Electronic Supplementary Information (ESI)

Potential molecular semiconductor devices: cyclo-C_n (n = 10 and 14) with higher stabilities and aromaticities than acknowledged cyclo-C_{18}

Mengyang Li,[a] Zhibin Gao,[b] Yanbo Han,[a] Yaoxiao Zhao,[a] Kun Yuan,[c] Shigeru Nagase,[d] Masahiro Ehara,[e] Xiang Zhao[a*]

[a] *Institute for Chemical Physics & Department of Chemistry, School of Science, State Key Laboratory of Electrical Insulation and Power Equipment & MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, Xi'an Jiaotong University, Xi'an710049, China.*

[b] Department of Physics, National University of Singapore, Singapore 117551, Republic of Singapore.

[c] College of Chemical Engineering and Technology, Tianshui Normal University, Tianshui, 741001, China.

[d] Fukui Institute for Fundamental Chemistry Kyoto University, Kyoto 606-8103, Japan.

[e] Institute for Molecular Science, Okazaki, 444-8585, Japan.

Corresponding author **E-mail: xzhao@mail.xjtu.edu.cn*

Table of Contents

1. **The geometries of cyclo-C_{18} on B3LYP/6-31G(d, p) and M062X/6-311G(d, p) Figure S1**

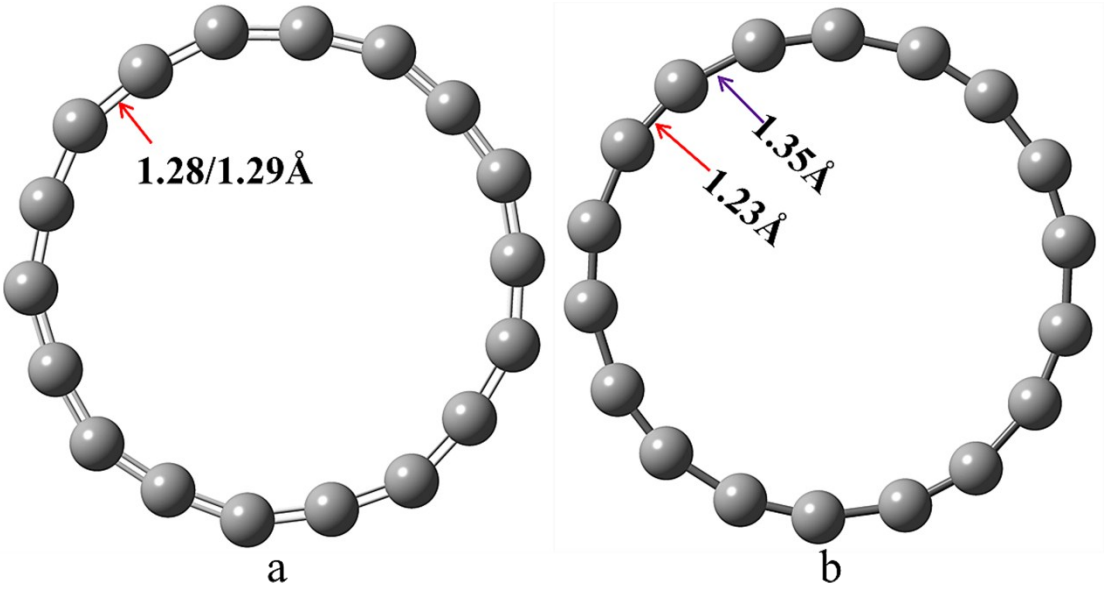

Fig. S1 The geometries of cyclo-C_{18} based on a) the B3LYP/6-31G(d,p) and b) the M062X/6-311G(d,p).

2. **The geometries of cyclo-C_n (n = 10, 14, and 18) on M062X/6-311G(d,p) and ωB97XD/def2-TZVP.**

