Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

$[Cs©C_{18}]^+$ and $[Na©C_{14}]^+$: perfect planar alkaline-metal-centered polyynic cyclo[n]carbon complexes with record coordination numbers

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Fig.S1 Optimized global minimum structures of D_{9h} C_{18} and D_{7h} C_{14} at M06-2X level.

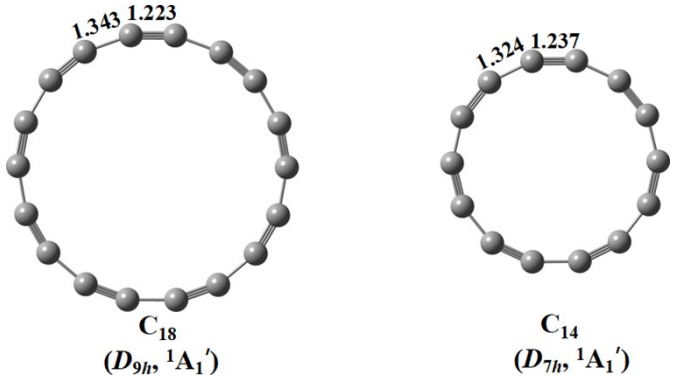


Fig. S2 Optimized global minimum structures of (a) M©C_{18}^{+} (M = Li, Na, K, Rb, Cs, and Fr) and (b) M©C_{14}^{+} (M = Li, Na and K) at M06-2X level.

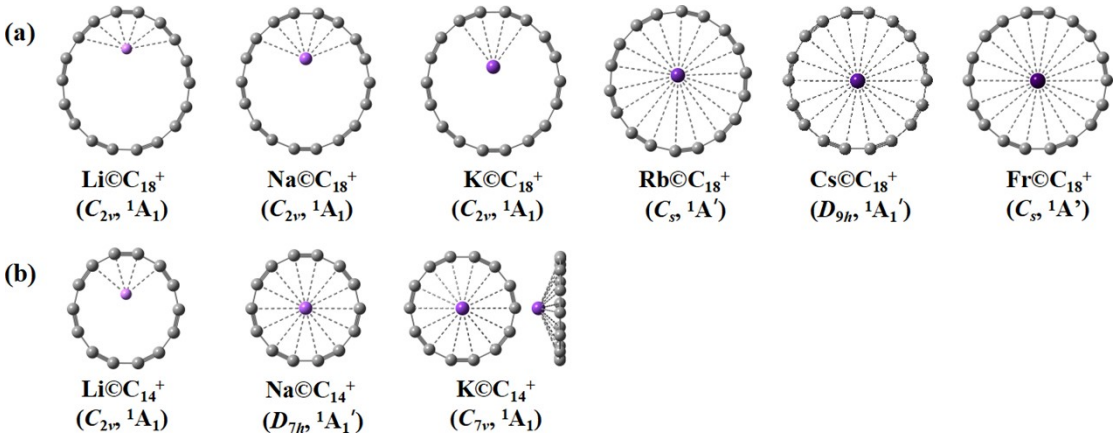


Fig. S3 Relative energies (in eV) of the low-lying isomers of $Cs©C_{18}^{+}$ at M06-2X and ωB97XD levels (parentheses).

