Supporting information

Metal-Centered Monocyclic Carbon Wheel Clusters with Record Coordination Numbers in Planar Species

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[La©C$_{13}$]$^+$L$_2$ (**8**) (L=Ar, Kr), [La©C$_{13}$]$_2$O (**9**), and C_{3v} N[La©C$_{13}$]$_3$ (**10**) at M06-2X

level.

Figure S1 Relative energies (in eV) of the low-lying isomers of La©C_{13}^+ calculated at M06-2X, PBE0 (parentheses), and CCSD(T) (square brackets) levels.

D_{13h} $^1A_1'$	C_s $^3A''$	C_s $^1A'$	C_1 ^1A	C_{2v} $^1A_1$
0.00	2.32	2.81	3.05	3.09
(0.00)	(2.17)	(2.93)	(3.45)	(2.76)
[0.00]	[2.41]	[2.97]	[3.16]	[3.08]

C_1 ^1A	C_{2v} $^1A_1$	C_1 ^1A	C_1 ^1A	C_s $^1A'$
3.09	3.36	3.46	3.99	4.17
(3.44)	(3.34)	(3.48)	(4.37)	(4.42)

C_s $^1A'$	C_1 ^1A	C_s $^1A'$	C_2 ^1A	C_1 ^1A
4.31	4.79	4.88	5.12	5.41
(4.73)	(5.03)	(5.30)	(5.42)	(5.51)
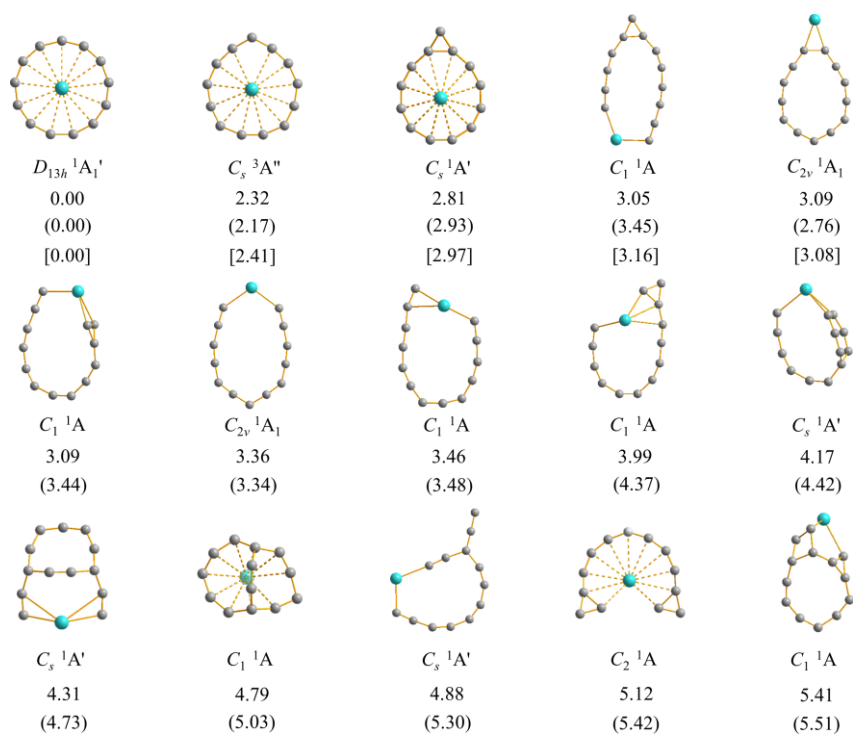
Figure S2 Relative energies (in eV) of the low-lying isomers of Ca©C$_{13}$ calculated at M06-2X, PBE0 (parentheses), and CCSD(T) (square brackets).

D_{13h} $^1A_1'$	C_{2v} $^3A_1$	C_s $^1A'$	C_s $^1A'$	C_{2v} $^3A_1$
0.00	1.99	2.09	2.37	2.41
(0.00)	(1.84)	(2.55)	(2.81)	(2.53)
[0.00]	[2.26]	[2.05]	[2.31]	[2.32]

C_s $^1A'$	C_s $^1A'$	C_1 ^1A	C_1 ^1A	C_{2v} $^1A_1$
2.41	2.77	3.05	3.14	3.16
(2.55)	(3.15)	(3.27)	(3.62)	(2.75)

C_s $^1A'$	C_s $^1A'$	C_1 ^1A	C_s $^1A'$	C_1 ^1A
3.20	3.36	3.47	3.76	3.98
(3.29)	(3.52)	(3.97)	(4.16)	(4.28)
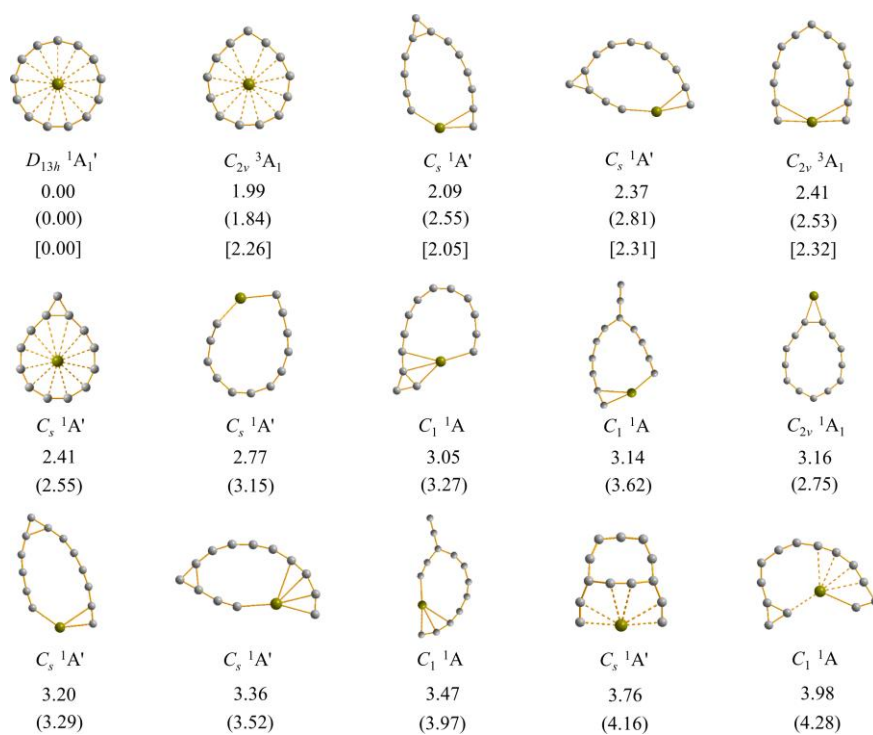
Figure S3 Relative energies (in eV) of the low-lying isomers of Ac©C_{13}^+ calculated at M06-2X, PBE0 (parentheses), and CCSD(T) (square brackets).