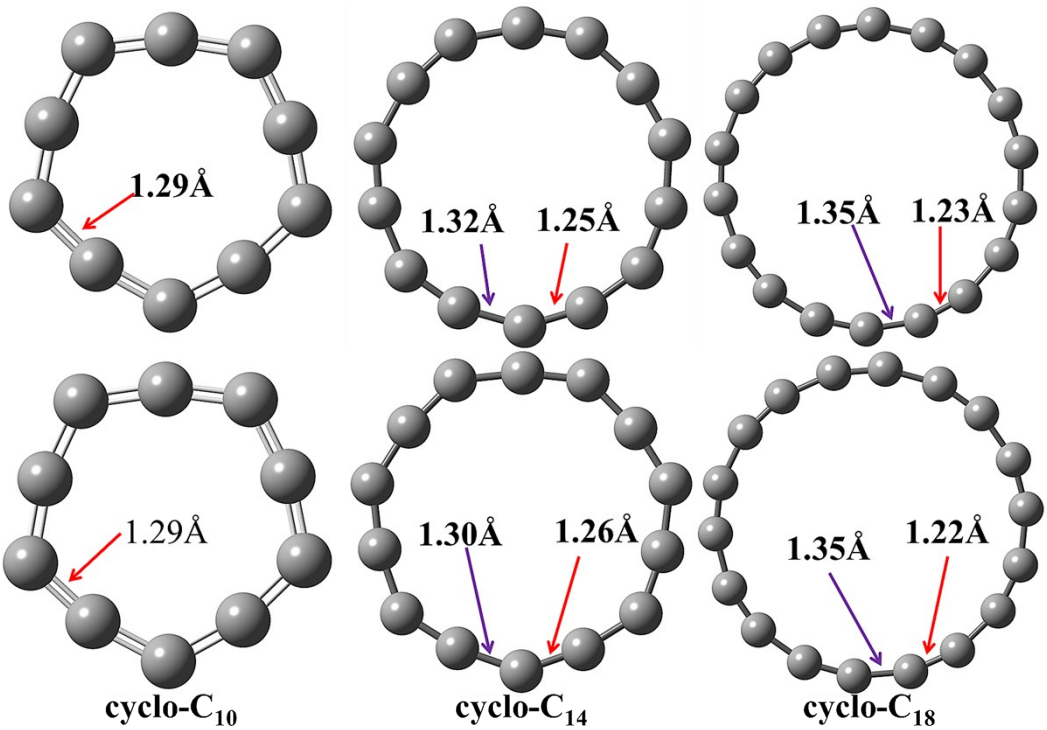

Fig. S2 The geometries of cyclo-C_n (n = 10, 14, and 18) based on M062X/6-311G(d,p) (top row) and ωB97XD/def2-TZVP (second row), respectively.

3. The relative energies of cyclo-C_n ($4 \le n \le 34$) with different spin multiplicity based on the M062X/6-311G(d,p)

Table S1 The relative energies of cyclo-C_n ($4 \le n \le 34$) with different spin multiplicity based on the M062X/6-311G(d,p).

	E[a] /a.u.			$\Delta E_{T\text{-}S}$[b]	$\Delta E_{Q\text{-}T}$[c]
	Singlet	Triplet	Quintet	kcal/mol	kcal/mol
cyclo-C_4	-152.055	-	-	-	-
cyclo-C_5	-190.064	-190.055	-190.008	6.0	29.3
cyclo-C_6	-228.220	-	-	-	-
cyclo-C_7	-266.278	-266.255	-	14.6	-
cyclo-C_8	-304.351	-304.328	-	14.2	-
cyclo-C_9	-342.424	-342.417	-342.362	4.5	34.4
cyclo-C_{10}	-380.593	-	-	-	-
cyclo-C_{11}	-418.619	-418.605	-418.511	8.5	59.3
cyclo-C_{12}	-456.703	-456.673	-	18.9	-
cyclo-C_{13}	-494.765	-494.768	-494.691	-2.1	48.8
cyclo-C_{14}	-532.900	-532.813	-	54.5	-
cyclo-C_{15}	-570.935	-570.936	-570.835	-0.4	63.1
cyclo-C_{16}	-609.037	-608.980	-	35.6	-
cyclo-C_{17}	-647.082	-647.094	-647.008	-7.8	54.1
cyclo-C_{18}	-685.210	-685.134	-	47.7	-
cyclo-C_{19}	-723.241	-723.251	-723.161	-6.1	56.7
cyclo-C_{20}	-761.355	-761.293	-	39.0	-
cyclo-C_{21}	-799.389	-799.406	-799.322	-10.3	52.4
cyclo-C_{22}	-837.515	-837.443	-	45.4	-
cyclo-C_{23}	-875.538	-875.559	-875.473	-12.8	53.9
cyclo-C_{24}	-913.663	-913.597	-	41.1	-
cyclo-C_{25}	-951.691	-951.711	-951.628	-12.4	51.7
cyclo-C_{26}	-989.817	-989.746	-	44.4	-
cyclo-C_{27}	-1027.840	-1027.861	-1027.784	-13.3	48.6
cyclo-C_{28}	-1065.965	-1065.898	-	42.3	-
cyclo-C_{29}	-1103.990	-1104.011	-1103.936	-13.2	47.5
cyclo-C_{30}	-1142.116	-1142.024	-	57.7	-
cyclo-C_{31}	-1180.139	-1180.161	-1180.086	-13.6	46.6
cyclo-C_{32}	-1218.264	-	-	-	-
cyclo-C_{33}	-1256.290	-1256.310	-1256.236	-12.5	45.9
cyclo-C_{34}	-1294.414	-1294.344	-	43.9	-

[a] The total energy of optimal cyclo-C_n ($4 \le n \le 34$) with different spin multiplicity;

[b] $\Delta E_{T\text{-}S}$ = E(triplet) – E(singlet) in kcal/mol;

[c] $\Delta E_{Q\text{-}T}$ = E(quintet) – E(triplet) in kcal/mol.