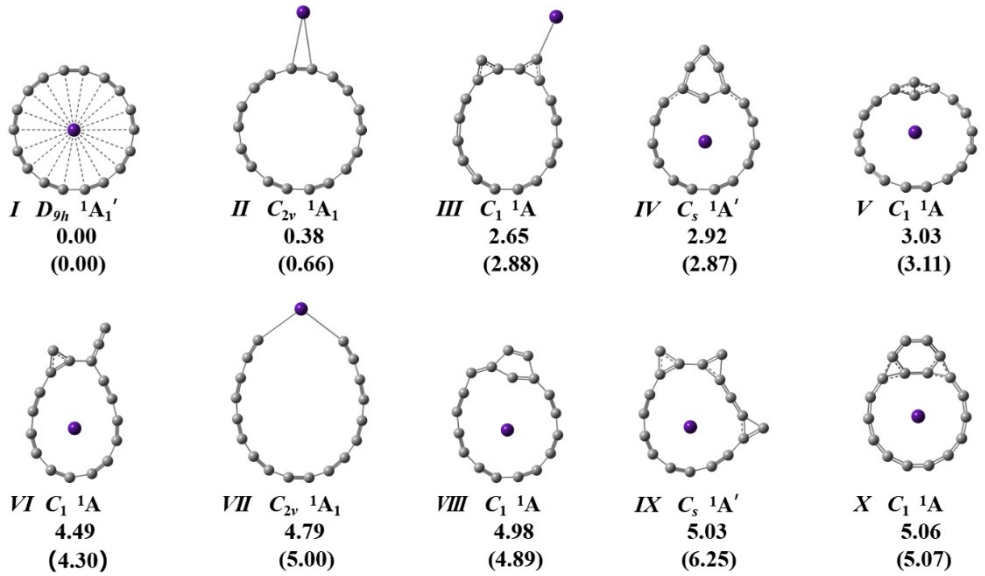


Fig. S4 Relative energies (in eV) of the low-lying isomers of $Cs©C_{17}B$ at M06-2X and ωB97XD levels (parentheses).

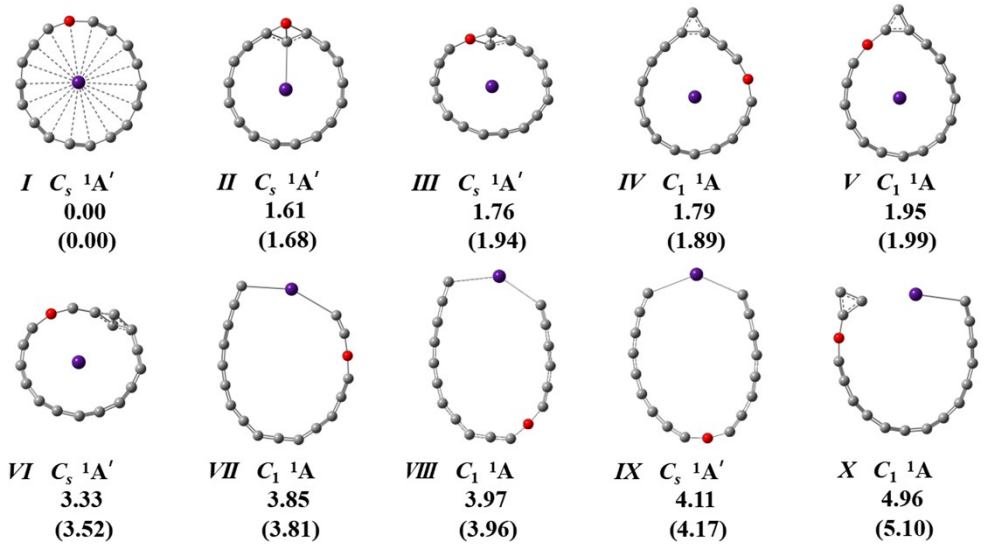


Fig. S5 Relative energies (in eV) of the low-lying isomers of $Cs©C_{17}^-$ at M06-2X and ωB97XD levels (parentheses).

