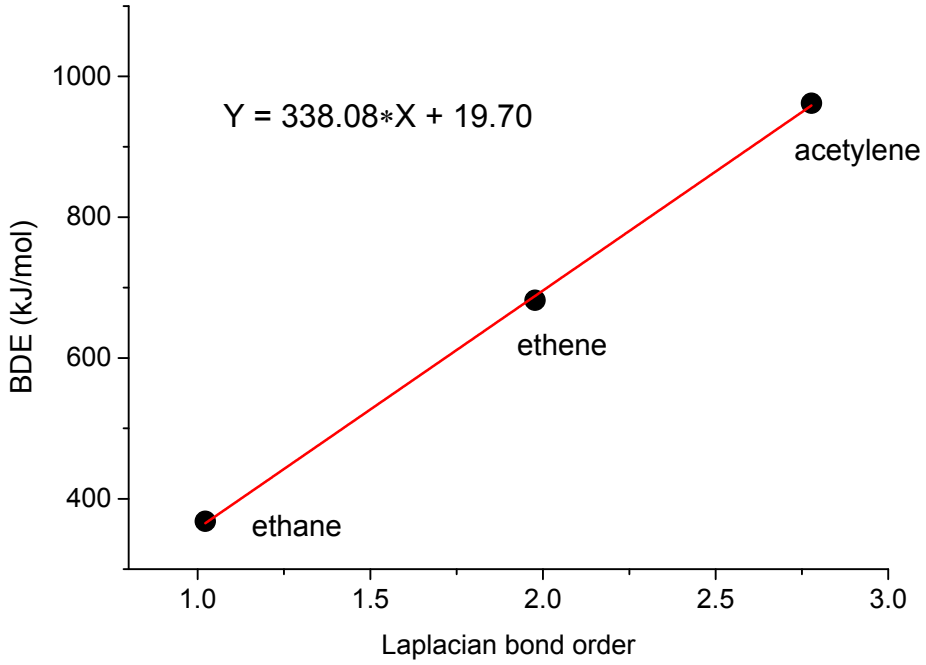

Fig S8 Relationship between the Laplacian bond order computed at ωB97XD/def2-TZVP level and experimental bond dissociation energy[2] of C-C bond in ethane, ethene and acetylene.

8. Optimized geometries

All geometries given below were optimized under ωB97XD/def2-TZVP level, no imaginary frequency can be found.

Cartesian coordinate of neutral state (in Å)

C	0.61036100	3.64174800	0.00000000
C	-0.61036100	3.64174800	0.00000000
C	-1.87330600	3.18207300	0.00000000
C	-2.80843400	2.39740800	0.00000000
C	-3.48043300	1.23347100	0.00000000
C	-3.69240900	0.03129400	0.00000000
C	-3.45902700	-1.29228500	0.00000000
C	-2.84866500	-2.34946200	0.00000000
C	-1.81910300	-3.21336800	0.00000000
C	-0.67199900	-3.63087900	0.00000000
C	0.67199900	-3.63087900	0.00000000
C	1.81910300	-3.21336800	0.00000000
C	2.84866500	-2.34946200	0.00000000
C	3.45902700	-1.29228500	0.00000000
C	3.69240900	0.03129400	0.00000000
C	3.48043300	1.23347100	0.00000000
C	2.80843400	2.39740800	0.00000000
C	1.87330600	3.18207300	0.00000000

Cartesian coordinate of cationic state (in Å)

