



Article

Structural, Aromatic, Optical and Reactive Features of $C_{12}-(CO)_n$ ($n = 2, 4, 6$): A DFT Study

Xin Chen , Pei-Pei Li * and Guang-Nian Xu *

School of Materials and Chemical Engineering, West Anhui University, Lu'an 237012, China; cx810101@163.com

* Correspondence: 22000043@wxc.edu.cn (P.-P.L.); 02000059@wxc.edu.cn (G.-N.X.)

Abstract

The geometric, electronic, spectroscopic, adsorption, and reactive properties of $C_{12}-(CO)_n$ ($n = 2, 4, 6$) were systematically investigated using density functional theory at the ω B97XD/def2-TZVP level. All three molecules adopt planar structures with pronounced bond length alternation along the C_{12} skeleton. Multi-index bonding analyses reveal significant π -electron localization at short C–C bonds rather than full-ring delocalization. As the number of OCCO fusion units increases, molecular symmetry evolves from C_{2v} to D_{2h} and further to D_{3h} . Aromaticity assessments using AV1245, HOMA, FLU- π , and ELF- π consistently indicate the absence of global aromaticity; OCCO fusion primarily disrupts π_{in} delocalization while leaving π_{out} conjugation comparatively less affected. Simulated UV-Vis spectra show that increasing OCCO units shifts the dominant absorption band toward the ultraviolet region, with low-energy excitations confirmed as locally excited states dominated by charge redistribution within the C_{12} ring. vdW potential calculations disclose an anomalous adsorption strength sequence for light noble gases (He > Ne), and it is contrary to the counterpoise-corrected interaction energy results. Local electron attachment energy (LEAE) and orbital-weighted dual descriptor (OWDD) jointly demonstrate that the intrinsic electron-accepting reactivity follows $C_{12}-(CO)_6 > C_{12}-(CO)_4 > C_{12}-(CO)_2$, qualitatively consistent with LUMO energy lowering yet modulated by electron-attachment relaxation effects. This work provides theoretical insights into the structure–bonding–reactivity relationships of OCCO-fused carbon macrocyclic systems.

Keywords: $C_{12}-(CO)_n$ ($n = 2, 4, 6$); Aromaticity; UV-Vis spectra; adsorption properties; reactive properties

1. Introduction

Cyclo[n]carbons are a family of monocyclic ring compounds which are composed entirely of sp-hybridized carbon atoms; they have attracted considerable attention in recent years. Among this family, cyclo[18]carbon (C_{18}) has been the subject of extensive theoretical [1–8] and experimental investigations since its first condensed-phase observation [9,10]. More recently, the on-surface method has been successfully applied to the syntheses of cyclo[n]carbon ($n = 10, 12, 14, 20$) [11,12], marking a significant advance in the experimental accessibility of smaller cyclocarbons. Acetylene pyrolysis in a neon atmosphere under pressure may provide another method for synthesizing the C_{12} ring [13].

Theoretical studies have revealed that C_{12} exhibits pronounced anti-aromatic character, with in-plane and out-of-plane double π anti-aromaticity [14,15]. Recently, the potential applications of cyclo[n]carbon systems have attracted growing theoretical interest. Screening of $M_3O@C_{2n}$ ($n = 5–10$, M = Li, Na, and K) confirmed that $Li_3O@C_{20}$ exhibits the best



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nonlinear optical (NLO) properties among all the involved species [16]. Anti-aromatic cyclo[4n]carbon-based frameworks ($n = 3-8$) may show nonlinear transport behavior when coupled with different electrodes [17]. Calculations on gas storage and sensing of cyclo[2n]carbon ($n = 6-8$) indicate that the adsorption strength for gases increases with the value of n and the polarity of gas molecules. Meanwhile, the adsorption stability is mainly due to London dispersion forces [18].

In contrast to cyclo[18]carbon (C_{18}), investigations into cyclo[12]carbon (C_{12}) are far less in-depth. $C_{18}-(CO)_6$ (the fusion of three ethylenedione OCCO units with the C_{18} ring) has been used as a precursor for synthesizing C_{18} [9]. But up to now, the precursors for synthesizing C_{12} are limited to halogenated polycyclic aromatic hydrocarbons (PAHs) and acetylene [11,13]. It remains an open question whether $C_{12}-(CO)_n$ ($n = 2, 4, 6$) could serve as potential precursors for preparing C_{12} . On the other hand, geometries, aromaticity and nonlinear properties of $C_{18}-(CO)_n$ ($n = 2, 4, 6$) have been comprehensively investigated. However, because the C_{12} and C_{18} rings have drastically different aromaticity, namely, doubly antiaromaticity [11,12] vs. doubly aromaticity [1,19], it is unclear whether the fusion of OCCO onto C_{12} and C_{18} rings induces identical effects. All these aspects are not well understood.

Inspired by these considerations, we designed $C_{12}-(CO)_n$ ($n = 2, 4, 6$), in which the C_{12} ring is fused with varying numbers of ethylenedione (OCCO) four-membered fragments. This series provides a suitable platform to investigate how the number of -CO groups modulates the geometric, electronic, spectroscopic, and reactive properties of the C_{12} -based macrocyclic framework. Through comprehensive density functional theory (DFT) calculations at the $\omega B97XD/def2-TZVP$ level, we have characterized these systems from multiple perspectives: geometric structures and bonding characteristics (bond lengths, bond orders), π -electron distribution (IRI- π , LOL- π), orbital interactions and charge transfer (EDD, ECDA), aromaticity (AV1245, HOMA, FLU- π , ELF- π), UV-Vis absorption spectra (including hole-electron analysis), van der Waals and electrostatic potentials, and local reactivity (LEAE and OWDD).