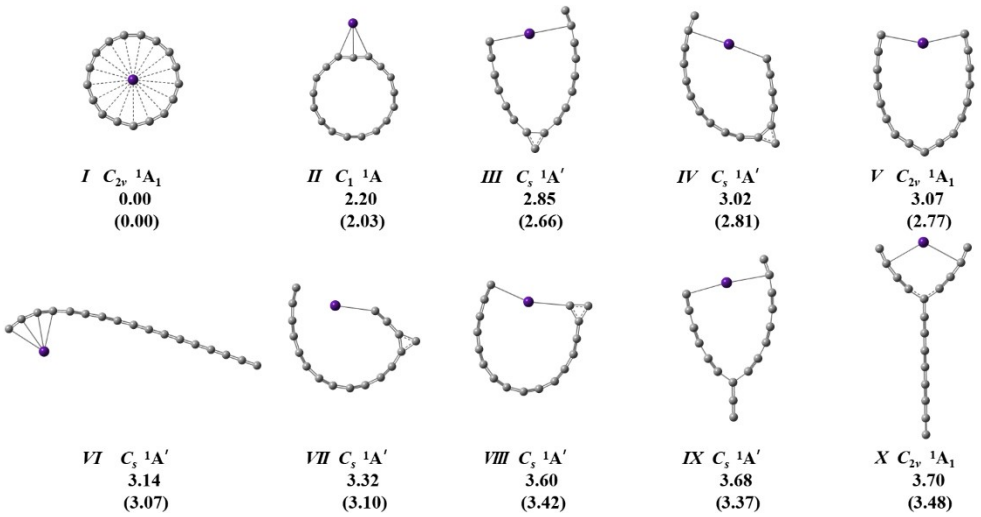


Fig. S6 Relative energies (in eV) of the low-lying isomers of $Na©C_{14}^+$ at M06-2X and ωB97XD levels (parentheses).

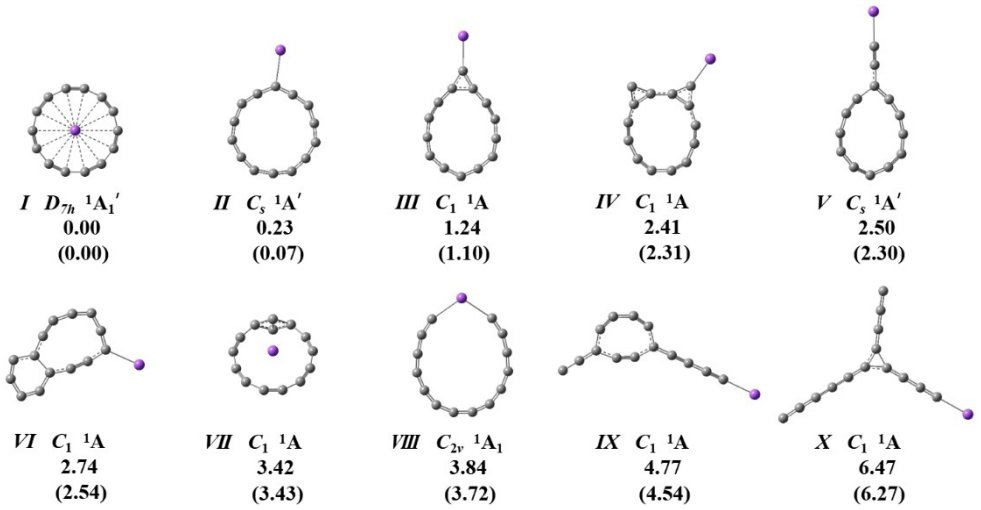


Fig. S7 Relative energies (in eV) of the low-lying isomers of Na©$C_{13}B$ at M06-2X and ωB97XD levels (parentheses).

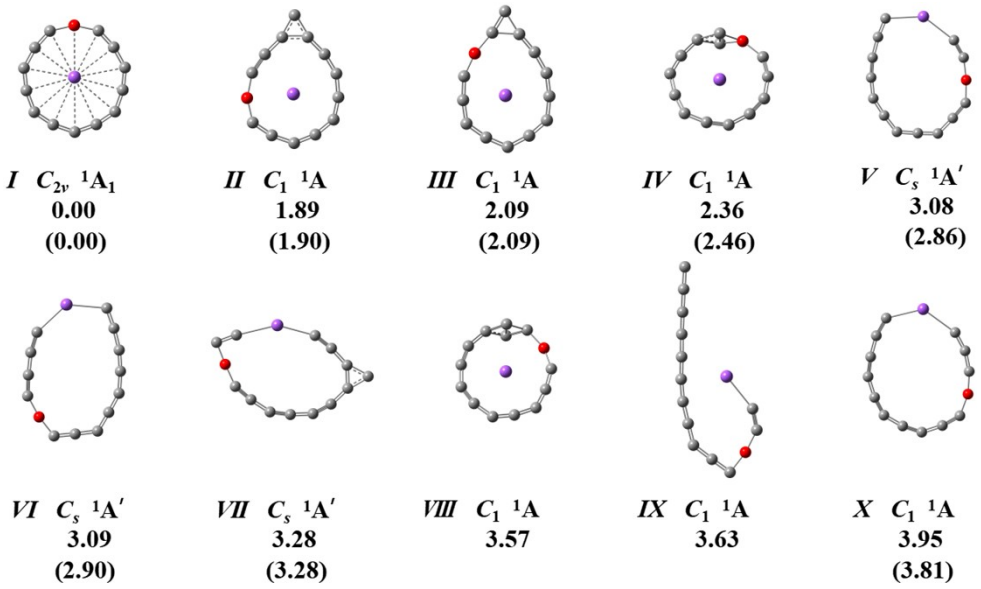


Fig. S8 Relative energies (in eV) of the low-lying isomers of Na©C_{13}^- at M06-2X level.