D_{13h} $^1A_1$	C_1 $^3A_1$	C_s $^1A'$	C_1 ^1A	C_s $^1A'$
0.00	2.20	2.74	2.91	2.99
(0.00)	(2.05)	(2.88)	(3.31)	(2.32)
[0.00]	[2.36]	[2.93]	[3.12]	[2.93]

C_1 ^1A	C_{2v} $^1A_1$	C_1 ^1A	C_{2v} $^1A_1$	C_1 ^1A
3.04	3.22	2.29	3.33	3.33
(3.31)	(3.20)	(3.38)	(2.94)	(3.38)

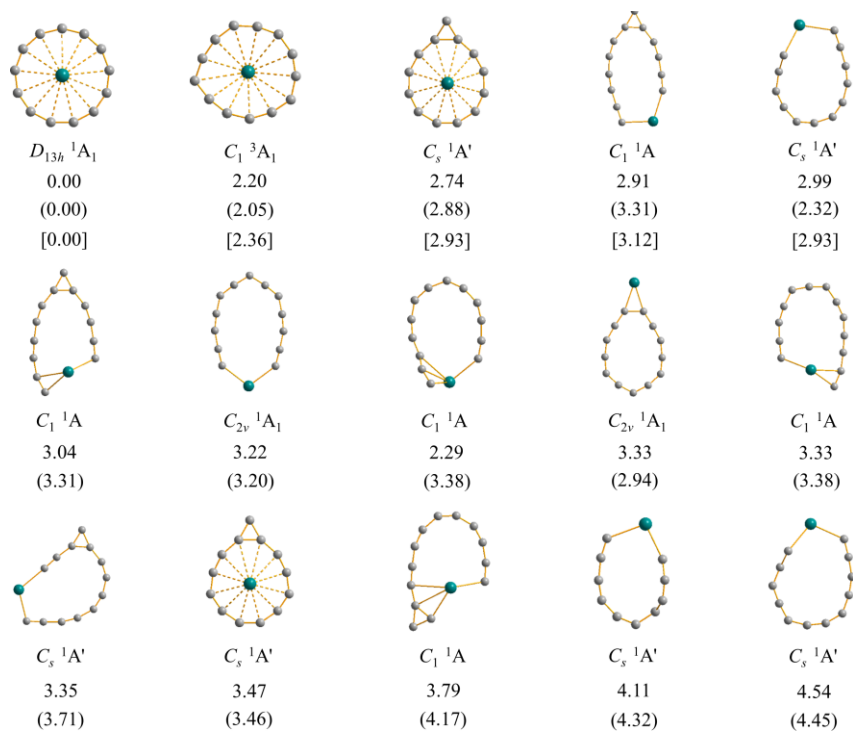|				
C_s $^1A'$	C_s $^1A'$	C_1 ^1A	C_s $^1A'$	C_s $^1A'$
3.35	3.47	3.79	4.11	4.54
(3.71)	(3.46)	(4.17)	(4.32)	(4.45)

Figure S4 Relative energies (in eV) of the low-lying isomers of La©C_{14}^+ calculated at M06-2X, PBE0 (parentheses), and CCSD(T) (square brackets).

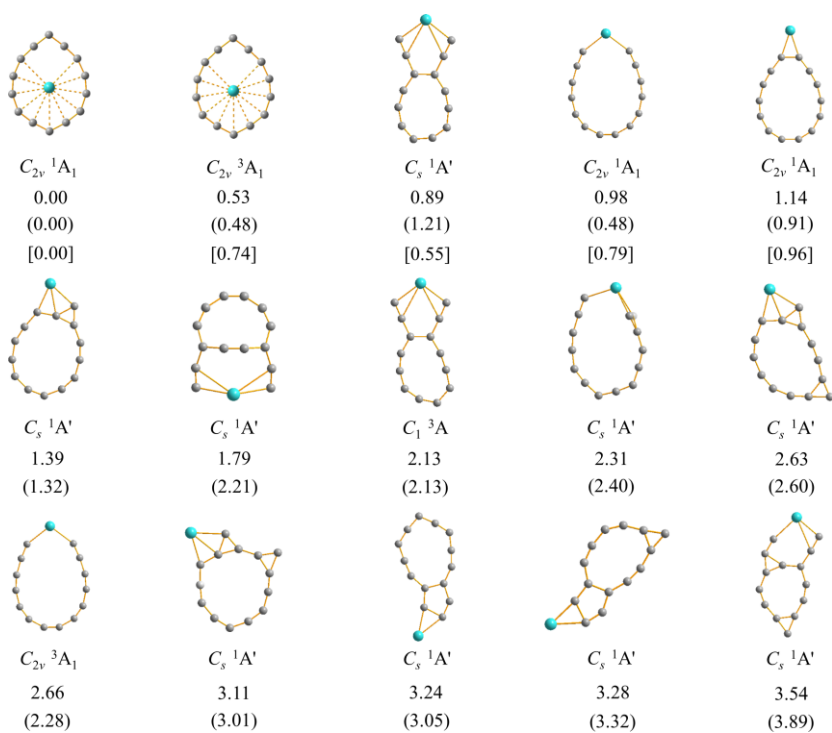| C_{2v} $^1A_1$	C_{2v} $^3A_1$	C_s $^1A'$	C_{2v} $^1A_1$	C_{2v} $^1A_1$
0.00	0.53	0.89	0.98	1.14
(0.00)	(0.48)	(1.21)	(0.48)	(0.91)
[0.00]	[0.74]	[0.55]	[0.79]	[0.96]

C_s $^1A'$	C_s $^1A'$	C_1 ^3A	C_s $^1A'$	C_s $^1A'$
1.39	1.79	2.13	2.31	2.63
(1.32)	(2.21)	(2.13)	(2.40)	(2.60)

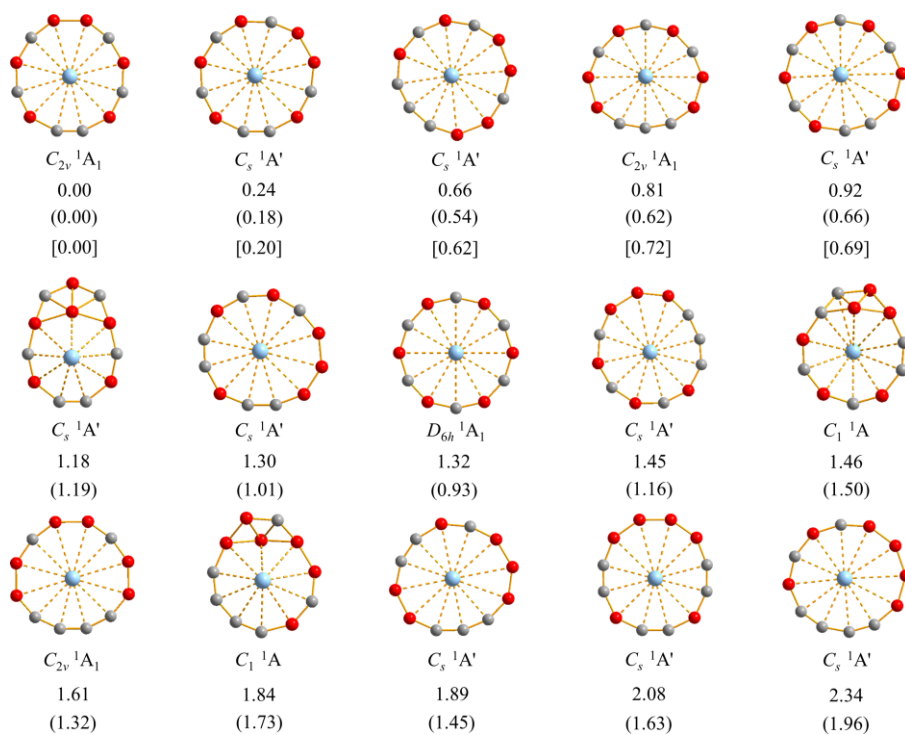| C_{2v} $^3A_1$	C_s $^1A'$	C_s $^1A'$	C_s $^1A'$	C_s $^1A'$
2.66	3.11	3.24	3.28	3.54
(2.28)	(3.01)	(3.05)	(3.32)	(3.89)

Figure S5 Relative energies (in eV) of the low-lying isomers of Y©$B_6C_6^+$ calculated at M06-2X, PBE0 (parentheses), and CCSD(T) (square brackets).