4. The spin density maps of triplet cyclo-C_n (n = 2m+1, m = 6-16) with isovalue 0.03 based on the M062X/6-311G(d,p)

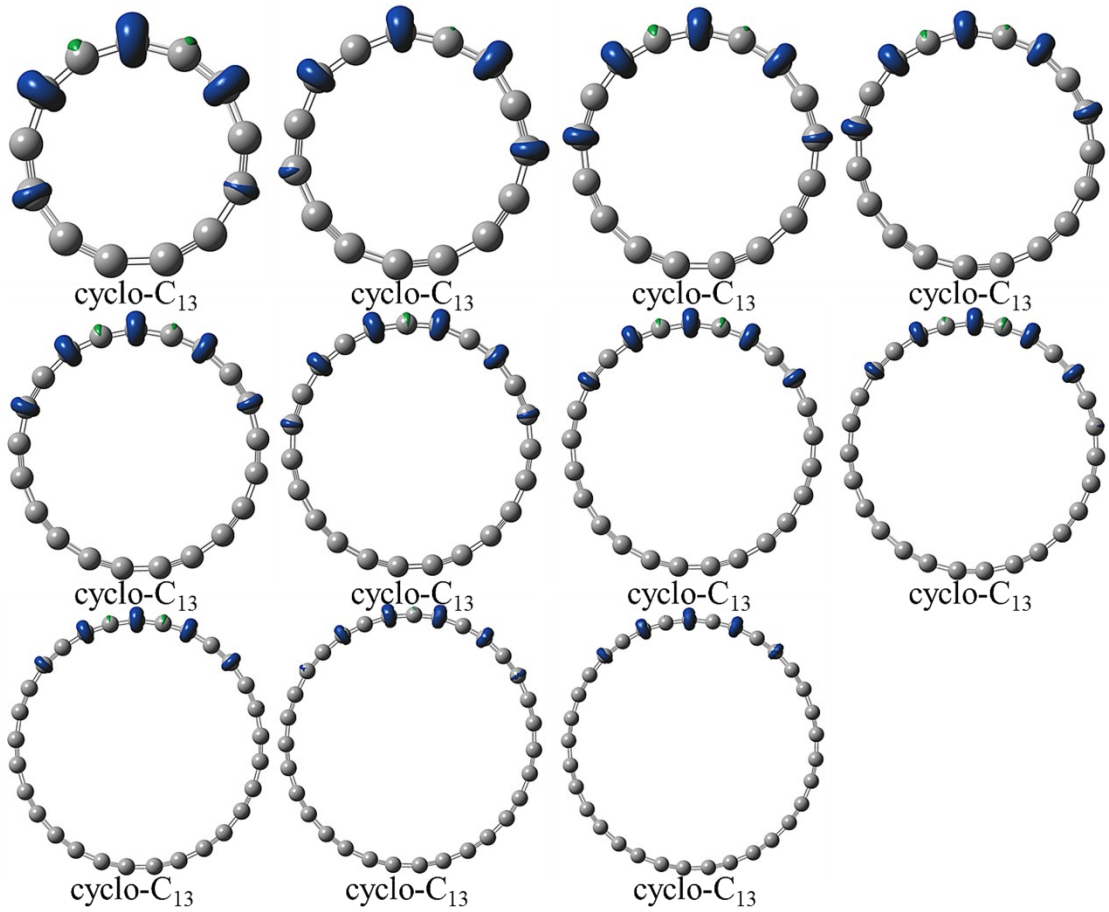

Fig. S3 The spin density maps of triplet cyclo-C_n (n = 2m+1, m = 6-16) with isovalue 0.03 based on the M062X/6-311G(d,p).