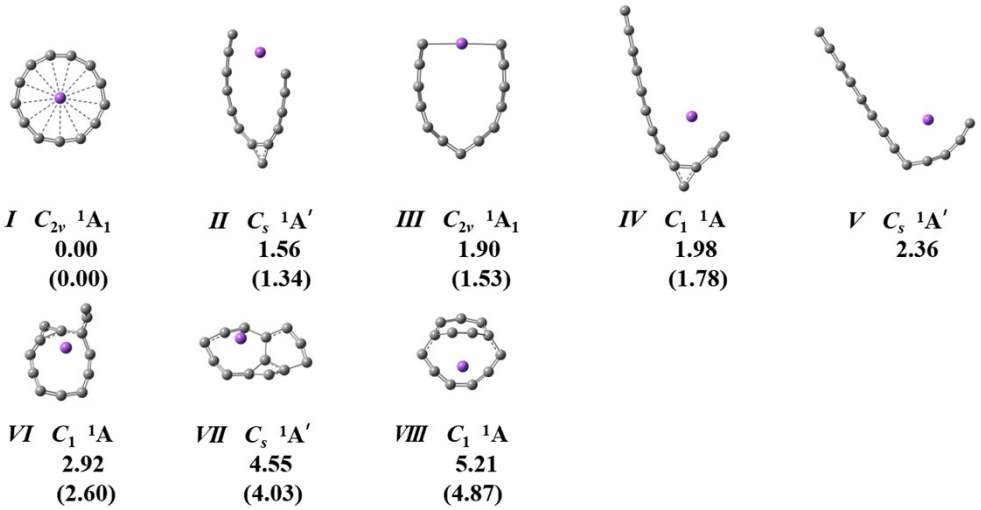


Fig. S9 Simulated IR, Raman, and UV-vis spectra (with 100 excited states included） of (a) D_{9h} Cs©C_{18}^{+} (**1**) and (b) D_{7h} Na©C_{14}^{+} (**4**) at M06-2X/aug-cc-pvtz level.