C_{2v} $^1A_1$	C_s $^1A'$	C_s $^1A'$	C_{2v} $^1A_1$	C_s $^1A'$
0.00	0.24	0.66	0.81	0.92
(0.00)	(0.18)	(0.54)	(0.62)	(0.66)
[0.00]	[0.20]	[0.62]	[0.72]	[0.69]

C_s $^1A'$	C_s $^1A'$	D_{6h} $^1A_1$	C_s $^1A'$	C_1 ^1A
1.18	1.30	1.32	1.45	1.46
(1.19)	(1.01)	(0.93)	(1.16)	(1.50)

C_{2v} $^1A_1$	C_1 ^1A	C_s $^1A'$	C_s $^1A'$	C_s $^1A'$
1.61	1.84	1.89	2.08	2.34
(1.32)	(1.73)	(1.45)	(1.63)	(1.96)

Figure S6 Relative energies (in eV) of the low-lying isomers of Sc©B_5C_6 calculated at M06-2X, PBE0 (parentheses), and CCSD(T) (square brackets).
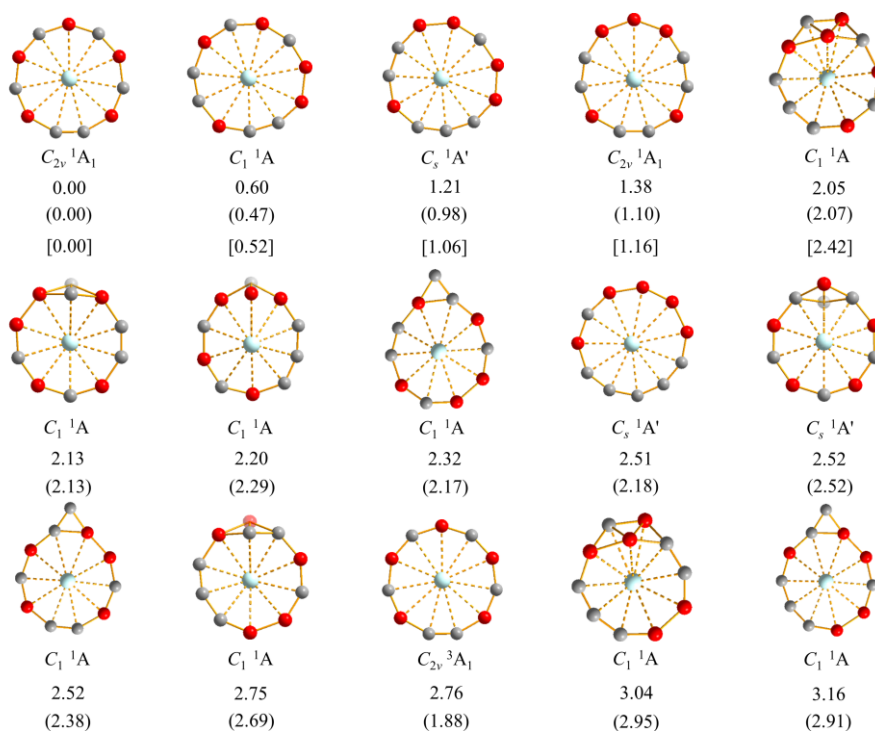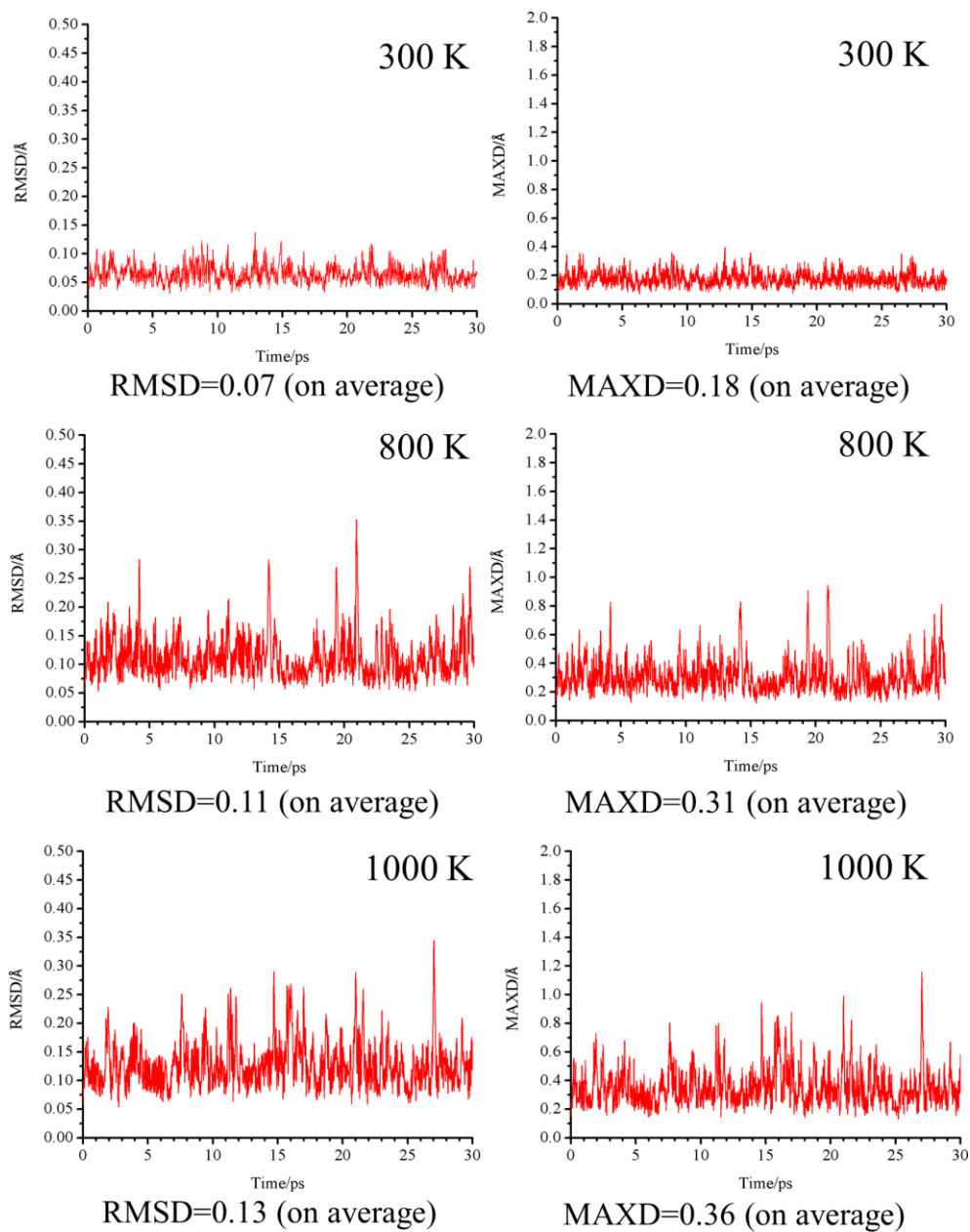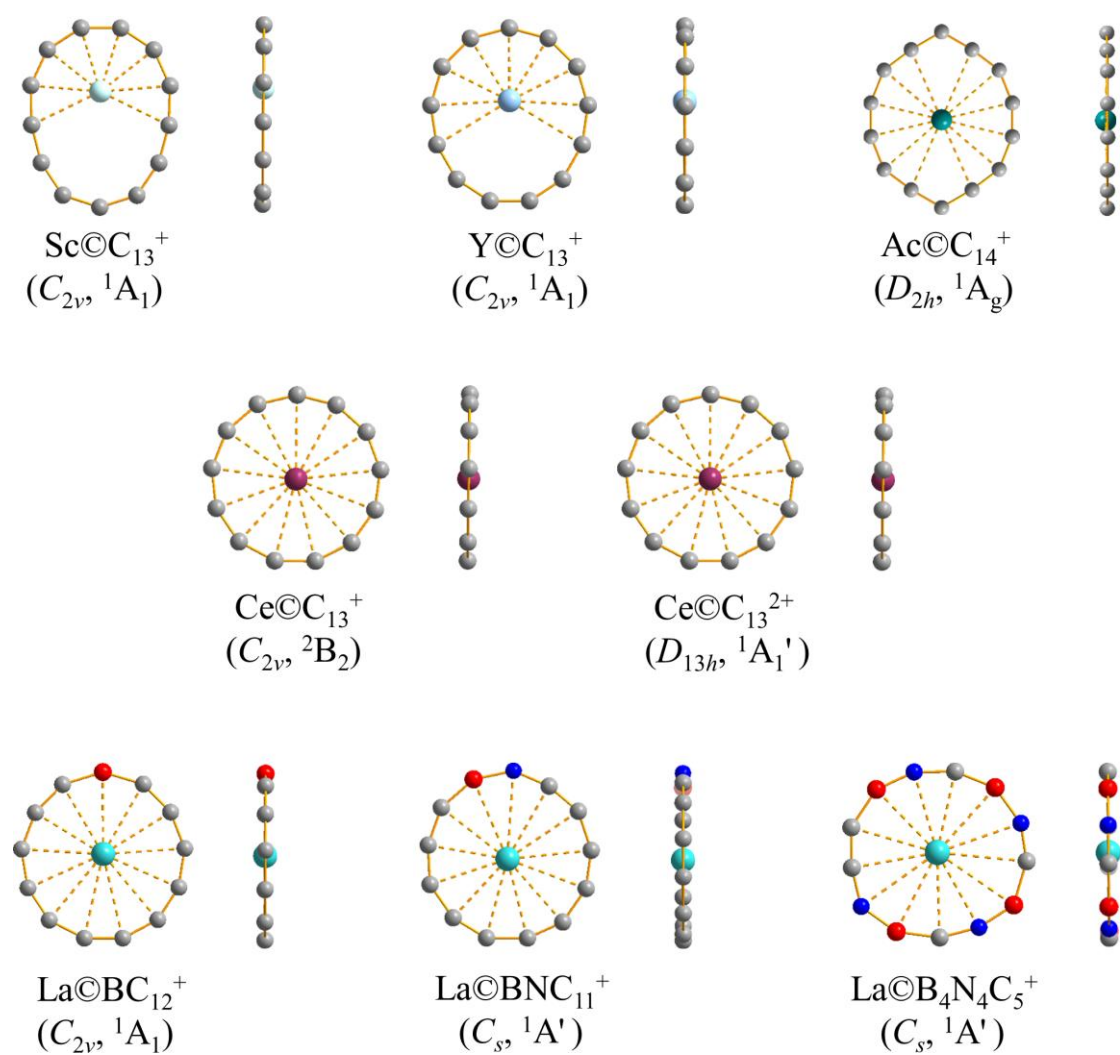