5. The energy profile for cyclo-C_n (n = 10, 14, and 18) at different temperatures Fig. S4-S6.

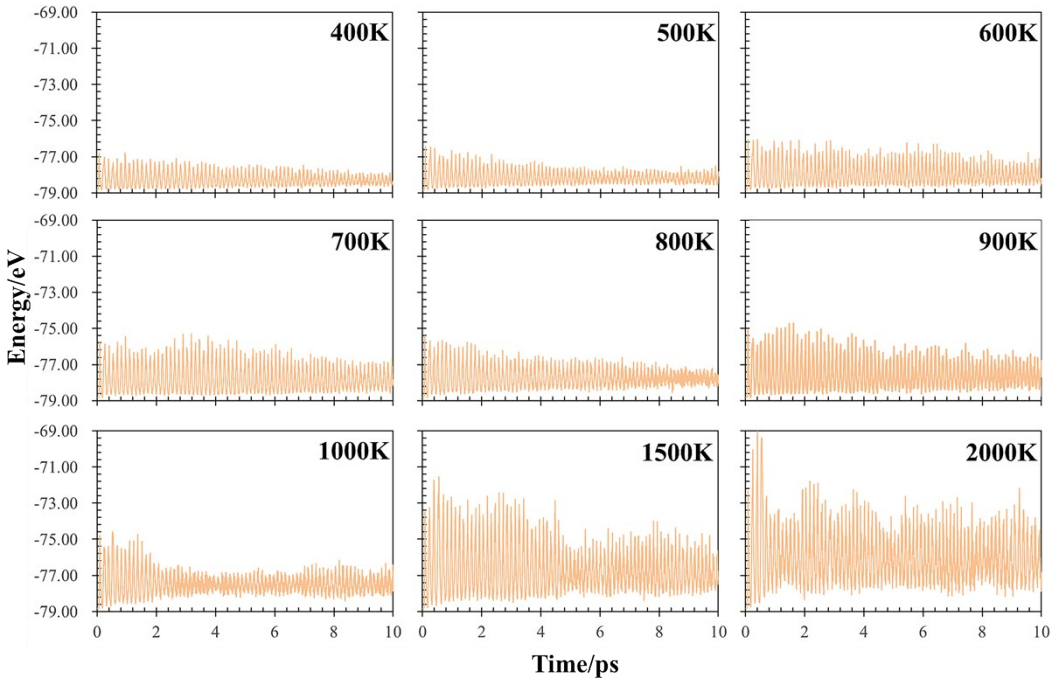

Fig. S4 The energies of cyclo-C_{10} at different time with different temperatures.

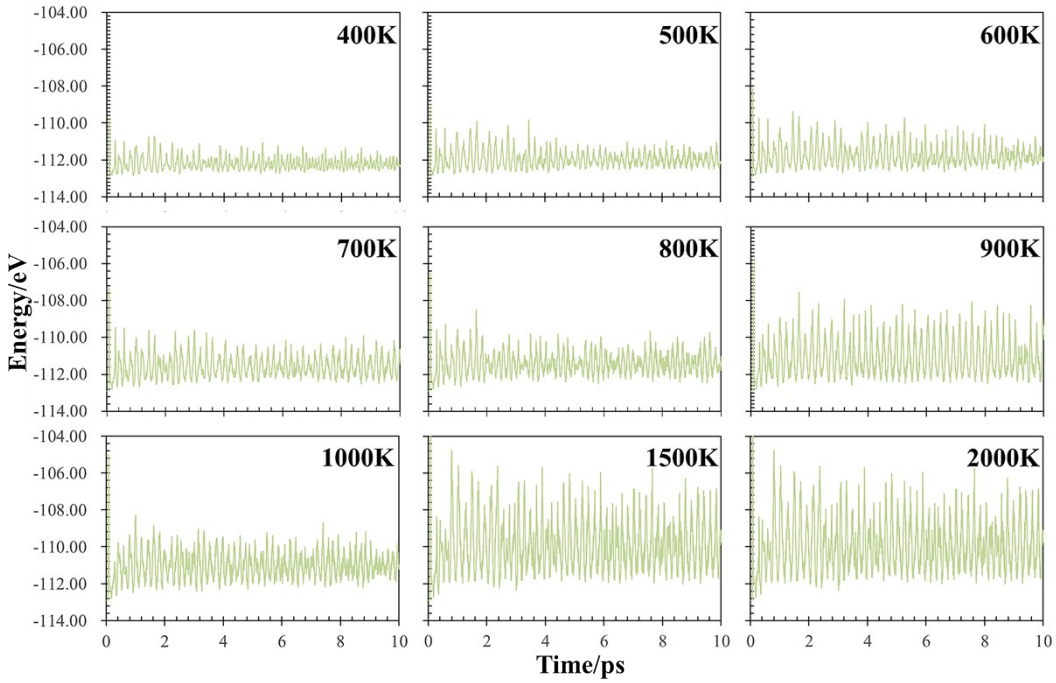

Fig. S5 The energies of cyclo-C_{14} at different time with different temperatures.