The present work intends to study the relationship between structure, properties and reactivity for $C_{12}-(CO)_n$ macrocycles, revealing how incremental carbonyl fusion progressively tunes the electronic structure and enhances the intrinsic electron-accepting reactivity. These findings may offer theoretical guidance for the rational design and functional modification of related carbon-oxide cyclic π -systems.

2. Computational Details

Geometry optimizations and frequency calculations (at the $\omega B97XD$ [20]/def2-TZVP [21] level) and UV-Vis spectra calculations (at the TD- $\omega B97XD/def2-TZVP$ level) were performed using Gaussian 16 Revision C.02 software [22]. All other calculations were carried out using Multiwfn 3.8 (dev) [23,24]. Except for ESP (electrostatic potential) and LEAE isosurfaces generated by VMD [25], all other graphics were produced with Multiwfn 3.8 (dev) [23,24]. The use of $\omega B97XD/def2-TZVP$ was based on many previous similar studies [2,3,5,8,26–30]. Tight self-consistent field (SCF) convergence criteria were used for structural optimization and TD-DFT calculations, with thresholds of 1.00×10^{-8} for the root mean square (RMS) variation in the density matrix, 1.00×10^{-6} for its maximum change, and 1.00×10^{-6} for the energy change.

3. Results

3.1. Geometric Structures

The optimized Cartesian coordinates for $C_{12}-(CO)_n$ ($n = 2, 4$, and 6) at the $\omega B97XD/def2-TZVP$ level are listed in Table S1. All three compounds are planar, with MPP (molecular

planarity parameters) and SDP (deviation from plane) [31] of 0 Å. C₁₂-(CO)_n can be regarded as a distorted closed-shell ethylenedione molecule (OCCO) bonded to the C₁₂ ring [32,33]. As shown in Figure 1, all the C–C bonds can be divided into five groups: C–C bonds of the C₁₂ ring (the shortest 1.20–1.21 Å, intermediate 1.36–1.37 Å, and the longest 1.40–1.41 Å), C–C bonds of OCCO moieties (1.57–1.58 Å), and C–C bonds linking the C₁₂ ring and OCCO (1.51–1.52 Å). For each classified bond type, the corresponding bond lengths vary by less than 0.01 Å across the three systems, indicating negligible bond length discrepancy. In contrast, distinct bond angle differences are observed. The internal angle of the four-membered ring (4MR) varies slightly across the three systems. The most prominent structural difference lies in the bond angles of the C₁₂ ring backbone and the junction between the C₁₂ ring and the 4-membered ring. For the latter, the outer angle changes from 138.8° (*n* = 2), to 141.5° (*n* = 4), and 137.6° (*n* = 6), while the corresponding inner angle varies from 127.3° (*n* = 2), to 124.5° (*n* = 4), and 128.3° (*n* = 6). Such systematic angular rearrangement is induced by directional stretching of the C₁₂ ring exerted by OCCO moieties at different positions. These bond length and bond angle values are nearly identical to those in the crystal structure data of C₁₈-(CO)₆ [33].

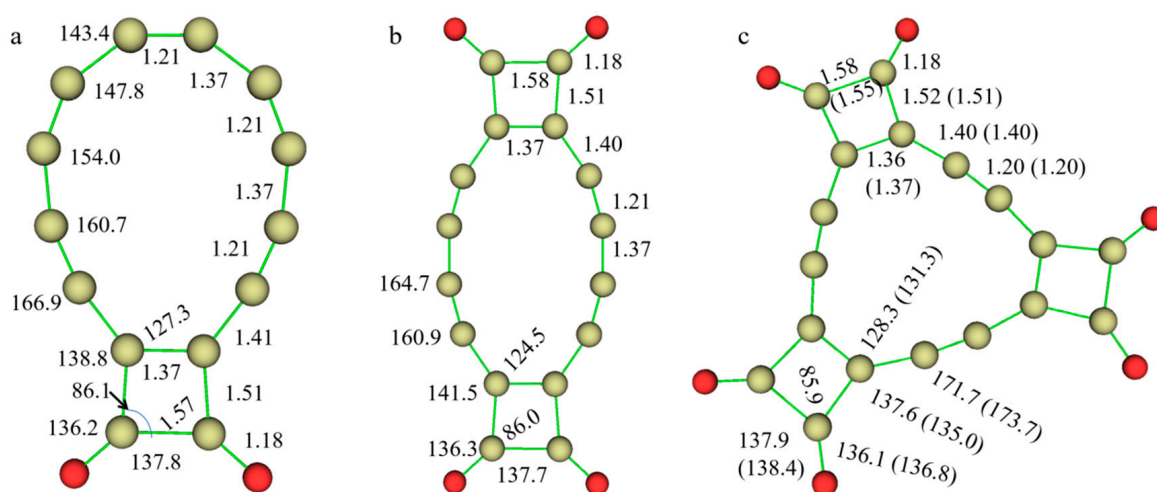


Figure 1. Optimized structural parameters of $C_{12}-(CO)_n$ ($n = 2$ (a), 4 (b) and 6 (c)) (data in parentheses are crystal structure data of $C_{18}-(CO)_6$). Bond angles (left) are given in $^\circ$ and bond lengths (right) are given in Å. C and O atoms are in orange and red, respectively.