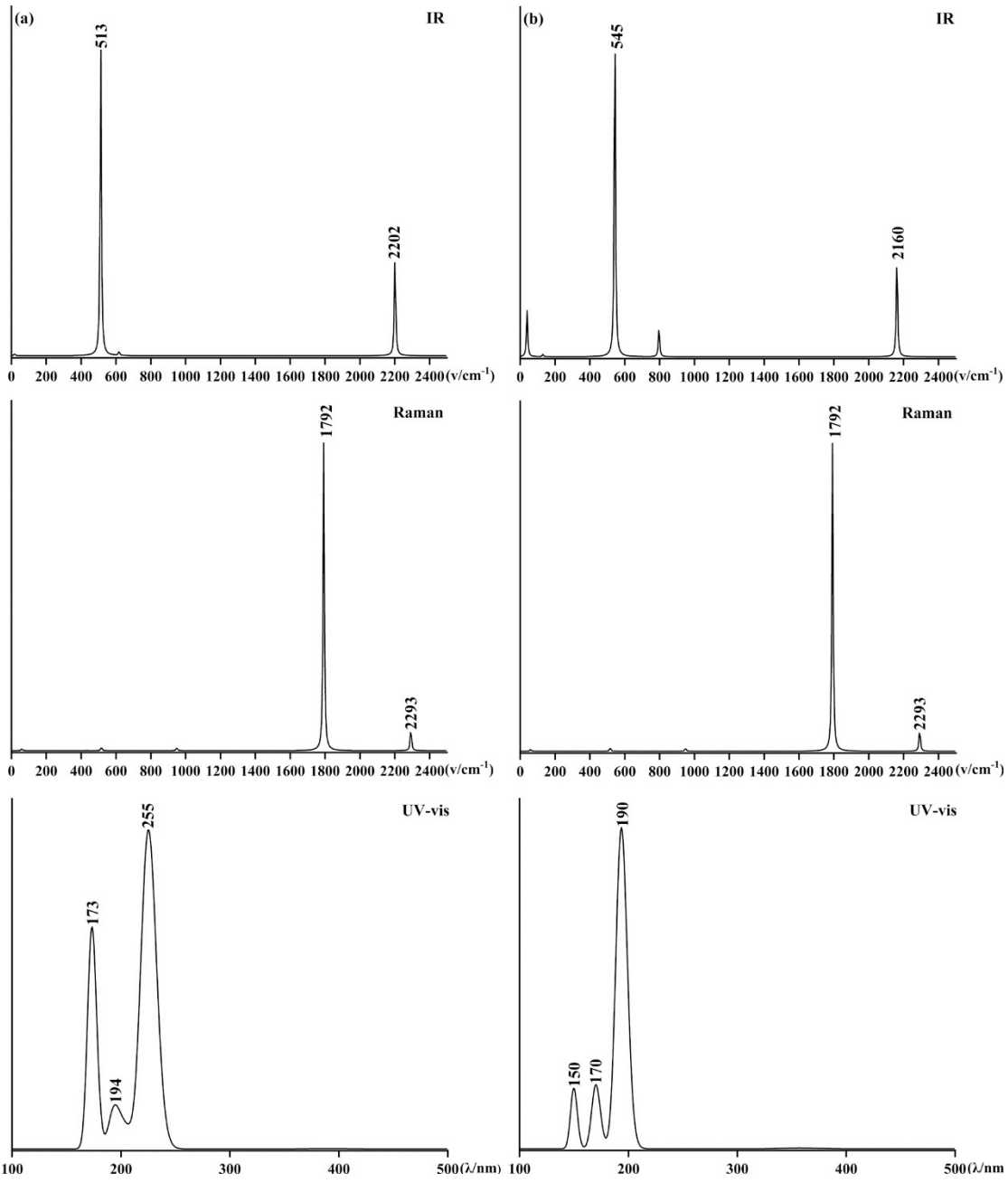
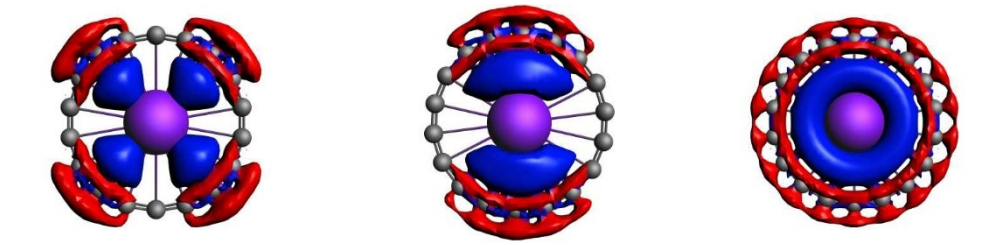


Fig. S10 Deformation densities $\Delta\rho_{(1)\text{-}(3)}$ Cs©C_{18}^{+} (**1**) associated with the orbital interactions $\Delta E_{(1)\text{-}(3)}$ tabulated in Table S2. Only one component of the orbital terms is shown. The color code of the charge flow is from red to blue.

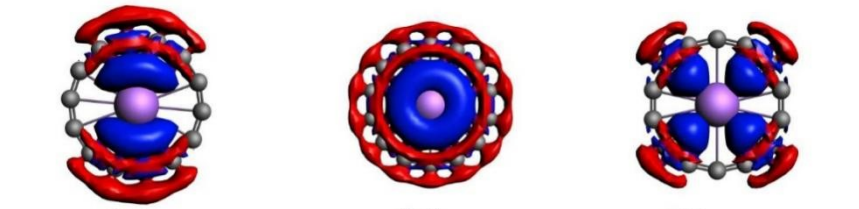


(a) $\triangle\rho_{(1)}$ $\triangle E_{\text{orb}(1)}$ = -1.92 kcal/mol (×2)