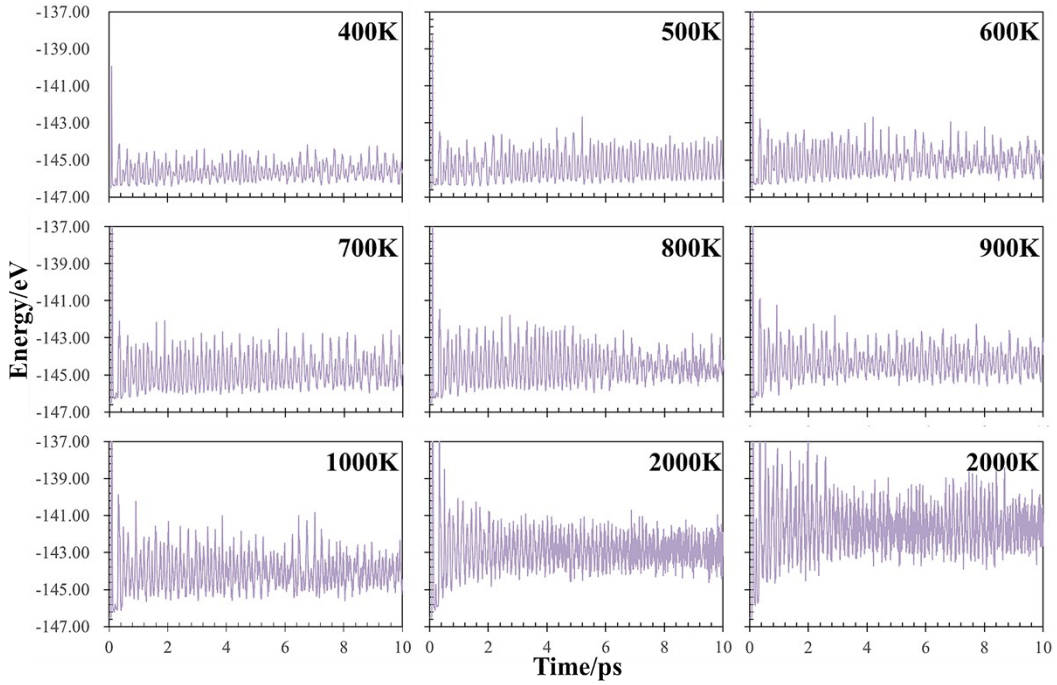

Fig. S6 The energies of cyclo-C_{18} at different time with different temperatures.

6. The geometrical parameters of the optimal cyclo-C_n (n = 10, 14, and 18) on the M062X/6-311G(d,p)

Table S2 The bond lengths and bond angles of the optimal cyclo-C_n (n = 10, 14, and 18) based on the optimization on M062X/6-311G(d,p).

	Bond Length/Å	d_{max}[a]	Length/		Angle/°
cyclo-C_{10}					
C1-C2	1.29	C1-C6	4.14	∠C1-C2-C10	164.60
C2-C10	1.29	C1-C8	4.14	∠C2-C10-C9	123.41
C10-C9	1.29	C2-C6	4.11	∠C10-C9-C8	164.60
C9-C8	1.29	C3-C8	4.11	∠C9-C8-C7	123.41
C8-C7	1.29	C4-C8	4.14	∠C8-C7-C6	164.58
C7-C6	1.29	C4-C10	4.14	∠C7-C6-C5	123.41
C6-C5	1.29	C5-C10	4.11	∠C6-C5-C4	164.60
C5-C4	1.29	C6-C10	4.14	∠C5-C4-C3	123.41
C4-C3	1.29	C7-C1	4.11	∠C4-C3-C1	164.59
C3-C1	1.29	C9-C4	4.11	∠C3-C1-C2	123.39
cyclo-C_{14}					
C1-C2	1.25	C1-C13	5.76	∠C1-C2-C3	161.05
C2-C3	1.32	C2-12	5.76	∠C2-C3-C4	147.51
C3-C4	1.25	C3-C11	5.76	∠C3-C4-C5	161.06
C4-C5	1.32	C4-C10	5.76	∠C4-C5-C6	147.52
C5-C6	1.25	C5-C9	5.76	∠C5-C6-C14	161.06
C6-C14	1.32	C6-C8	5.76	∠C6-C14-C13	147.54
C14-C13	1.25	C7-C14	5.76	∠C14-C13-C12	161.03
C13-C12	1.32	-	-	∠C13-C12-C11	147.55
C12-C11	1.25	-	-	∠C12-C11-C10	161.01
C11-C10	1.32	-	-	∠C11-C10-C9	147.56
C10-C9	1.25	-	-	∠C10-C9-C8	161.01
C9-C8	1.32	-	-	∠C9-C8-C7	147.52
C8-C7	1.25	-	-	∠C8-C7-C1	161.04
C7-C1	1.32	-	-	∠C7-C1-C2	147.52
cyclo-C_{18}					
C1-C2	1.35	C1-C8	7.40	∠C1-C2-C3	160.08
C2-C3	1.23	C2-C16	7.40	∠C2-C3-C4	159.94
C3-C4	1.35	C3-C15	7.40	∠C3-C4-C5	160.06
C4-C5	1.23	C4-C14	7.40	∠C4-C5-C6	159.93
C5-C6	1.35	C5-C13	7.40	∠C5-C6-C17	160.04
C6-C17	1.23	C6-C12	7.40	∠C6-C17-C18	159.97
C17-C18	1.35	C7-C9	7.40	∠C17-C18-C7	160.02
C18-C7	1.23	C10-C18	7.40	∠C18-C7-C8	159.99
C7-C8	1.35	C11-C17	7.40	∠C7-C8-C16	160.04
C8-C16	1.23	-	-	∠C8-C16-C15	159.94
C16-C15	1.35	-	-	∠C16-C15-C14	160.05
C15-C14	1.23	-	-	∠C15-C14-C13	159.95
C14-C13	1.35	-	-	∠C14-C13-C12	160.06
C13-C12	1.23	-	-	∠C13-C12-C11	159.95
C12-C11	1.35	-	-	∠C12-C11-C10	160.03
C11-C10	1.23	-	-	∠C11-C10-C9	159.96
C10-C9	1.35	-	-	∠C10-C9-C1	160.05
C9-C1	1.23	-	-	∠C9-C1-C2	159.94

[a] The maximum distances betwwen each atom and the others.

