Supporting Information

Bonding character, electron delocalization, and aromaticity of cyclo[18]carbon (C\textsubscript{18}) precursors, C\textsubscript{18}-(CO)\textsubscript{n} (n = 6, 4, and 2): Focusing on the effect of -CO groups

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Table S1 Optimized Cartesian coordinates for studied precursors C_{18-(CO)}_n (n = 6, 4, and 2) at the ωB97XD/def2-TZVP level of theory

|   | x            | y            | z            |
|---|--------------|--------------|--------------|
| C | 3.24966659   | -2.66417240  | 0.00000000   |
| C | 1.88194072   | -2.91419814  | 0.00000000   |
| C | 0.67811438   | -3.02397837  | 0.00000000   |
| C | -0.67816777  | -3.02379520  | 0.00000000   |
| C | -1.88199645  | -2.91403269  | 0.00000000   |
| C | -3.24974722  | -2.66414362  | 0.00000000   |
| C | -3.93581418  | -1.48052714  | 0.00000000   |
| C | -3.47196216  | -0.16972226  | 0.00000000   |
| C | -2.96488518  | 0.92764304   | 0.00000000   |
| C | -2.28581203  | 2.10173299   | 0.00000000   |
| C | -1.58653975  | 3.08779618   | 0.00000000   |
| C | -0.68405830  | 4.14556403   | 0.00000000   |
| C | 0.68405151   | 4.14555722   | 0.00000000   |
| C | 1.58652437   | 3.08777518   | 0.00000000   |
| C | 2.28617912   | 2.10198119   | 0.00000000   |
| C | 2.96525790   | 0.92789879   | 0.00000000   |
| C | 3.47180659   | -0.16971246  | 0.00000000   |
| C | 3.93567632   | -1.48051811  | 0.00000000   |
| C | 4.50970759   | -3.51461135  | 0.00000000   |
| C | 5.30000945   | -2.15173394  | 0.00000000   |
| O | 4.75582235   | -4.66841350  | 0.00000000   |
| O | 6.42364400   | -1.79219398  | 0.00000000   |
| C | -0.78769561  | 5.66242543   | 0.00000000   |
| C | 0.78770138   | 5.66241538   | 0.00000000   |
| O | 1.66236925   | 6.45410995   | 0.00000000   |
| O | 1.66238080   | 6.45409444   | 0.00000000   |
| C | -5.30011963  | -2.15180712  | 0.00000000   |
| C | -4.50974251  | -3.51464903  | 0.00000000   |
| O | -6.42377005  | -1.79232271  | 0.00000000   |
| O | -4.75580300  | -4.66846189  | 0.00000000   |
| atom | x      | y      | z      |
|------|--------|--------|--------|
| C    | 4.15817096 | 0.38227472 | 0.00000000 |
| C    | 3.91808999 | -0.98424738 | 0.00000000 |
| C    | 3.52357179 | -2.12942996 | 0.00000000 |
| C    | 2.78970963 | -3.26470588 | 0.00000000 |
| C    | 1.86956647 | -4.05658178 | 0.00000000 |
| C    | 0.60734633 | -4.53698870 | 0.00000000 |
| C    | -0.60734633 | -4.53698870 | 0.00000000 |
| C    | -1.86956647 | -4.05658178 | 0.00000000 |
| C    | -2.78970963 | -3.26470588 | 0.00000000 |
| C    | -3.52357179 | -2.12942996 | 0.00000000 |
| C    | -3.91808999 | -0.98424738 | 0.00000000 |
| C    | -4.15817096 | 0.38227472 | 0.00000000 |
| C    | -3.27914680 | 1.43525045 | 0.00000000 |
| C    | -1.88838335 | 1.49719748 | 0.00000000 |
| C    | -0.67899834 | 1.53485613 | 0.00000000 |
| C    | 0.67899834 | 1.53485613 | 0.00000000 |
| C    | 1.88838335 | 1.49719748 | 0.00000000 |
| C    | 3.27914680 | 1.43525045 | 0.00000000 |
| C    | 5.38675055 | 1.27490473 | 0.00000000 |
| C    | 4.37933527 | 2.48356329 | 0.00000000 |
| O    | 6.55575040 | 1.11000619 | 0.00000000 |
| O    | 4.42905785 | 3.66291873 | 0.00000000 |
| C    | -5.38675055 | 1.27490473 | 0.00000000 |
| C    | -4.37933527 | 2.48356329 | 0.00000000 |
| O    | -6.55575040 | 1.11000619 | 0.00000000 |
| O    | -4.42905785 | 3.66291873 | 0.00000000 |
$$\text{C}_{18}-(\text{CO})_2 \text{ (charge = 0, spin multiplicity = 1)}$$