OCCO can significantly distort the shape of the C₁₂ ring. The point groups for C₁₂-(CO)_n (*n* = 2, 4, and 6) are C_{2v}, D_{2h}, and D_{3h}, respectively. And the respective cavity diameters of the C₁₂ ring are 1.006 Å, 0.445 Å, and 1.042 Å (Figure S1). The cavity diameter of the C₁₂ ring for C₁₂-(CO)₄ is far smaller than those of C₁₂-(CO)₂ and C₁₂-(CO)₆; this is because of the strong stretching effect from the two opposite terminal OCCO groups. This discrepancy in cavity diameter can significantly modulate their van der Waals (vdW) adsorption and steric effects.

To evaluate the bond orders of C–C bonds and C–O bonds, five types of bond orders (Mayer [34], Wiberg [35], Laplacian [36], Mulliken [37] and Fuzzy [38]) were calculated (Figure S2 and Table S2). Mulliken bond order (MBO) is excluded from further analysis, because its arbitrary equal partitioning of overlap cross-terms leads to quantitative and qualitative errors for chemical bonds in $C_{12}-(CO)_n$ [37].

Mayer, Wiberg, Fuzzy and Laplacian bond orders show consistent trends that correlate well with computed bond lengths. Distinct bond-order alternation is observed along the C₁₂ backbone for all three species. High-order C–C bonds (Mayer > 2.5, Wiberg > 2.4) feature prominent multiple-bond character; they originate from local π -electron accumulation, and

correspond to short bond lengths near 1.21 Å. The adjacent linkages exhibit intermediate bond-order values (1.1–1.5) and intermediate bond lengths (~1.37 Å). This alternation reveals π -electrons are localized more on high-order sites instead of uniformly delocalized over the whole ring.

Within the four-membered cycle of all three species, the Mayer, Wiberg, Fuzzy and Laplacian bond orders of the C–C bonds in OCCO moieties and the C–C bonds between OCCO and C_{12} ring are all slightly lower than 1.0. It indicates that these C–C bonds are all single bond. But for the fused C–C bonds between the four-membered cycle and the C_{12} ring, the four kinds of bond orders are all about 1.5, and slightly larger than those of other C–C bonds with the same bond lengths (~1.37 Å). Hence, it can be concluded that the fused C–C bond has more π -electrons delocalized. Mayer, Wiberg and Fuzzy bond orders of C–O bonds are all in the range of 2–3; it implies that C–O bonds lie between those of double and triple bonds. But Laplacian bond orders (LBO) of C–O bonds of all three species are all lower than 2.0, it yields relatively low values for these C–O bonds.

To verify the reliability of structural optimization based on the range-separated ω B97XD functional (22.2% short-range HF exchange and 100% long-range HF exchange, with range separation scale $\omega = 0.2 \text{ bohr}^{-1}$), geometry optimizations were also performed using cam-B3LYP (19% short-range HF exchange and 65% long-range HF exchange, with range separation scale $\omega = 0.33 \text{ bohr}^{-1}$) [39] and pbe1pbe functionals (25% HF exchange at all ranges) [40,41] with the unified def2-TZVP basis set. The maximum structural deviations among the three methods were 0.01 Å for bond lengths and 0.5° for bond angles (Figure S3 and Table S3), demonstrating that all functionals afforded almost consistent geometric configurations for the studied system. A comparison of Mayer bond orders of chemical bonds of $C_{12}-(CO)_n$ ($n = 2, 4$, and 6) calculated with the three functionals ω B97XD, CAM-B3LYP, and PBE1PBE using the def2-TZVP basis set was also performed (Table S4). The three methods yield consistent trends for the variation in Mayer bond order. (1) The C–C bond orders on the C_{12} ring exhibit an uneven bond order alternation. (2) All C–O bond orders are slightly greater than 2. (3) The C–C bonds within the OCCO moiety and the C–C bonds linking OCCO to the C_{12} ring are lower than 1.0. Hence, the ω B97XD/def2-TZVP level is reliable for analyzing the structures and chemical bonds of these compounds. Unless otherwise specified, the structures optimized at the ω B97XD/def2-TZVP level were adopted for all subsequent calculations.

3.2. Character of Bonding

To further visualize the π -electron distribution and intramolecular π interactions and verify the above bonding characteristics, IRI- π analyses were conducted for all three $C_{12}-(CO)_n$ systems (Figure 2). For the three kinds of C–C bonds of the C_{12} ring (the shortest C–C bonds of 1.20–1.21 Å, intermediate C–C bonds of 1.36–1.37 Å, and the longest C–C bonds of 1.40–1.41 Å), there are only annular IRI- π isosurfaces around the two former C–C bonds. And IRI- π isosurfaces of the shortest C–C bonds are broader than those of intermediate C–C bonds of 1.36–1.37 Å, implying that the shortest C–C bonds have larger π electron density. For the longest C–C bonds of 1.40–1.41 Å, the absence of annular IRI- π isosurfaces predict the weakest π electron density. The IRI- π color-filled maps can provide the same perspective as IRI- π isosurfaces. The blue IRI- π isosurfaces in the cavity of the C_{12} ring indicate the vdW interaction (Figure S4), and the fatter blue IRI- π isosurfaces within the C_{12} ring of $C_{12}-(CO)_4$ than in the other two species reveal the stronger vdW interaction. This is consistent with its smallest cavity diameter. The red IRI- π isosurfaces in the four-membered cycle demonstrate the notable repulsion in the four-membered cycle. In general, IRI- π isosurfaces imply that π -electrons are delocalized mainly at the shortest

and the intermediate C–C bonds of the C_{12} ring, demonstrating the localized nature of π -electron distribution within the C_{12} skeleton.