7. The molecular π orbitals of cyclo-C_n (n = 10, 14, and 18) Figure S3-S5

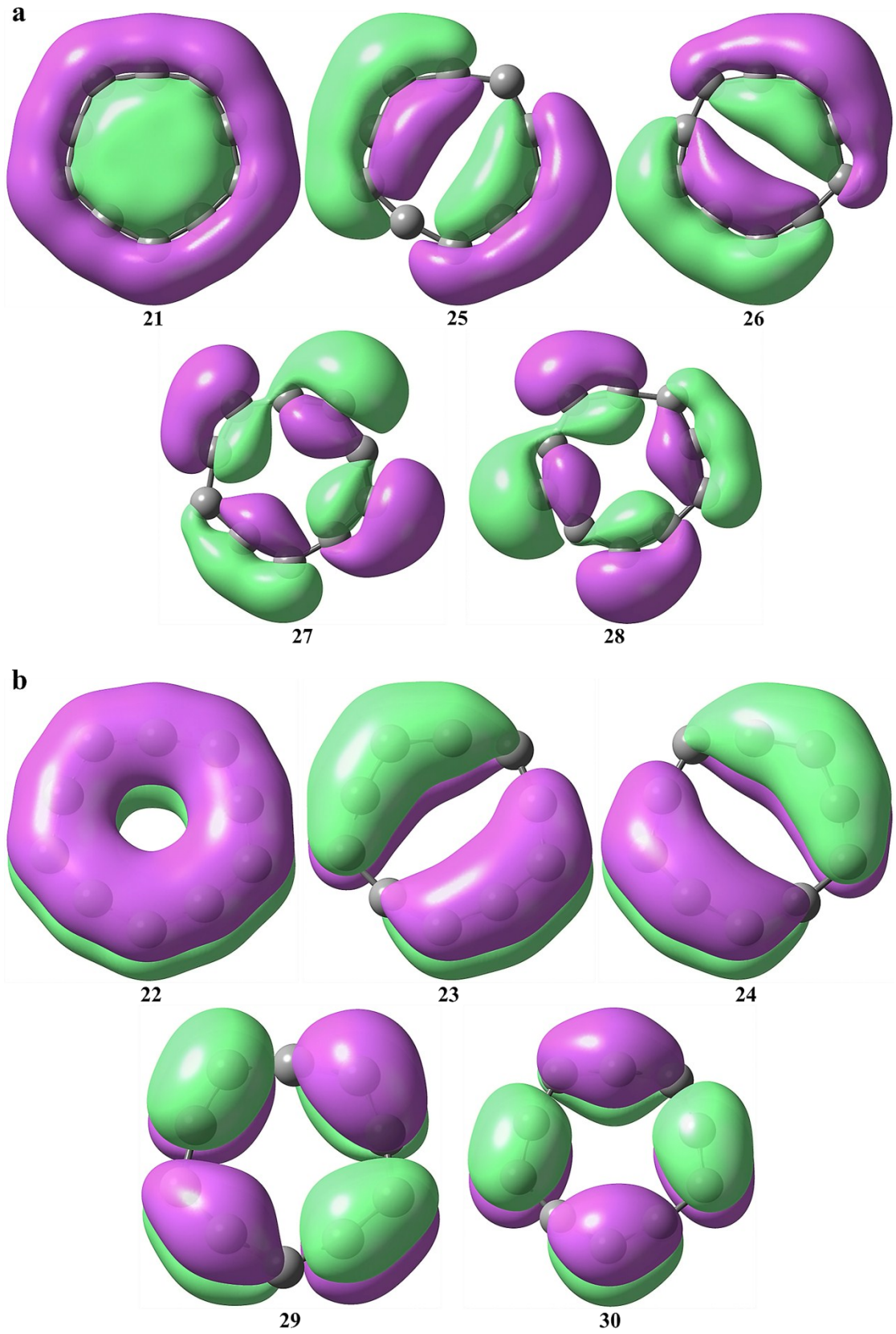

Fig. S7 The a) in-plainπ orbitals and b) out –plain π orbitals for cyclo-C_{10}. The numbers below the orbitals are the labels of corresponding π orbitals.