C_{2v} $^1A_1$	C_1 ^1A	C_s $^1A'$	C_{2v} $^1A_1$	C_1 ^1A
0.00	0.60	1.21	1.38	2.05
(0.00)	(0.47)	(0.98)	(1.10)	(2.07)
[0.00]	[0.52]	[1.06]	[1.16]	[2.42]

C_1 ^1A	C_1 ^1A	C_1 ^1A	C_s $^1A'$	C_s $^1A'$
2.13	2.20	2.32	2.51	2.52
(2.13)	(2.29)	(2.17)	(2.18)	(2.52)

| C_1 ^1A | C_1 ^1A | C_{2v} $^3A_1$ | C_1 ^1A | C_1 ^1A |
| 2.52 | 2.75 | 2.76 | 3.04 | 3.16 |
| (2.38) | (2.69) | (1.88) | (2.95) | (2.91) |

Figure S7 Born-Oppenheimer molecular dynamics simulations of La©C_{13}^+ at 300, 800, and 1000 K. The root-mean-square deviation (RMSD) and maximum bond length deviation (MAXD) values (on average) are indicated in Å

RMSD=0.07 (on average) MAXD=0.18 (on average)

RMSD=0.11 (on average) MAXD=0.31 (on average)

RMSD=0.13 (on average) MAXD=0.36 (on average)

Figure S8. Optimized structures of $Sc©C_{13}^{+}$, $Y©C_{13}^{+}$, $Ac©C_{14}^{+}$, $Ce©C_{13}^{+}$, $Ce©C_{13}^{2+}$, $La©BC_{12}^{+}$, $La©BNC_{11}^{+}$, and $La©B_4N_4C_5^{+}$ at M06-2X level.