(b) $\triangle\rho_{(2)}$ $\triangle E_{\text{orb}(2)}$ = -1.17 kcal/mol (×2)

(c) $\triangle\rho_{(3)}$ $\triangle E_{\text{orb}(3)}$ = -1.96 kcal/mol

Fig. S11 Deformation densities $\Delta\rho_{(1)\text{-}(3)}$ of Na©C_{14}^{+} (**4**) associated with the orbital interactions $\Delta E_{(1)\text{-}(3)}$ tabulated in Table S3. Only one component of the orbital terms is shown. The color code of the charge flow is red to blue.



(a) $\triangle\rho_{(1)}$ $\triangle E_{\text{orb}(1)}$ = -2.79 kcal/mol (×2)

(b) $\triangle\rho_{(2)}$ $\triangle E_{\text{orb}(2)}$ = -4.30 kcal/mol

(c) $\triangle\rho_{(3)}$ $\triangle E_{\text{orb}(3)}$ = -2.03 kcal/mol (×2)

Fig. S12 AdNDP bonding pattern of C_s Cs©C_{17}B (**2**), with the occupation numbers indicated.

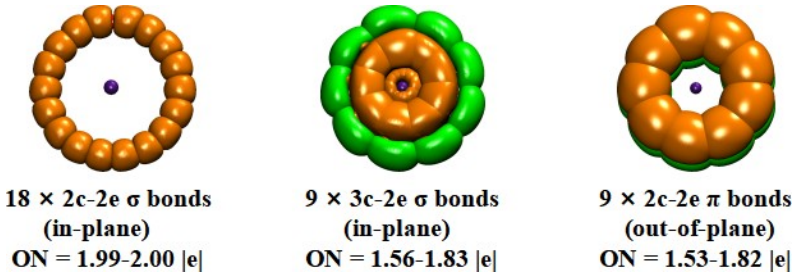
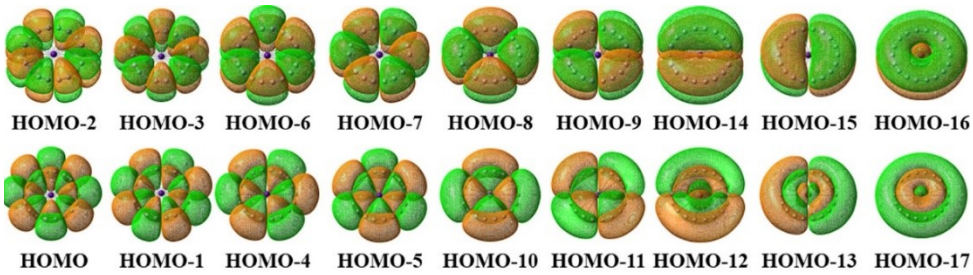


Fig. S13 The nine delocalized out-of-plane π MOs and nine delocalized in-plane σ MOs of D_{9h} Cs©C_{18}^+ (**1**) (a) and seven delocalized out-of-plane π MOs and seven delocalized in-plane σ MOs of D_{7h} Na©C_{14}^+ (**4**).

(a) Cs©C_{18}^+ (**1**)



(b) Na©C_{14}^+ (**4**)

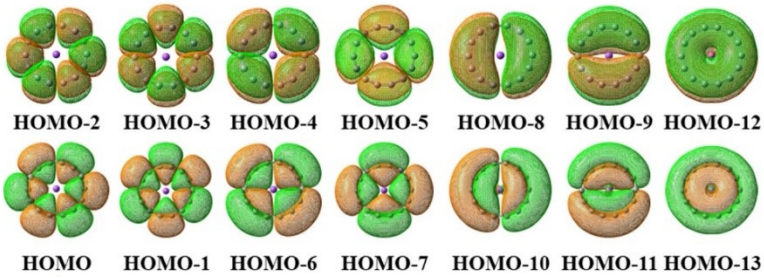


Table S1 Comparison of the calculated HOMO-LUMO gaps (ΔE_{gap}) and optimized bond lengths (r_{C-C} and $r_{C\equiv C}$) of D_{9h} $[Cs©C_{18}]^+$ (**1**) and D_{7h} $[Na©C_{14}]^+$ (**4**) and their polyynic cyclo[n]carbon ligands D_{9h} C_{18} and D_{7h} C_{14}.