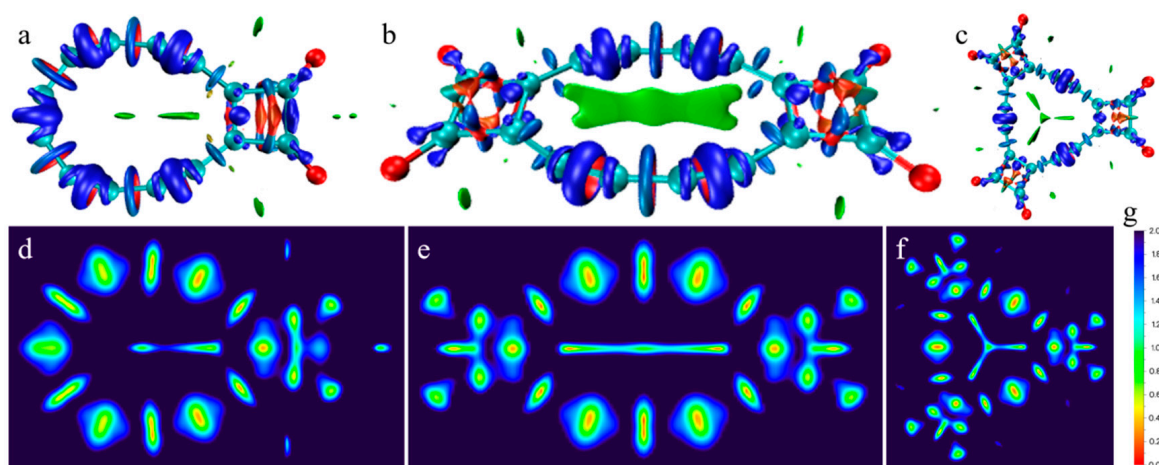


Figure 2. IRI- π isosurfaces (the first row, isovalue = 1.2 a.u.) and IRI- π color-filled maps (the second row) at 0.5 Å above the ring plane of $C_{12}-(CO)_n$ ((a,d) for $n = 2$, (b,e) for $n = 4$, (c,f) for $n = 6$). The scale of color bar for IRI- π color-filled maps (g) is given in a.u.

The IRI- π color-filled maps can provide the same perspective as IRI- π isosurfaces. The simulated STM (Scanning Tunneling Microscopy, Figure S5) image of $C_{12}-(CO)_n$ ($n = 2, 4$, and 6) also confirms the electron density difference as IRI- π isosurface.

The π delocalization character can be intuitively reflected by localized orbital locator for π electrons (LOL- π) [42]. As seen in Figure 3, isosurfaces of LOL- π_{in} and LOL- π_{out} of $C_{12}-(CO)_n$ ($n = 2, 4$, and 6) show the following characteristics: (1) -CO groups can exert a more pronounced effect on LOL- π_{in} than on LOL- π_{out} ; local delocalization is more obvious for LOL- π_{in} than LOL- π_{out} , and this effect increases with the number of -CO groups. (2) Whether for LOL- π_{in} or LOL- π_{out} , the C–C bonds of 1.40–1.41 Å bears relative smaller π electrons compared to other C–C bonds of the C_{12} ring, as can be seen in the truncated positions of LOL- π_{in} and LOL- π_{out} isosurfaces. (3) The electron localization of π electrons on the fused C–C bonds and the C–O bonds of -CO groups mainly arises from π_{out} electrons.

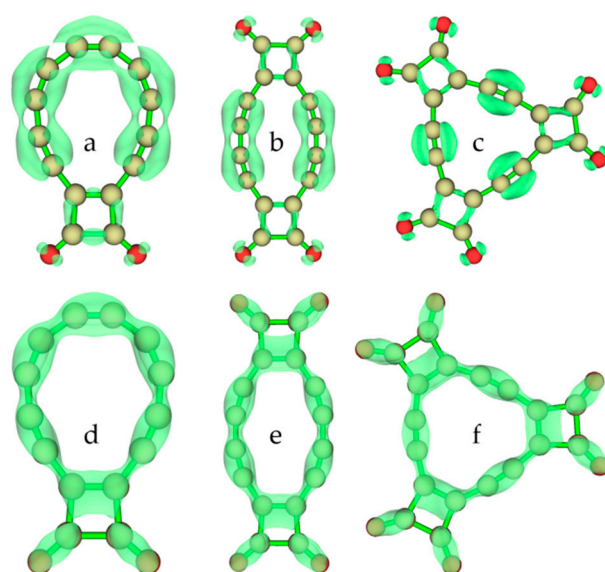


Figure 3. Isosurfaces of LOL- π_{in} (the first row) and LOL- π_{out} (the second row) of $C_{12}-(CO)_n$ ($n = 2$ (a,d), 4 (b,e), and 6 (c,f)). (Isovalue = 0.4 a.u.).

3.3. Orbital Interaction Analyses

When OCCO are bonded to the C_{12} ring, electron density difference (EDD) calculations were performed for $C_{12}-(CO)_n$ ($n = 2, 4, 6$). The calculation results confirm that electron density changes mainly occur on the OCCO and the C–C bonds of 4MR (Figure S6). Extended charge decomposition analyses (ECDA) [43,44] results indicate that for $C_{12}-(CO)_n$ ($n = 2, 4, 6$), the net numbers of electrons transferred from the C_{12} ring to OCCO are 0.1004 e, 0.1395 e, and 0.2258 e, respectively. In other words, each -CO group obtains 0.0502 e, 0.0349 e, and 0.0376 e from the C_{12} ring in $C_{12}-(CO)_n$ ($n = 2, 4, 6$), respectively.