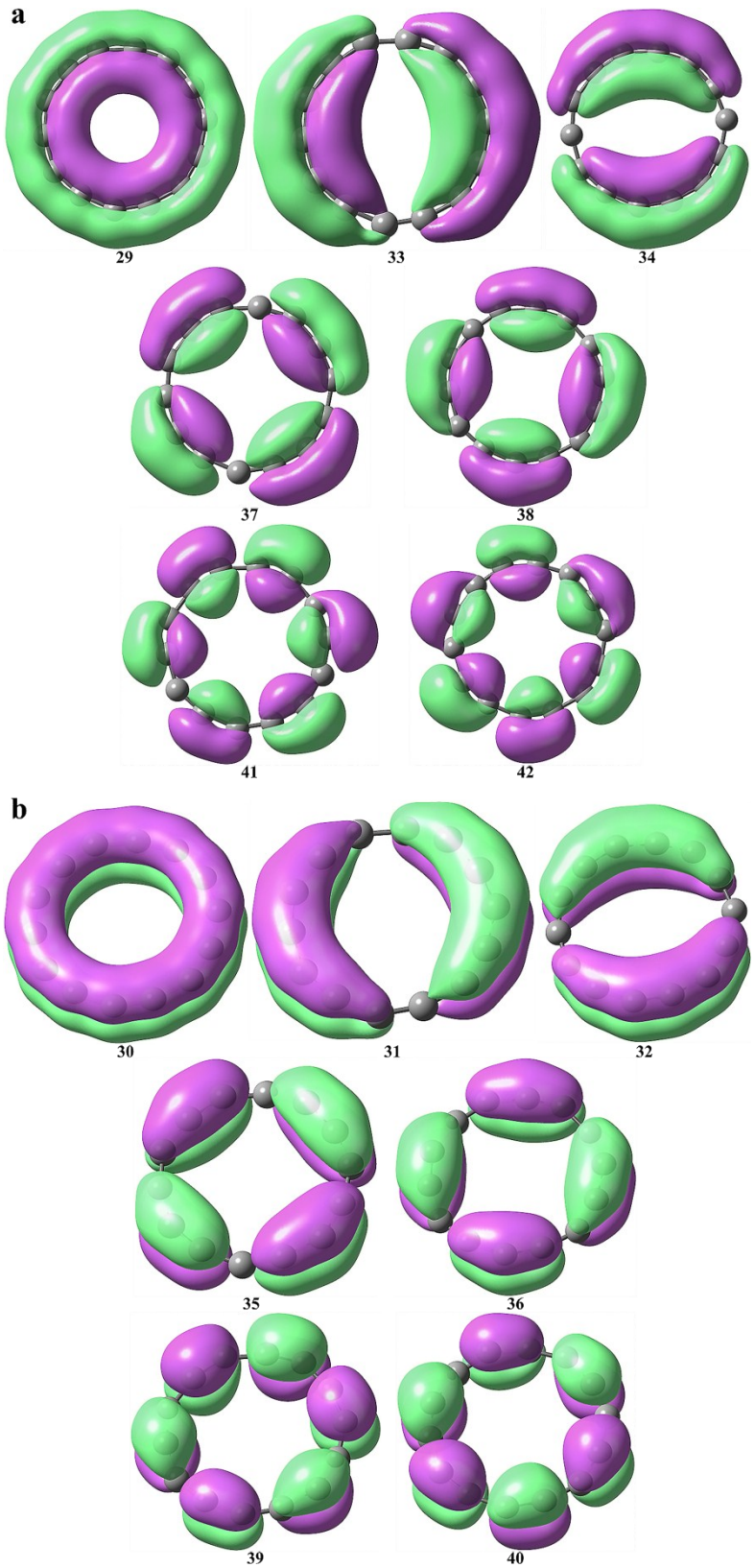

Fig. S8 The a) in-plainπ orbitals and b) out –plain π orbitals for cyclo-C_{14}. The numbers below the orbitals are the labels of corresponding π orbitals.