	ΔE_{gap}/eV	r_{C-C}/Å	$r_{C\equiv C}$/Å
D_{9h} $[Cs©C_{18}]^+$	5.38	1.343	1.224
D_{9h} C_{18}	5.31	1.345	1.226
D_{7h} $[Na©C_{14}]^+$	5.87	1.326	1.240

D_{7h} C_{14}	5.77	1.324	1.237

Table S2 Comparison of EDA analyses of D_{9h} Cs©C_{18}^+ (**1**) in two different schemes ($Cs^+ + C_{18}$ and $Cs + C_{18}^+$) at M06-2X/TZ2P-ZORA level. All energy values are in kcal mol^{-1}.

Energy terms	**Interacting fragments**	
	$Cs^+ + C_{18}$	$Cs + C_{18}^+$
ΔE_{int}	-15.22	-1102.48
ΔE_{Pauli}	1.89	263.26
ΔE_{elstat}	-3.16	-261.13
ΔE_{orb}	-13.95	-1104.61

Table S3 Compositions from the C_{18} and Cs^+ to the $20e_1$', $19e_1$' and $15a_1$' MOs of D_{3h} Cs©C_{18}^+.

MOs	**Compositions**
$20e_1$'	98.05% (C_{18} $14e_1$') + 1.89% (Cs^+ $14e_1$')
$19e_1$'	96.61% (C_{18} $13e_1$') + 2.81% (Cs^+ $6e_1$') + 0.59% ($10e_1$')
$15a_1$'	98.10% (C_{18} $8a_1$') + 0.85% (Cs^+ $8a_1$')

Table S4 Compositions from the C_{14} and Na^+ to the $5e_2$', $6e_1$' and $6a_1$' MOs of D_{7h} Na©C_{14}^+.

MOs	**Compositions**

$5e_2'$	98.28% (C_{14} $5e_2'$) + 1.24% (Na^+ $1e_2'$)
$6e_1'$	96.26% (C_{14} $3e_1'$) + 3.42% (Na^+ $2e_1'$)
$6a_1'$	96.27% (C_{14} $4a_1'$) + 2.53% (Na^+ $3a_1'$)

Table S5 Optimized coordinates (x, y, z) of D_{9h} Cs©C_{18}^+ (**1**), C_s Cs©C_{17}B (**2**), C_{2v} Cs©C_{17}^- (**3**), D_{7h} Na©C_{14}^+ (**4**), C_{2v} Na©C_{13}B (**5**), and C_{2v} Na©C_{13}^- (**6**) at M06-2X level.

Cs©C_{18}^+ (**1**)

C	-0.61185300	3.64473100	0.00000000
C	-1.87408200	3.18531800	0.00000000
C	-2.81149500	2.39873500	0.00000000
C	-3.48311200	1.23545800	0.00000000
C	-3.69560700	0.03034400	0.00000000
C	-3.46235600	-1.29248600	0.00000000
C	-0.67161800	-3.63419300	0.00000000
C	0.67161800	-3.63419300	0.00000000
C	0.61185300	3.64473100	0.00000000
C	1.87408200	3.18531800	0.00000000
C	2.81149500	2.39873500	0.00000000
C	3.48311200	1.23545800	0.00000000
C	3.69560700	0.03034400	0.00000000
C	3.46235600	-1.29248600	0.00000000
C	2.85050300	-2.35224600	0.00000000
C	1.82152500	-3.21566100	0.00000000
C	-2.85050300	-2.35224600	0.00000000
C	-1.82152500	-3.21566100	0.00000000
Cs	0.00000000	0.00000000	0.00000000

Cs©C_{17}B (**2**)

C	-3.50078000	-1.29928000	0.00000000
C	-3.59256600	-0.05583100	0.00000000
C	-3.42944600	1.24615000	0.00000000
C	-2.71672900	2.27906400	0.00000000
C	-1.80615200	3.20987100	0.00000000
C	-0.59225300	3.57395600	0.00000000