$Sc©C_{13}^{+}$
$(C_{2v}, {}^1A_1)$

$Y©C_{13}^{+}$
$(C_{2v}, {}^1A_1)$

$Ac©C_{14}^{+}$
$(D_{2h}, {}^1A_g)$

$Ce©C_{13}^{+}$
$(C_{2v}, {}^2B_2)$

$Ce©C_{13}^{2+}$
$(D_{13h}, {}^1A_1')$

$La©BC_{12}^{+}$
$(C_{2v}, {}^1A_1)$

$La©BNC_{11}^{+}$
$(C_s, {}^1A')$

$La©B_4N_4C_5^{+}$
$(C_s, {}^1A')$

Figure S9. Eigenvalue spectrum of D_{13h} La©C_{13}^+ (**1**) at M062x level, with its 7 π-CMOs, 7 σ-CMOs, and the 13 σ-CMOs corresponding to 13 two-center-two-electron (2c-2e) C-C σ bonds depicted. The calculated HOMO-LUMO energy gap is indicated in eV.
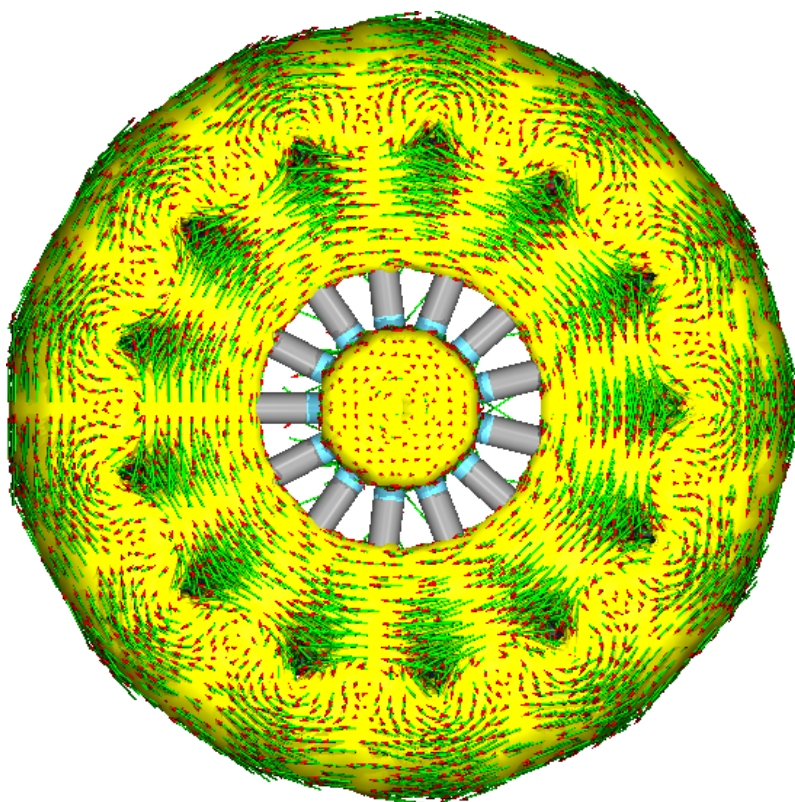
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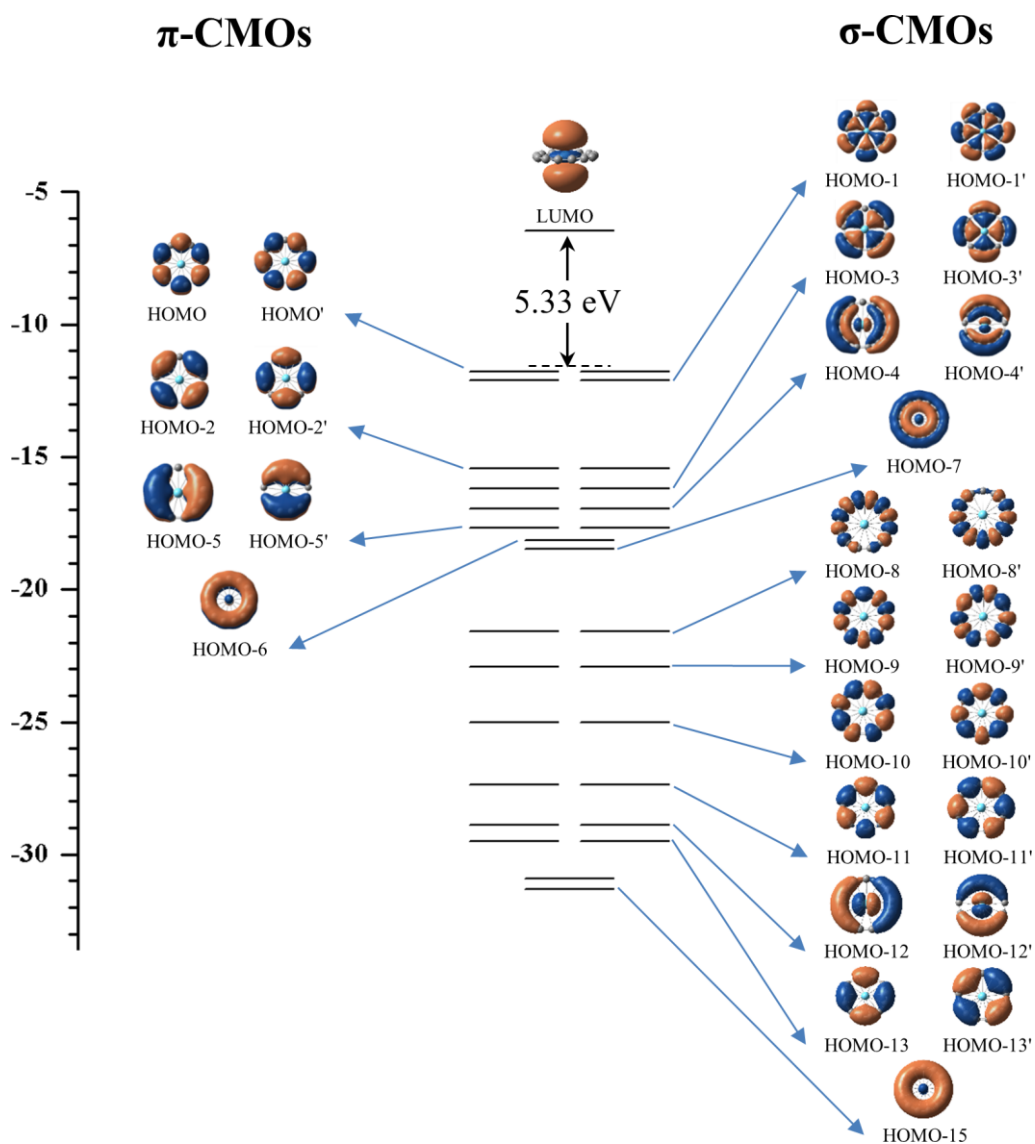
Figure S10. The high-resolution π- and σ-ring current maps of La©C_{13}^+ (**1**), Y©$B_6C_6^+$ (**5**), and Sc©B_5C_6 (**6**), respectively, in comparison with the π-ring current map of D_{6h} C_6H_6. The external magnetic field is perpendicular to the wheel plane. The red arrows represent directions and magnitudes of the ring currents at various positons on the ACID iso-surfaces.
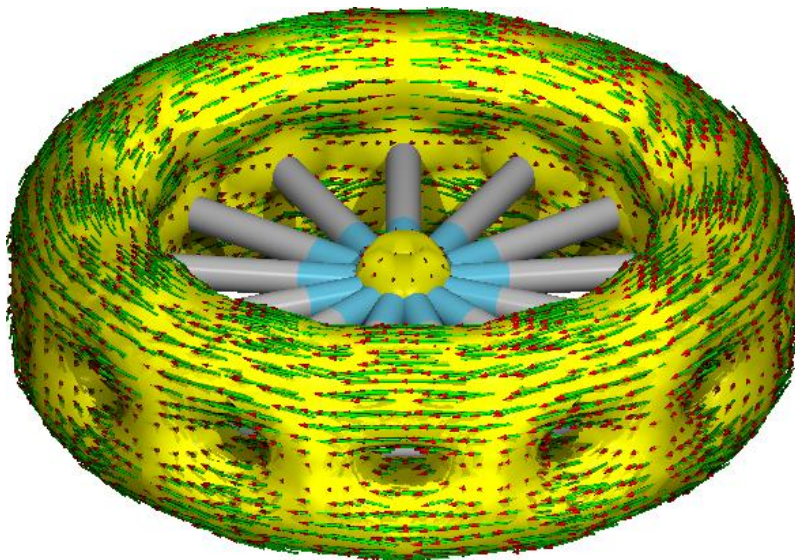
π-ring current maps of La©C_{13}^+ (**1**)

σ-ring current maps of La©C_{13}^+ (**1**)

π-ring current maps of Y©B$_6$C$_6$$^+$ (**5**)