| atom | $x$  | $y$  | $z$     |
|------|------|------|---------|
| C    | 0.68776658 | 3.12191398 | 0.00000000 |
| C    | 1.59790167  | 2.07538066  | 0.00000000  |
| C    | 2.28730243  | 1.07785509  | 0.00000000  |
| C    | 2.85806442  | -0.14709834 | 0.00000000  |
| C    | 3.14137415  | -1.32903814 | 0.00000000  |
| C    | 3.08924402  | -2.67744632 | 0.00000000  |
| C    | 2.67356906  | -3.82117652 | 0.00000000  |
| C    | 1.77866177  | -4.83150897 | 0.00000000  |
| C    | 0.67504344  | -5.34629299 | 0.00000000  |
| C    | -0.67504344 | -5.34629299 | 0.00000000  |
| C    | -1.77866177 | -4.83150897 | 0.00000000  |
| C    | -2.67356906 | -3.82117652 | 0.00000000  |
| C    | -3.08924402 | -2.67744632 | 0.00000000  |
| C    | -3.14137415 | -1.32903814 | 0.00000000  |
| C    | -2.85806442 | -0.14709834 | 0.00000000  |
| C    | -2.28730243 | 1.07785509  | 0.00000000  |
| C    | -1.59790167 | 2.07538066  | 0.00000000  |
| C    | -0.68776658 | 3.12191398  | 0.00000000  |
| C    | 0.78627460  | 4.63602501  | 0.00000000  |
| C    | -0.78627460 | 4.63602501  | 0.00000000  |
| O    | 1.65984748  | 5.43103988  | 0.00000000  |
| O    | -1.65984748 | 5.43103988  | 0.00000000  |
Fig. S1 Optimized structural parameters and crystal structure data (in parentheses, from J Am Chem Soc 1991; 113: 495–500) of C_{18}-(CO)$_6$ molecule. Bond angles (left) in ° and bond lengths (right) in Å.
Fig. S2 STM image of constant height mode for precursors $C_{18}(CO)_n$ ($n = 6, 4, \text{ and } 2$) above 0.7 Å of the ring plane with a bias voltage of -3.5 V. The color scale is given in arbitrary unit.
**Fig. S3** Plot of the bond length versus bond order for precursors $\text{C}_{18}^-$$(\text{CO})_6$. 
Fig. S4 Plot of the bond length versus bond order for precursors C_{18}-(CO)_{4}.
Fig. S5 Plot of the bond length versus bond order for precursors $C_{18}$(CO)$_2$. 
**Fig. S6** Isosurface map of occupied π molecular orbitals ($\pi^\text{out}$ and $\pi^\text{in}$, isovalue = 0.05 au) for $\text{C}_{18^-}\text{(CO)}_6$. Green and blue regions denote the positive and negative orbital phases, respectively. Orbital indices are labelled.
Fig. S7 Isosurface map of occupied $\pi$ molecular orbitals ($\pi^\text{out}$ and $\pi^\text{in}$, isovalue = 0.05 au) for C$_{18}$(CO)$_4$. Green and blue regions denote the positive and negative orbital phases, respectively. Orbital indices are labelled.
Fig. S8 Isosurface map of occupied $\pi$ molecular orbitals ($\pi^{\text{out}}$ and $\pi^{\text{in}}$, isovalue = 0.05 au) for $\text{C}_{18^-}(\text{CO})_2$. Green and blue regions denote the positive and negative orbital phases, respectively. Orbital indices are labelled.
**Table S2** Bifurcation values of isosurface except for the breakpoint near -CO groups

| Species      | LOL out | LOL in | ELF out | ELF in |
|--------------|---------|--------|---------|--------|
| $\text{C}_{18}^-\text{(CO)}_6$ | 0.50    | 0.42   | 0.51    | 0.41   |
| $\text{C}_{18}^-\text{(CO)}_4$ | 0.49    | 0.39   | 0.53    | 0.36   |
| $\text{C}_{18}^-\text{(CO)}_2$ | 0.48    | 0.38   | 0.55    | 0.34   |
Fig. S9 Isosurfaces of ELF-\(\pi\) of \(\text{C}_{18-}(\text{CO})_{n}\) \((n = 6, 4,\) and 2\). The isovalues are set to be their respective bifurcation value (see Table S2) of isosurface except for the breakpoint near -CO groups.
**Fig. S10** Color-filled map of ELF-$\pi^{\text{out}}$ at 0.5 Å above the ring and ELF-$\pi^{\text{in}}$ on the ring plane of $\text{C}_{18}-(\text{CO})_n$ ($n = 6, 4, \text{and} 2$). The scales of color bars are in au.
**Fig. S11** Isosurfaces (isovalue = 0.03 au) of ACID for all $\pi$ electrons of $C_{18-}(CO)_n$ ($n = 6, 4, \text{ and } 2$). The external magnetic field is perpendicular to the ring plane and points outward. The green arrows represent direction and magnitude of the ring current at various positions on the ACID isosurfaces.