Orbital interaction diagrams of $C_{12}-(CO)_n$ ($n = 2, 4, 6$), and contributions of fragment (C_{12} ring and closed-shell OCCO) orbitals to their frontier molecular orbitals are shown in Figure S7 and Table S5. The LUMO (the lowest unoccupied molecular orbital) of $C_{12}-(CO)_6$ is composed of C_{12} π_{out} orbital (89.97%) and OCCO σ orbital (8.21%), while its HOMO (the highest occupied orbital) consists of C_{12} π_{in} orbital (38.27%), OCCO π_{in} orbital (25.22%) and OCCO σ orbital (31.22%). These compositional differences result in the different bonding characters of the longer C–C bonds of the C_{12} ring of its LUMO and HOMO. The former bears more π -bond character, and the latter has only σ -bond character. Orbital interaction analyses are helpful for understanding bonding character, π electrons delocalization and localization scenario. The combination of OCCO with the C_{12} ring will lead to the dramatic C–C–C angle distortions (124.5 – 128.3° , Figure 1) in C_{12} ring near OCCO, and obviously decrease π_{in} electron delocalization in this region. Hence, the junction C–C bonds between the C_{12} ring and OCCO moieties have no annular IRI- π isosurfaces, and no LOL- π_{in} delocalization.

3.4. Aromaticity Analyses

The aromaticity and π -conjugation characteristics of the C_{12} ring of $C_{12}-(CO)_n$ ($n = 2, 4$, and 6) were systematically analyzed using geometric (HOMA, Harmonic Oscillator Model of Aromaticity [45]), real-space topological (ELF- π , Electron Localization Function- π [46]), and orbital/electron-delocalization (AV1245 [47] and FLU- π , Aromatic Fluctuation Index [48]) descriptors to reveal their intrinsic conjugation features. The physical meaning and limitations of HOMA, FLU- π , ELF- π and AV1245, together with the rationale for their combined application, are given in Text S1. The π_{in} and π_{out} molecular orbitals of $C_{12}-(CO)_n$ ($n = 2, 4$, and 6) are shown in Figure S8. Unless otherwise specified, the subsequent aromaticity discussion is restricted to the C_{12} ring of $C_{12}-(CO)_n$ ($n = 2, 4, 6$). Physical meaning, thresholds, and limitations of the aromaticity descriptors are listed in Text S1 [45,47–55].

The larger the AV1245 values, the stronger the delocalization and the higher the aromaticity. For $C_{12}-(CO)_n$ ($n = 2, 4, 6$), the total AV1245- π decreases monotonically from 1.04 ($n = 2$) to 0.56 ($n = 4$) and further to 0.40 ($n = 6$), indicating a progressive attenuation of π -aromatic character upon increasing -CO substitution (Table 1). An interesting inversion between AV1245- π_{in} and AV1245- π_{out} is observed along this series. At $n = 2$, AV1245- π_{in} (0.60) exceeds AV1245- π_{out} (0.44). As the number of -CO groups increases to $n = 4$ and $n = 6$, AV1245- π_{in} drops sharply to 0.14 and 0.09, respectively, becoming substantially smaller than the corresponding AV1245- π_{out} values (0.42 and 0.31). This reversal reveals that -CO groups exert a strong destructive effect predominantly on the π_{in} delocalization of $C_{12}-(CO)_n$, while the π_{out} delocalization is comparatively less perturbed. A similar overall downward trend in AV1245- π is found for the $C_{18}-(CO)_n$ ($n = 2, 4, 6$), which falls from 2.69 ($n = 2$) to 2.12 ($n = 4$) and 1.07 ($n = 6$). Distinct from the C_{12} series, AV1245- π_{in} is persistently lower than AV1245- π_{out} across all n values for $C_{18}-(CO)_n$. Even though AV1245- π_{in} turns negative (-0.53) at $n = 6$, the AV1245- π_{out} remains considerably high (2.18, 1.89, and 1.60

for $n = 2, 4$, and 6 , respectively). Analogous to the C_{12} series, the $-CO$ groups influence π_{in} delocalization more significantly than π_{out} delocalization for $C_{18}-(CO)_n$ [5].

Table 1. AV1245- π multicenter indices (total, π_{in} , and π_{out}) and minimum multicenter indices ($AV_{min-\pi}$, $AV_{min-\pi_{in}}$, $AV_{min-\pi_{out}}$) for C_{12} ring of $C_{12}-(CO)_n$ ($n = 2, 4$ and 6).

	AV1245- π_{in}	AV1245- π_{out}	AV1245	$AV_{min-\pi_{in}}$	$AV_{min-\pi_{out}}$	$AV_{min-\pi}$
$C_{12}-(CO)_2$	0.60 (0.51)	0.44 (2.18)	1.04 (2.69)	0.006	0.358	0.323
$C_{12}-(CO)_4$	0.14 (0.22)	0.42 (1.89)	0.56 (2.12)	0.016	0.107	0.229
$C_{12}-(CO)_6$	0.09 (−0.53)	0.31 (1.60)	0.40 (1.07)	0.013	0.153	0.317
C_{18}	1.73	2.52	4.25	–	–	–

Note: The values in parentheses are the corresponding values for $C_{18}-(CO)_n$ ($n = 2, 4$ and 6) [5].