C	0.00000000	0.61053600	3.60389400
C	0.00000000	-0.61053600	3.60389400
C	0.00000000	-1.86661100	3.13938400
C	0.00000000	-2.83327900	2.38870600
C	0.00000000	-3.47152500	1.21946300
C	0.00000000	-3.74306100	0.01825400
C	0.00000000	-3.45090400	-1.26893100
C	0.00000000	-2.85940500	-2.35988500
C	0.00000000	-1.82120700	-3.15397400
C	0.00000000	-0.65064200	-3.58691000
C	0.00000000	0.65064200	-3.58691000
C	0.00000000	1.82120700	-3.15397400
C	0.00000000	2.85940500	-2.35988500
C	0.00000000	3.45090400	-1.26893100
C	0.00000000	3.74306100	0.01825400
C	0.00000000	3.47152500	1.21946300
C	0.00000000	2.83327900	2.38870600
C	0.00000000	1.86661100	3.13938400

Cartesian coordinate of anionic state (in Å)

C	-3.29688900	-1.77498000	0.00000000
C	-3.65016800	-0.59623500	0.00000000
C	-3.82773700	0.73109100	0.00000000
C	-3.22448900	1.82071100	0.00000000
C	-2.47186400	2.90681000	0.00000000
C	-1.27811100	3.31582700	0.00000000
C	0.00000000	3.54475600	0.00000000
C	1.24456600	3.32061100	0.00000000
C	2.36128100	2.65778700	0.00000000
C	3.33604600	1.85665400	0.00000000
C	3.65942800	0.57513200	0.00000000
C	3.84019400	-0.65685900	0.00000000
C	3.20895900	-1.83807600	0.00000000
C	2.46353200	-2.81688100	0.00000000
C	1.23841000	-3.37546400	0.00000000
C	0.03413100	-3.59189400	0.00000000
C	-1.29298700	-3.35257000	0.00000000
C	-2.34430300	-2.72642000	0.00000000

Cartesian coordinate of dimer structure (in Å)

C	-0.60999570	3.64233294	1.80590841
C	-1.87396277	3.18228653	1.80590841
C	-2.80853031	2.39809124	1.80590841
C	-3.48107312	1.23321286	1.80590841
C	-3.69292237	0.03175598	1.80590841
C	-3.45935067	-1.29289481	1.80590841
C	-2.84935501	-2.34943824	1.80590841
C	-1.81895959	-3.21404263	1.80590841
C	-0.67254277	-3.63130421	1.80590841
C	0.67254289	-3.63130418	1.80590841
C	1.81895970	-3.21404257	1.80590841
C	2.84935508	-2.34943815	1.80590841
C	3.45935071	-1.29289470	1.80590841
C	3.69292236	0.03175610	1.80590841
C	3.48107308	1.23321298	1.80590841
C	2.80853023	2.39809133	1.80590841
C	1.87396267	3.18228659	1.80590841
C	0.60999559	3.64233296	1.80590841
C	-1.81895970	3.21404257	-1.80590841
C	-2.84935508	2.34943815	-1.80590841
C	-3.45935071	1.29289470	-1.80590841
C	-3.69292236	-0.03175610	-1.80590841

C	-3.48107308	-1.23321298	-1.80590841
C	-2.80853023	-2.39809133	-1.80590841
C	-1.87396267	-3.18228659	-1.80590841
C	-0.60999559	-3.64233296	-1.80590841
C	0.60999570	-3.64233294	-1.80590841
C	1.87396277	-3.18228653	-1.80590841
C	2.80853031	-2.39809124	-1.80590841
C	3.48107312	-1.23321286	-1.80590841
C	3.69292237	-0.03175598	-1.80590841
C	3.45935067	1.29289481	-1.80590841
C	2.84935501	2.34943824	-1.80590841
C	1.81895959	3.21404263	-1.80590841
C	0.67254277	3.63130421	-1.80590841
C	-0.67254289	3.63130418	-1.80590841

References

[1] K. Kaiser, L. M. Scriven, F. Schulz, P. Gawel, L. Gross, H. L. Anderson, An sp-hybridized molecular carbon allotrope, cyclo[18]carbon. *Science* **2019**, *365*, 1299.

[2] J. A. Dean, Lange's Handbook of Chemistry (in Chinese), Science Press: Beijing, 2003.