σ-ring current maps of Y©B$_6$C$_6$$^+$ (**5**)
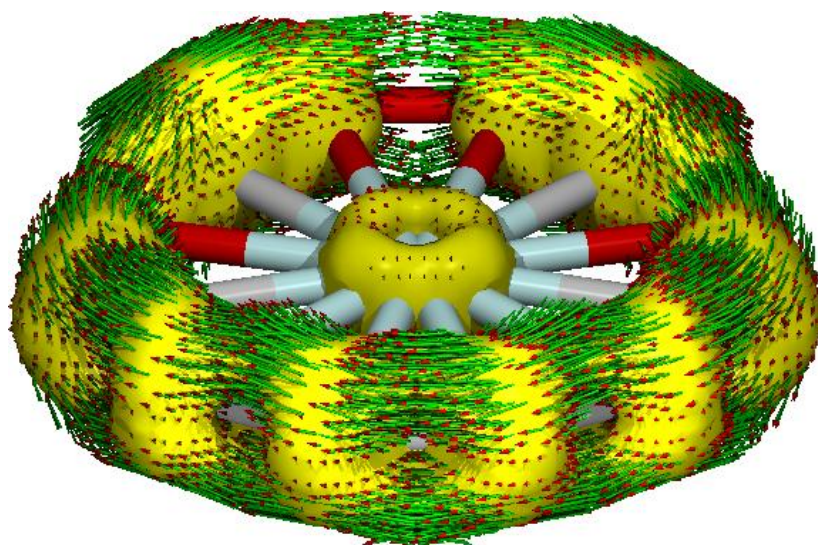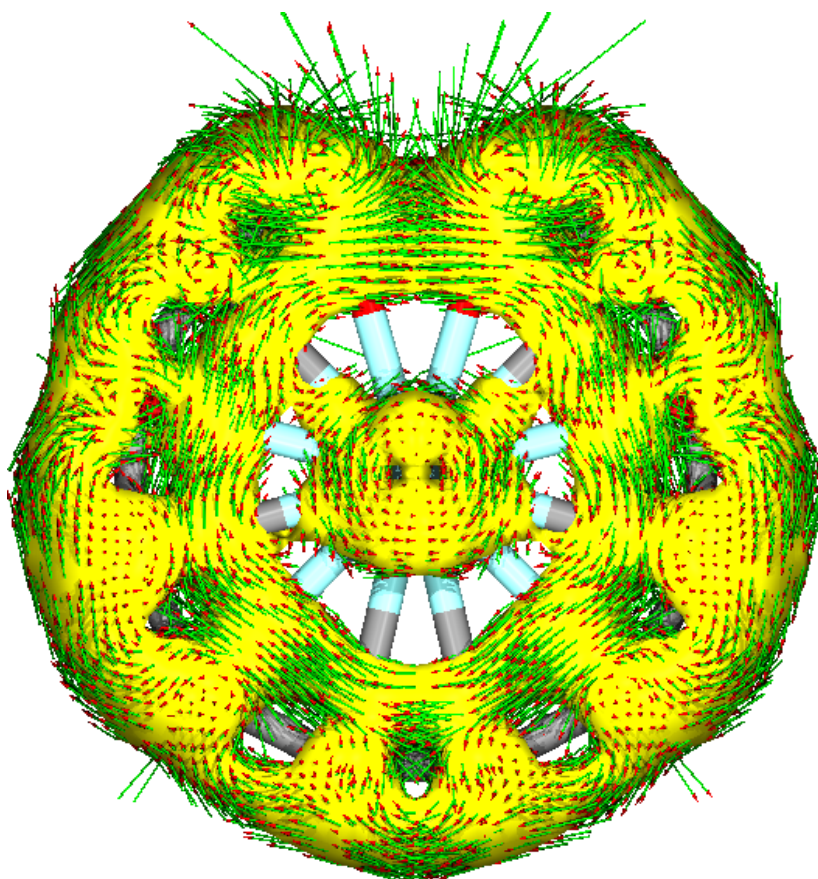
π-ring current maps of Sc©B$_5$C$_6$ (**6**)
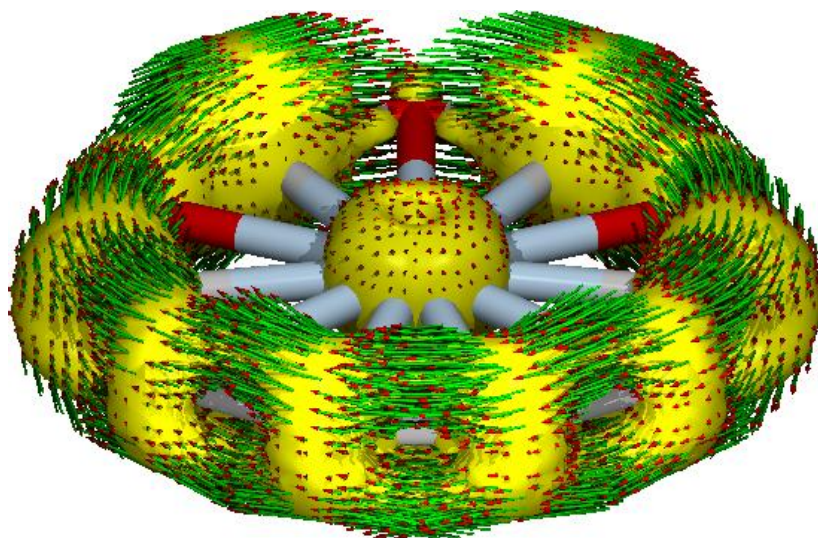
σ-ring current maps of Sc©B$_5$C$_6$ (**6**)
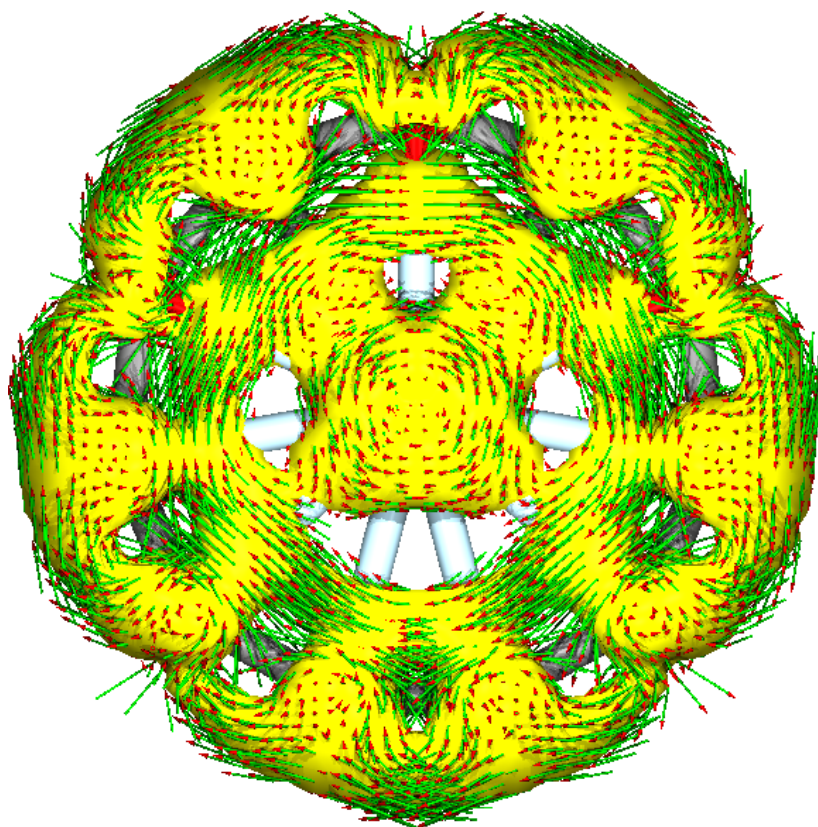
π-ring current maps of D_{6h} C_6H_6
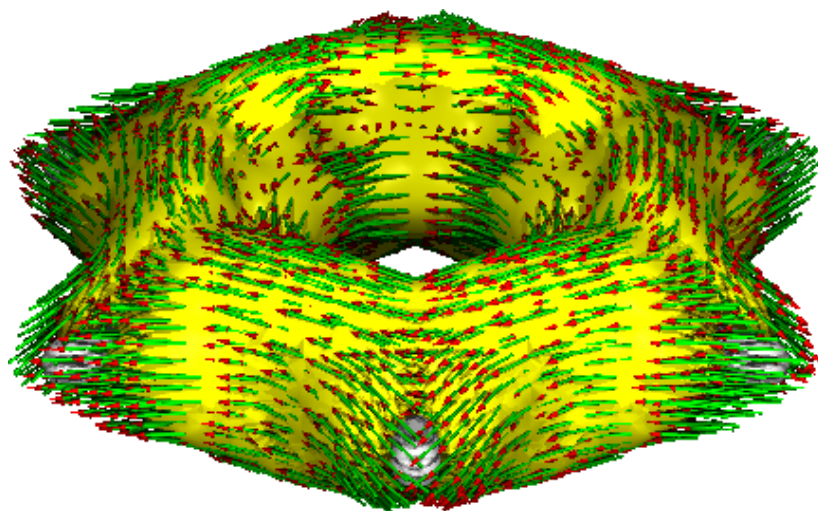
Figure S11. Simulated IR, Raman, and UV-Vis spectra of La©C_{13}^+ (**1**) (a) and Y©$B_6C_6^+$ (**5**) (b) at M06-2X level.