The HOMA values for $C_{12}-(CO)_n$ are -2.41 , -1.87 , and -1.26 for $n = 2, 4$, and 6 , respectively. All values are negative, and their gradual increase toward zero suggests a modest geometric regularization with increasing CO substitution. Concurrently, the AV1245- π_{out} value decreases continuously from 0.44 to 0.31 , while FLU- π increases from 0.498 to 0.773 , indicative of deteriorated multicenter conjugation and growing π -electron inhomogeneity. $C_{12}-(CO)_4$ exhibits the lowest $AV_{min-\pi_{out}}$ (0.107), indicating a pronounced local disruption of cyclic conjugation at specific sites. The higher-symmetry $C_{12}-(CO)_6$ shows a slightly higher $AV_{min-\pi_{out}}$ (0.153) and a more uniform π distribution, yet retains the weakest overall multicenter delocalization within the series.

The real-space ELF- π_{out} results exhibit a slight trend opposite to that of the orbital descriptor AV1245- π_{out} (Figure S9, Tables 1 and 2). The ELF- π_{out} bifurcation values marginally increase from 0.415 to 0.425 with increasing $-CO$ substitution (Table 2). This difference arises mainly from the different ways in which the two descriptors are constructed. Some selected ELF- π_{in} /ELF- π_{out} orbitals are not strictly confined to the C_{12} ring; they may include contributions from the π orbitals and even partial σ orbitals of the 4MRs (Figure S9). In contrast, the evaluation of AV1245- π_{in} /AV1245- π_{out} , HOMA, and FLU- π involves only the atoms and bonds of the C_{12} ring and therefore does not directly include contributions from the 4MRs. Consequently, ELF- π_{out} reflects the real-space π -basin connectivity that may include contributions from the 4MRs, whereas AV1245- π_{out} provides a more direct measure of the intrinsic π delocalization within the C_{12} ring itself. This difference in construction does not affect the main conclusion, since ELF- π_{in} remains nearly zero (0.0012 – 0.0065) and far below ELF- π_{out} (0.415 – 0.425), while AV1245, HOMA, and FLU- π consistently indicate negligible π -aromaticity of the C_{12} ring.

Table 2. ELF- π bifurcation values (total, π_{in} , and π_{out}), HOMA indices, and FLU- π values for C_{12} ring of $C_{12}-(CO)_n$ ($n = 2, 4$ and 6). (All values are dimensionless.)

	ELF- π_{in}	ELF- π_{out}	ELF- π	HOMA	FLU- π
$C_{12}-(CO)_2$	0.0065	0.415	0.187	-2.410	0.498
$C_{12}-(CO)_4$	0.0025	0.425	0.195	-1.866	0.652
$C_{12}-(CO)_6$	0.0012	0.425	0.288	-1.258	0.773

Together with the qualitative LOL- π_{in} /LOL- π_{out} analysis (Figure 3), the quantitative AV1245- π_{in} /AV1245- π_{out} and ELF- π_{in} /ELF- π_{out} indices consistently indicate uneven π_{in} and π_{out} electron delocalization, with the π_{in} delocalization strength gradually decreasing as n increases.

In summary, for the C_{12} ring in $C_{12}-(CO)_n$ ($n = 2, 4$, and 6), the four descriptors consistently indicate negligible π -aromaticity. HOMA is strongly negative (-2.410 , -1.866 , and -1.258 for $n = 2, 4$, and 6 , respectively), far from the aromatic threshold of 1 , indicating

pronounced bond-length alternation. FLU- π is large (0.498, 0.652, and 0.773), well above aromatic threshold of 0 and consistent with nonaromatic or antiaromatic character. ELF- π is low (0.187, 0.195, and 0.288), far below the aromatic threshold of 0.70. In particular, ELF- π_{in} is nearly 0 (0.0012–0.0065), whereas ELF- π_{out} is 0.415–0.425, indicating that π localization occurs mainly outside the C_{12} ring rather than along the ring pathway. AV1245 is only 0.40–1.04, much lower than the benzene reference value 10.5–10.7, and AV $_{min}$ - π_{in} is only 0.006–0.016, further indicating very weak multicenter π delocalization along the C_{12} ring. Therefore, the present results provide reasonable converging evidence against aromaticity in the C_{12} ring within the limitations of the employed descriptors.

3.5. UV-Vis Spectra

The lowest-energy UV-Vis absorption spectra (oscillator strength $f > 0.003$) [56] and their CTS (charge-transfer spectra) of $C_{12}-(CO)_n$ ($n = 2, 4$, and 6) simulated with a full width at half maximum (FWHM) of 0.3 eV are shown in Figure 4. Simulated absorption spectra and CTS of $C_{12}-(CO)_2$ at 200–715 nm and 200–425 nm are displayed in Figure S10. Main excited-state parameters of the first 20 excited states of $C_{12}-(CO)_n$ ($n = 2, 4$, and 6) in the gas phase are listed in Table S6.