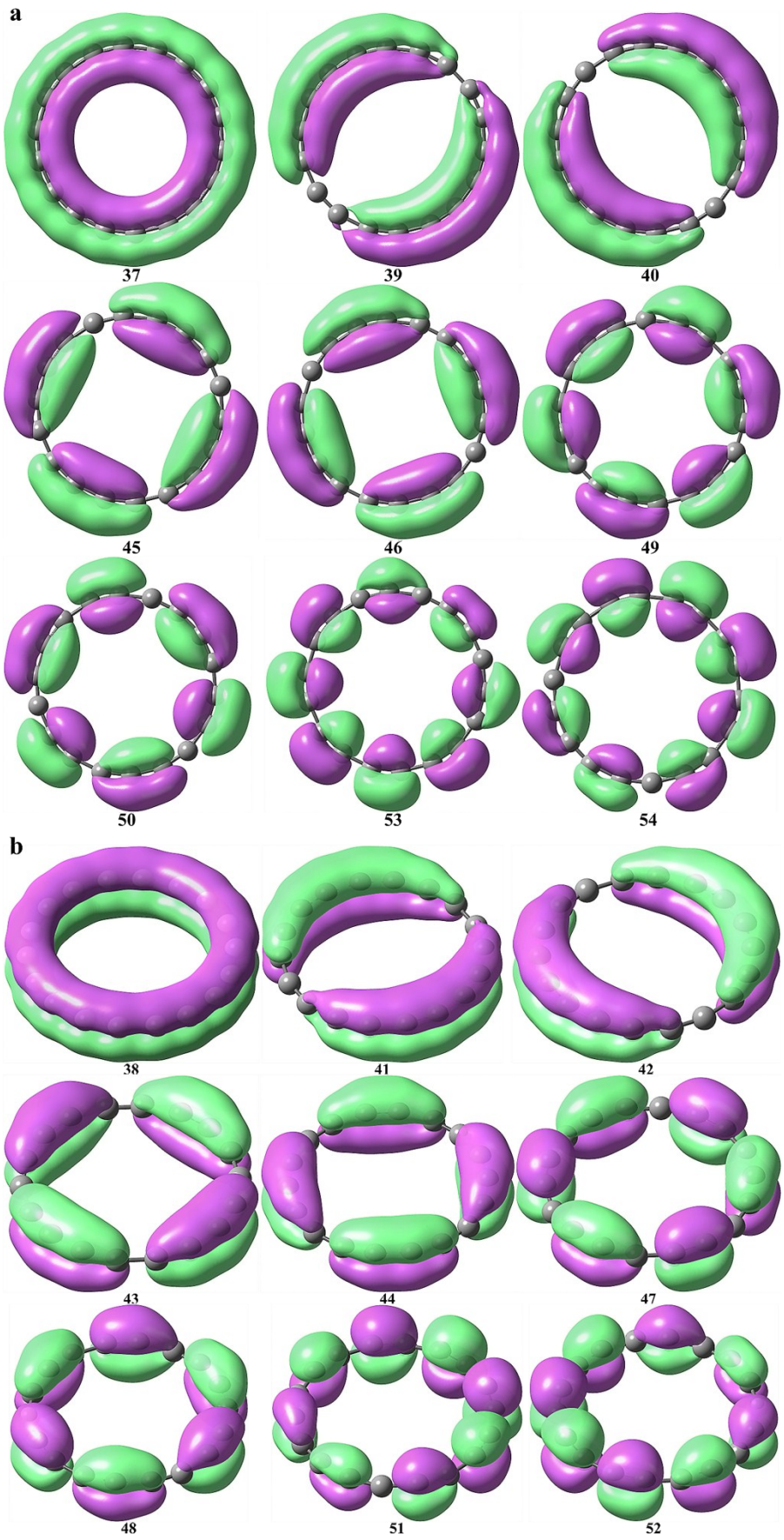

Fig. S9 The a) in-plainπ orbitals and b) out –plain π orbitals for cyclo-C_{18}. The numbers below the orbitals are the labels of corresponding π orbitals.

8. The coordinates for cyclo-C_n (n = 10, 14, and 18) optimized on the M062X/6-311G(d,p)

Cyclo-C_{10}

C	-3.91903300	2.19950400	-1.89291200
C	-4.38237600	3.05296300	-2.74272600
C	-4.66953300	1.45717000	-1.15091200
C	-5.67206000	0.88300000	-0.57604400
C	-6.90219400	1.16019200	-0.84944800
C	-7.98487900	1.65874400	-1.34389800
C	-7.99491400	2.57255400	-2.25477900
C	-7.66148800	3.45507600	-3.13520900
C	-6.43740100	3.74242500	-3.42474900
C	-5.14877400	3.78898800	-3.47463700

Cyclo-C_{14}

C	-3.45547700	1.16038500	-0.85699900
C	-2.80536500	1.91219700	-1.60777300
C	-2.51919300	2.82535900	-2.51822700
C	-2.94476700	3.65485000	-3.34420800
C	-3.77455100	4.38371600	-4.06862200
C	-4.95504400	4.66606700	-4.34808000
C	-4.64210400	0.75063000	-0.44626400
C	-5.87817900	0.64278900	-0.33655600
C	-7.07188300	1.04453300	-0.73440200
C	-7.96286000	1.66189500	-1.34809000
C	-8.26504600	2.57298300	-2.25535000
C	-8.13987600	3.45051900	-3.13044000
C	-7.32271700	4.18478600	-3.86367900

C	-6.27587200	4.66178000	-4.34112500

Cyclo-C_{18}

C	-3.56538700	0.94323000	-0.64178700
C	-2.58571000	1.59764100	-1.29121200
C	-2.03257700	2.37453100	-2.06168700
C	-1.87433200	3.32292300	-3.00261700
C	-2.15392300	4.17041300	-3.84329800
C	-2.89154100	4.96935600	-4.63546600
C	-6.38570800	5.71897300	-5.37514100
C	-7.62187200	5.34247600	-5.00118600
C	-4.69233800	0.60071200	-0.30134200
C	-6.03545000	0.54709800	-0.24708900
C	-7.20925600	0.79932700	-0.49566000
C	-8.28700600	1.37169000	-1.06187600
C	-8.95816100	2.10051000	-1.78406800
C	-9.26650600	3.03007800	-2.70635300
C	-9.12132700	3.89431800	-3.56380500
C	-8.51576200	4.74684000	-4.41011500
C	-3.87342800	5.49108800	-5.15201000
C	-5.16161300	5.76719100	-5.42437000