Table S1 Optimized coordinates (x, y, z) of D_{13h} La©C$_{13}^+$ (**1**), D_{13h} Ca©C$_{13}$ (**2**), C_{13v} Ac©C$_{13}^+$ (**3**), C_{2v} La©C$_{14}^+$ (**4**), C_{2v} Y©B$_6$C$_6^+$ (**5**), and C_{2v} Sc©B$_5$C$_6$ (**6**) at M06-2X level.
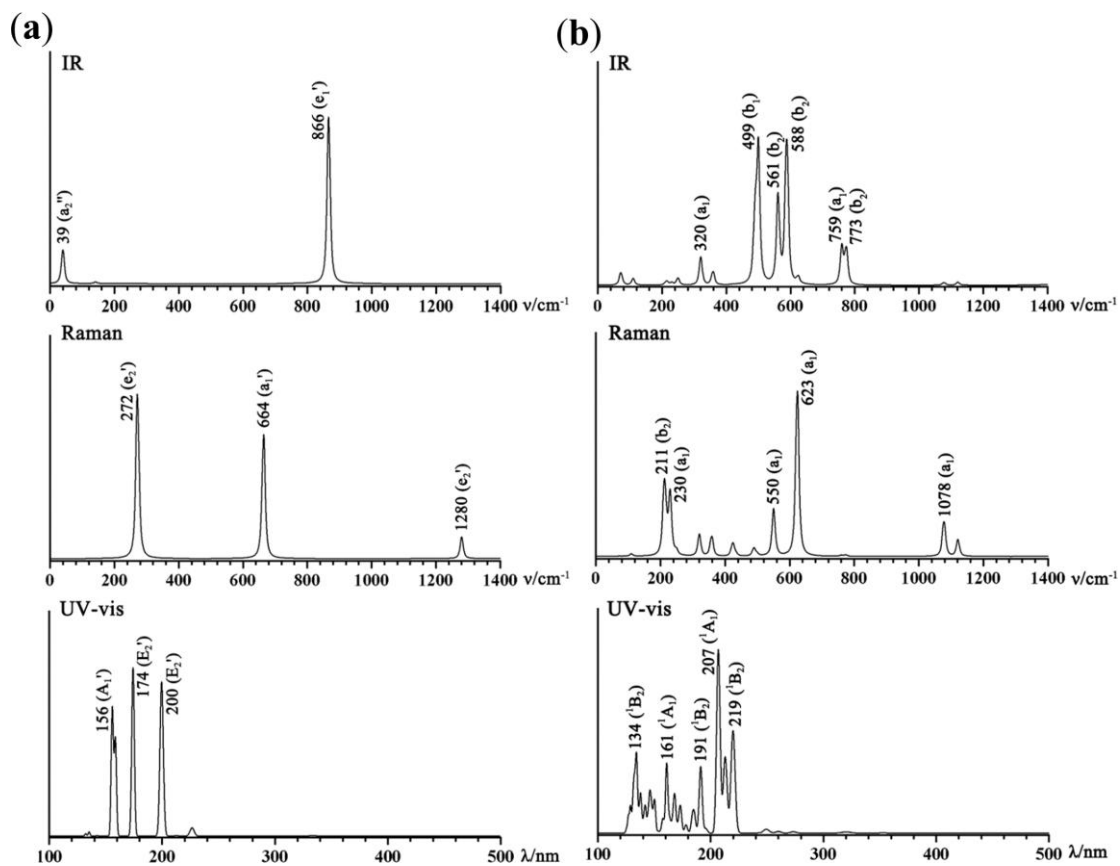
D_{13h} La©C$_{13}^+$ (**1**)

La	0.00000000	0.00000000	0.00000000
C	0.00000000	2.70031100	0.00000000
C	1.25489700	2.39100600	0.00000000
C	2.22231200	1.53395100	0.00000000
C	2.68062200	0.32548600	0.00000000
C	2.52483400	-0.95754300	0.00000000
C	1.79063700	-2.02121200	0.00000000
C	0.64622700	-2.62184500	0.00000000
C	-0.64622700	-2.62184500	0.00000000
C	-1.79063700	-2.02121200	0.00000000
C	-2.52483400	-0.95754300	0.00000000
C	-2.68062200	0.32548600	0.00000000
C	-2.22231200	1.53395100	0.00000000
C	-1.25489700	2.39100600	0.00000000

D_{13h} Ca©C$_{13}$ (**2**)

Ca	0.00000000	0.00000000	0.00000000
C	0.00000000	2.69495700	0.00000000
C	-1.25240900	2.38626600	0.00000000
C	-2.21790600	1.53091000	0.00000000
C	-2.67530800	0.32484100	0.00000000
C	-2.51982900	-0.95564500	0.00000000
C	-1.78708700	-2.01720400	0.00000000
C	-0.64494500	-2.61664600	0.00000000
C	0.64494500	-2.61664600	0.00000000
C	1.78708700	-2.01720400	0.00000000
C	2.51982900	-0.95564500	0.00000000
C	2.67530800	0.32484100	0.00000000
C	2.21790600	1.53091000	0.00000000
C	1.25240900	2.38626600	0.00000000

C_{13v} Ac©C_{13}^+ (**3**)

Ac	0.00000000	0.00000000	0.27445900
C	0.00000000	2.70503500	-0.31316500
C	-1.25709200	2.39519000	-0.31316500
C	-2.22620000	1.53663500	-0.31316500
C	-2.68531200	0.32605600	-0.31316500
C	-2.52925200	-0.95921900	-0.31316500
C	-1.79377000	-2.02474800	-0.31316500
C	-0.64735700	-2.62643200	-0.31316500
C	0.64735700	-2.62643200	-0.31316500
C	1.79377000	-2.02474800	-0.31316500
C	2.52925200	-0.95921900	-0.31316500
C	2.68531200	0.32605600	-0.31316500
C	2.22620000	1.53663500	-0.31316500
C	1.25709200	2.39519000	-0.31316500

C_{2v} La©C_{14}^+ (**4**)

C	0.00000000	1.06442400	-2.77909800
C	0.00000000	0.00000000	-3.58381600
C	0.00000000	-1.06442400	-2.77909800
C	0.00000000	-1.97746600	-1.90237600
C	0.00000000	-2.51687100	-0.69833800
C	0.00000000	-2.60159900	0.56258400
C	0.00000000	1.97746600	-1.90237600
C	0.00000000	2.51687100	-0.69833800
C	0.00000000	2.60159900	0.56258400
C	0.00000000	2.17259200	1.81234100
C	0.00000000	1.16174800	2.58919500
C	0.00000000	0.00000000	3.20312200
C	0.00000000	-1.16174800	2.58919500
C	0.00000000	-2.17259200	1.81234100
La	0.00000000	0.00000000	0.12758700

C_{2v} Y©B$_6$C$_6^+$ (**5**)

C	0.00000000	0.61934300	-2.58453600
C	0.00000000	2.52889600	-0.70979100
C	0.00000000	1.86516600	1.90464200
C	0.00000000	-1.86516600	1.90464200
C	0.00000000	-2.52889600	-0.70979100
C	0.00000000	-0.61934300	-2.58453600
Y	0.00000000	0.00000000	0.03761300
B	0.00000000	1.91654000	-1.91861200
B	0.00000000	-1.91654000	-1.91861200
B	0.00000000	-2.58199300	0.69850300
B	0.00000000	-0.78940700	2.74104200
B	0.00000000	2.58199300	0.69850300
B	0.00000000	0.78940700	2.74104200

C_{2v} Sc©B$_5$C$_6$ (**6**)

C	0.00000000	1.33240400	2.06357200
C	0.00000000	2.41814500	-0.37764100
C	0.00000000	0.62482100	-2.33794800
C	0.00000000	-0.62482100	-2.33794800
C	0.00000000	-2.41814500	-0.37764100
C	0.00000000	-1.33240400	2.06357200
B	0.00000000	0.00000000	2.49451500
B	0.00000000	-2.25334300	1.03591200
B	0.00000000	-1.88347400	-1.62452000
B	0.00000000	2.25334300	1.03591200
B	0.00000000	1.88347400	-1.62452000
Sc	0.00000000	0.00000000	0.05923600

*C*_{13*v*} [La©C₁₃]F (**7**)

La	0.00000000	0.00000000	0.23089700
C	0.00000000	2.70008300	-0.43339900
C	1.25479100	2.39080500	-0.43339900
C	2.22212500	1.53382200	-0.43339900
C	2.68039600	0.32545900	-0.43339900
C	2.52462200	-0.95746300	-0.43339900
C	1.79048600	-2.02104100	-0.43339900
C	0.64617200	-2.62162400	-0.43339900
C	-0.64617200	-2.62162400	-0.43339900
C	-1.79048600	-2.02104100	-0.43339900
C	-2.52462200	-0.95746300	-0.43339900
C	-2.68039600	0.32545900	-0.43339900
C	-2.22212500	1.53382200	-0.43339900
C	-1.25479100	2.39080500	-0.43339900
F	0.00000000	0.00000000	2.29377800