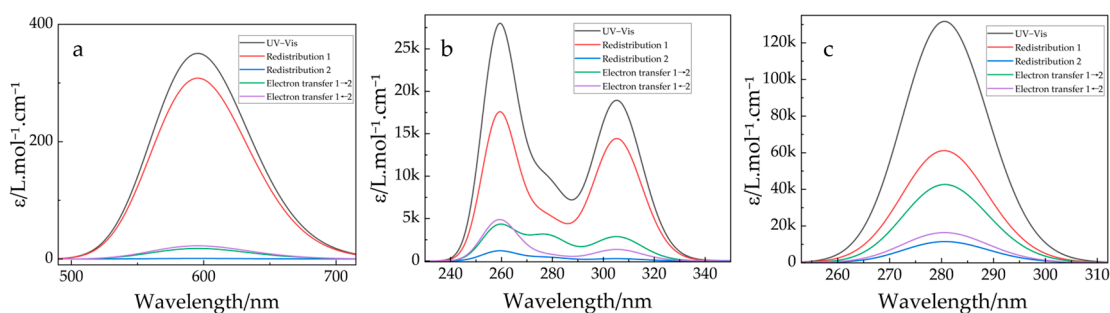


Figure 4. Simulated UV-Vis spectra (black curves) and charge-transfer spectra (CTSs, colored curves) of $C_{12}-(CO)_n$ ($n = 2$ (a), $n = 4$ (b), and $n = 6$ (c)) with FWHM 0.3 eV. For (a–c), fragment 1 and 2 are C_{12} ring and $(CO)_n$, respectively.

Increasing n in $C_{12}-(CO)_n$ ($n = 2, 4$, and 6) changes the absorption profile from weak transitions to intense UV absorption (Figure 4 and Table S6), and redistributes the oscillator strength from low-lying dark states to higher-energy mixed configurations. For $n = 2$, the absorption band near 595.5 nm is very weak ($S2, f = 0.0039$) and is not the main absorption; the strongest transition lies in the UV region around 260 nm ($S11, f \approx 0.07$). For $n = 4$ and 6, intense UV bands appear at 305.4 nm ($S8, f = 0.2100$) and 280.7 nm ($S11/S12, f = 0.7228$), respectively, and the maximum oscillator strength increases from 0.07 ($n = 2$) to 0.31 ($n = 4$) and 0.72 ($n = 6$). In contrast, the maximum absorption of $C_{18}-(CO)_n$ red-shifts from 225.0 to 294.5 and 344.0 nm [8]. This contrast reflects the distinct electronic response of the doubly anti-aromatic C_{12} ring [11,12] versus the doubly aromatic C_{18} ring [1,2].

To verify the reliability of the UV-Vis spectrum calculations at the TD- ω B97XD/def2-TZVP level, TD-CAM-B3LYP/def2-TZVP calculations were also performed based on the optimized structure at the ω B97XD/def2-TZVP level. As seen in Figure S11, Tables S7 and S8, the differences in the simulated UV-Vis spectra and related excited states parameters (excited energy, excited wavelength, oscillator strength and main molecular orbital transitions) between these two methods are minor. This indicates that the UV-Vis spectrum calculation results at the TD- ω B97XD/def2-TZVP level are reliable. Natural transition orbitals (NTO) analyses (Figure S12) reveal that $S8$ state of $C_{12}-(CO)_4$ has mixed characteristics of $\pi_{in} \rightarrow \pi_{in}^*$ and $\pi_{out} \rightarrow \pi_{out}^*$, while $S2$ state of $C_{12}-(CO)_2$ and $S11/S12$ state of $C_{12}-(CO)_6$ are almost solely $\pi_{out} \rightarrow \pi_{out}^*$ excitations.

For the overall CTS of both $C_{12}-(CO)_n$ and $C_{18}-(CO)_n$ ($n = 2, 4$, and 6), the main charge transfer occurs in the following sequence: inside the carbon (C_{12} or C_{18}) ring, from the carbon ring to OCCO, from OCCO to the carbon ring, and inside OCCO. The electron redistribution within the carbon ring dominates the electron excitations, and the electron redistribution within the OCCO group is almost negligible [8].

Hole–electron analyses [19] were performed to characterize the excited states responsible for the above-mentioned absorption bands. As shown in Table 3, the relevant states (S2 of $C_{12}-(CO)_2$, S8 of $C_{12}-(CO)_4$, and S11/S12 of $C_{12}-(CO)_6$) all exhibit small D values, large Sr values (about 0.8), and negative t values. According to the criteria given in Text S2, these features indicate that the hole and electron are not significantly separated, consistent with locally excited (LE) character. The hole and electron distributions in Figure S13 are mainly located on the C_{12} ring and the $-(CO)_n$ ($n = 2, 4$, and 6) groups and overlap substantially. Consistent with the CTS results (Figure 4), charge redistribution within the C_{12} ring provides the main contribution to these excitations, while the contributions from the OCCO moiety and C_{12} ring $\rightarrow$ OCCO charge transfer differ among the systems.

Table 3. Key electronic descriptors for selected excited states of $C_{12}-(CO)_n$ ($n = 2, 4$, and 6) in the gas phase (HDI and EDI are dimensionless.).

n	State	Sr (a.u.)	D (Å)	t (Å)	H (Å)	HDI	EDI	E_{coul} (eV)	Excitation Types
2	S2	0.773	0.413	−1.828	2.886	6.57	6.23	5.32	LE
4	S8	0.857	0	−0.885	3.047	5.74	4.78	5.21	LE
6	S11	0.809	0.255	−2.270	3.458	5.65	5.52	4.51	LE
	S12	0.818	0.256	−1.939	3.458	5.65	5.52	4.52	LE

Note: Sr , D , t , H , HDI, EDI and E_{coul} denote Sr index (integral of Sr function), D index, H index, t index, hole delocalization index, Electron delocalization index and Coulomb attractive energy, respectively.