C	3.03714500	2.30727600	0.00000000
C	3.50860200	1.16777200	0.00000000
C	-2.80903800	-2.42264800	0.00000000
C	-1.93335900	-3.30178500	0.00000000
C	-0.67555300	-3.71666500	0.00000000
C	0.55889300	-3.79050500	0.00000000
C	1.78574200	-3.28105700	0.00000000
C	2.75700700	-2.52017200	0.00000000
C	3.39799700	-1.35356200	0.00000000
C	3.68337000	-0.15532500	0.00000000
C	0.68968900	3.73847300	0.00000000
Cs	0.00000000	0.18013900	0.00000000
B	1.96491800	3.26759100	0.00000000

$Cs©C_{17}^-$ (**3**)

C	0.00000000	2.81836000	2.10611200
C	0.00000000	3.32079700	0.95158400
C	0.00000000	3.51825400	-0.34047400
C	0.00000000	3.08066800	-1.52952600
C	0.00000000	2.38021500	-2.62250800
C	0.00000000	1.24043700	-3.19830700
C	0.00000000	0.00000000	-3.54429200
C	0.00000000	-1.24043700	-3.19830700
C	0.00000000	-2.38021500	-2.62250800
C	0.00000000	-3.08066800	-1.52952600
C	0.00000000	-3.51825400	-0.34047400
C	0.00000000	-3.32079700	0.95158400
C	0.00000000	-2.81836000	2.10611200
C	0.00000000	-1.81873400	2.95755500
C	0.00000000	-0.65764900	3.43295500
C	0.00000000	0.65764900	3.43295500
C	0.00000000	1.81873400	2.95755500
Cs	0.00000000	0.00000000	0.00321900

$Na©C_{14}^+$ (**4**)

C	0.61977300	2.81465100	0.00000000
C	1.81416100	2.23946400	0.00000000
C	2.58700500	1.27034900	0.00000000
C	2.88199500	-0.02208500	0.00000000
C	2.60617000	-1.23055200	0.00000000

C	1.77962700	-2.26700400	0.00000000
C	-0.61977300	2.81465100	0.00000000
C	-1.81416100	2.23946400	0.00000000
C	-2.58700500	1.27034900	0.00000000
C	-2.88199500	-0.02208500	0.00000000
C	-2.60617000	-1.23055200	0.00000000
C	-1.77962700	-2.26700400	0.00000000
C	-0.66283600	-2.80482300	0.00000000
C	0.66283600	-2.80482300	0.00000000
Na	0.00000000	0.00000000	0.00000000

Na©$C_{13}B$ (**5**)

C	0.00000000	1.36516500	2.71479300
C	0.00000000	2.21557500	1.78203200
C	0.00000000	2.84087900	0.63856100
C	0.00000000	2.71276000	-0.62285600
C	0.00000000	2.27396700	-1.83892300
C	0.00000000	1.21350200	-2.54939600
C	0.00000000	-1.36516500	2.71479300
C	0.00000000	-2.21557500	1.78203200
C	0.00000000	-2.84087900	0.63856100
C	0.00000000	-2.71276000	-0.62285600
C	0.00000000	-2.27396700	-1.83892300
C	0.00000000	-1.21350200	-2.54939600
C	0.00000000	0.00000000	-2.97103200
Na	0.00000000	0.00000000	0.11157800
B	0.00000000	0.00000000	3.02166000

Na©C_{13}^{-} (**6**)

C	0.00000000	0.00000000	2.62603200
C	0.00000000	1.27381400	2.43815900
C	0.00000000	2.16824000	1.49434100
C	0.00000000	2.71777900	0.34364600
C	0.00000000	2.47868300	-0.94549100
C	0.00000000	1.81136300	-2.02100300
C	0.00000000	0.63103000	-2.60631900
C	0.00000000	-0.63103000	-2.60631900
C	0.00000000	-1.81136300	-2.02100300
C	0.00000000	-2.47868300	-0.94549100

C	0.00000000	-2.71777900	0.34364600
C	0.00000000	-2.16824000	1.49434100
C	0.00000000	-1.27381400	2.43815900
Na	0.00000000	0.00000000	-0.01783500