*C*_{13*v*} [La©C₁₃]Cl (**7**)

La	0.00000000	0.00000000	0.00879100
C	0.00000000	2.70102300	-0.56629200
C	1.25522800	2.39163700	-0.56629200
C	2.22289800	1.53435600	-0.56629200
C	2.68132900	0.32557200	-0.56629200
C	2.52550000	-0.95779600	-0.56629200
C	1.79111000	-2.02174500	-0.56629200
C	0.64639700	-2.62253600	-0.56629200
C	-0.64639700	-2.62253600	-0.56629200
C	-1.79111000	-2.02174500	-0.56629200
C	-2.52550000	-0.95779600	-0.56629200
C	-2.68132900	0.32557200	-0.56629200
C	-2.22289800	1.53435600	-0.56629200
C	-1.25522800	2.39163700	-0.56629200
Cl	0.00000000	0.00000000	2.56880600

C_{13v} [La©C$_{13}$]Br (**7**)

La	0.00000000	0.00000000	0.29829600
C	0.00000000	2.70085900	0.87268500
C	-1.25515200	2.39149200	0.87268500
C	-2.22276400	1.53426300	0.87268500
C	-2.68116700	0.32555300	0.87268500
C	-2.52534700	-0.95773800	0.87268500
C	-1.79100100	-2.02162200	0.87268500
C	-0.64635800	-2.62237700	0.87268500
C	0.64635800	-2.62237700	0.87268500
C	1.79100100	-2.02162200	0.87268500
C	2.52534700	-0.95773800	0.87268500
C	2.68116700	0.32555300	0.87268500
C	2.22276400	1.53426300	0.87268500
C	1.25515200	2.39149200	0.87268500
Br	0.00000000	0.00000000	-2.43063700

D_{13h} [La©C$_{13}$]$^+$Ar$_2$ (**8**)

La	0.00000000	0.00000000	0.00000000
C	0.00000000	2.70130000	0.00000000
C	1.25535700	2.39188200	0.00000000
C	2.22312600	1.53451300	0.00000000
C	2.68160400	0.32560600	0.00000000
C	2.52575900	-0.95789400	0.00000000
C	1.79129300	-2.02195200	0.00000000
C	0.64646300	-2.62280500	0.00000000
C	-0.64646300	-2.62280500	0.00000000
C	-1.79129300	-2.02195200	0.00000000
C	-2.52575900	-0.95789400	0.00000000
C	-2.68160400	0.32560600	0.00000000
C	-2.22312600	1.53451300	0.00000000
C	-1.25535700	2.39188200	0.00000000
Ar	0.00000000	0.00000000	3.03439600
Ar	0.00000000	0.00000000	-3.03439600

D$_{13h}$ [La©C$_{13}$]$^+$Kr$_2$ (**8**)

La	0.00000000	0.00000000	0.00000000
C	0.00000000	2.70191300	0.00000000
C	1.25564200	2.39242500	0.00000000
C	2.22363100	1.53486200	0.00000000
C	2.68221300	0.32568000	0.00000000
C	2.52633300	-0.95811200	0.00000000
C	1.79170000	-2.02241100	0.00000000
C	0.64661000	-2.62340000	0.00000000
C	-0.64661000	-2.62340000	0.00000000
C	-1.79170000	-2.02241100	0.00000000
C	-2.52633300	-0.95811200	0.00000000
C	-2.68221300	0.32568000	0.00000000
C	-2.22363100	1.53486200	0.00000000
C	-1.25564200	2.39242500	0.00000000
Kr	0.00000000	0.00000000	3.17108300
Kr	0.00000000	0.00000000	-3.17108300

C$_{2v}$ [La©C$_{13}$]$_2$O (**9**)

O	0.00000000	0.00000000	0.91849300
La	0.00000000	2.04846100	0.34376700
C	-2.24054500	2.47090100	-1.20541700
C	-1.62645500	1.65214700	-1.93541500
C	-2.49304700	3.21215700	-0.13506300
C	-0.72572900	0.75304900	-2.39645200
C	-2.05578800	3.84679100	0.87217200
C	0.72572900	0.75304900	-2.39645200
C	-1.28237200	4.21321100	1.87601400
C	1.62645500	1.65214700	-1.93541500
C	0.00000000	4.36305400	1.97020900
C	2.24054500	2.47090100	-1.20541700
C	1.28237200	4.21321100	1.87601400
C	2.49304700	3.21215700	-0.13506300
C	2.05578800	3.84679100	0.87217200
La	0.00000000	-2.04846100	0.34376700
C	-0.72572900	-0.75304900	-2.39645200
C	0.72572900	-0.75304900	-2.39645200
C	-1.62645500	-1.65214700	-1.93541500

C	1.62645500	-1.65214700	-1.93541500
C	-2.24054500	-2.47090100	-1.20541700
C	2.24054500	-2.47090100	-1.20541700
C	-2.49304700	-3.21215700	-0.13506300
C	2.49304700	-3.21215700	-0.13506300
C	-2.05578800	-3.84679100	0.87217200
C	2.05578800	-3.84679100	0.87217200
C	-1.28237200	-4.21321100	1.87601400
C	1.28237200	-4.21321100	1.87601400
C	0.00000000	-4.36305400	1.97020900

C_{3v} N[La©C$_{13}$]$_3$ (**10**)

N	0.00000000	0.00000000	0.59400600
La	1.99002800	1.14894300	0.32842400
C	0.75090100	3.62570000	-1.02380100
C	0.75550800	2.63160600	-2.07261900
C	1.64696500	3.88817000	-0.04035000
C	1.61017400	1.65302200	-2.44407000
C	2.40969900	3.80059000	0.95561300
C	2.23664600	0.56794100	-2.44407000
C	3.12026800	3.28104000	1.95156200
C	2.65679100	-0.66151400	-2.07261900
C	3.91420100	2.25986500	1.99630300
C	3.51539900	-1.16255100	-1.02380100
C	4.40159800	1.06171100	1.95156200
C	4.19073700	-0.51777100	-0.04035000
C	4.49625600	0.18656500	0.95561300
La	0.00000000	-2.29788700	0.32842400
C	2.76449800	-2.46314900	-1.02380100
C	1.90128300	-1.97009200	-2.07261900
C	2.54377200	-3.37039900	-0.04035000
C	0.62647200	-2.22096200	-2.44407000
C	2.08655800	-3.98715500	0.95561300
C	-0.62647200	-2.22096200	-2.44407000
C	1.28133000	-4.34275100	1.95156200
C	-1.90128300	-1.97009200	-2.07261900
C	0.00000000	-4.51973000	1.99630300
C	-2.76449800	-2.46314900	-1.02380100
C	-1.28133000	-4.34275100	1.95156200

C	-2.54377200	-3.37039900	-0.04035000
C	-2.08655800	-3.98715500	0.95561300
La	-1.99002800	1.14894300	0.32842400
C	-3.51539900	-1.16255100	-1.02380100
C	-2.65679100	-0.66151400	-2.07261900
C	-4.19073700	-0.51777100	-0.04035000
C	-2.23664600	0.56794100	-2.44407000
C	-4.49625600	0.18656500	0.95561300
C	-1.61017400	1.65302200	-2.44407000
C	-4.40159800	1.06171100	1.95156200
C	-0.75550800	2.63160600	-2.07261900
C	-3.91420100	2.25986500	1.99630300
C	-0.75090100	3.62570000	-1.02380100
C	-3.12026800	3.28104000	1.95156200
C	-1.64696500	3.88817000	-0.04035000
C	-2.40969900	3.80059000	0.95561300