3.6. Analyses of van der Waals (vdW) Potential and Electrostatic Potential (ESP)

In this section, a multi-step computational strategy is used to analyze rare gas adsorption on $C_{12}-(CO)_n$. The UFF (Universal Force Field)-based van der Waals potential (VvdW) [57] delivers preliminary qualitative screening under fixed molecular geometries. SAPT (symmetry-adapted perturbation theory) [58] energy decomposition using Psi4 [59] was performed on geometries optimized at the ω B97XD/def2-TZVP level to compare the relative magnitude of interaction components. BSSE (basis set superposition error)-corrected [60] DFT calculations on fully optimized structures at the ω B97XD/def2-TZVP level were carried out to provide quantitative binding energies and serve as the primary benchmark for adsorption strength.

UFF calculations show that the overall interaction order is $Xe > Ar > He > Ne$ for all $C_{12}-(CO)_n$ ($n = 2, 4$, and 6) species (Table S9 and Figure S14). SAPT0 energy decomposition analyses using the SAPT0/jun-cc-pVDZ method indicate that for a given n of $C_{12}-(CO)_n@He/Ne$ complexes, all four energy components (electrostatic, exchange repulsion, induction and dispersion) of the $C_{12}-(CO)_n@Ne$ exhibit larger magnitudes than those of the $C_{12}-(CO)_n@He$ (Table S10).

To verify the reliability of qualitative analysis results of van der Waals potential, the structures of $C_{12}-(CO)_n@He/Ne$ ($n = 2, 4, 6$) were optimized at the ω B97XD/def2-TZVP level using Gaussian 16 C.02 to provide geometries for ORCA [61] calculations. ORCA software (version 5.0.4) was utilized to assess basis set convergence and BSSE via multiple computational methods based on the optimized structures at the ω B97XD/def2-TZVP level, owing to its high computational efficiency. Benchmark calculations at the ω B97X-D3BJ level demonstrate that the counterpoise-corrected binding energies ΔE_{CP} of the six $C_{12}-(CO)_n@He/Ne$ systems exhibit only minor differences between def2-TZVP and the

larger, more polarized def2-QZVP basis set (Table S11). For $C_{12}-(CO)_2@He$, the ΔE_{CP} value obtained with def2-TZVP also agrees closely with that calculated using the diffuse augmented ma-def2-TZVP basis set. For instance, ΔE_{CP} of $C_{12}-(CO)_n@He$ is -0.392 kcal/mol (def2-TZVP), -0.393 kcal/mol (def2-QZVP), and -0.404 kcal/mol (ma-def2-TZVP). These benchmark results validate that the def2-TZVP basis set is adequate for the subsequent data analysis in this work.

Although the UFF-based van der Waals potential correctly captures the qualitative trend of vertical distances between He/Ne and the C_{12} ring, i.e., the vertical distance follows the order ($n = 4 > n = 6 > n = 2$) for $C_{12}-(CO)_n@He/Ne$ (Table S12), it underestimates the absolute values of these vertical distances. As exemplified by $C_{12}-(CO)_2@He$ (2.886 Å, DFT vs. 1.91 Å, UFF) and $C_{12}-(CO)_2@Ne$ (2.889 Å, DFT vs. 2.62 Å, UFF), this underestimation is especially pronounced for He, which may explain the anomalous V_{vdW} trend.

Figure 5 further characterizes the electrostatic properties of these planar $C_{12}-(CO)_n$ systems by mapping electrostatic potential (ESP) extrema [62,63] on electron-density isosurfaces. Their most negative ESP values are -26.97 ($n = 2$), -22.81 ($n = 4$) and -20.18 kcal·mol $^{-1}$ ($n = 6$), respectively. And these negative ESP extrema are concentrated around oxygen atoms of $-CO$ groups. The most positive ESP extrema of them are 28.98 ($n = 2$), 34.80 ($n = 4$) and 39.19 kcal·mol $^{-1}$ ($n = 6$), respectively. And these positive ESP extrema are all located on both sides of the C–C bonds of OCCO moieties. The second-largest positive ESP extrema are all situated on both sides of the fused C–C bonds between the 4MR and C_{12} ring, and the values are on average 19.56 ($n = 2$), 25.62 ($n = 4$), and 30.45 kcal·mol $^{-1}$ ($n = 6$), respectively. The positions of ESP extrema differ substantially from those of the vdW potential.

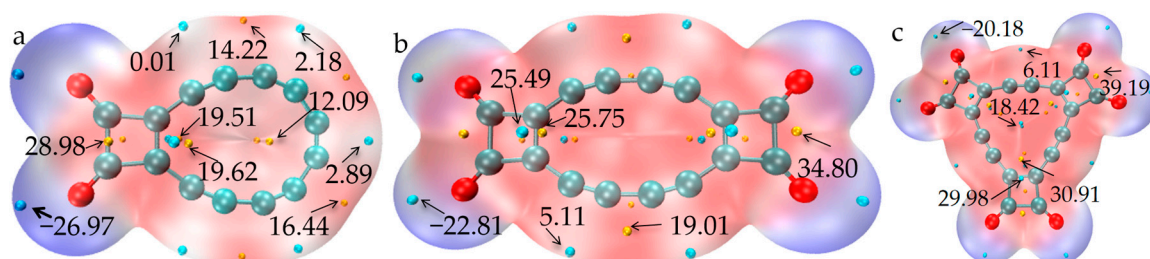


Figure 5. Molecular electrostatic potential extrema of $C_{12}-(CO)_n$: (a) ($n = 2$); (b) ($n = 4$); (c) ($n = 6$). The marked values correspond to ESP extrema in kcal·mol $^{-1}$. The small yellow spheres and cyan spheres denote local ESP maxima ($V_{S,max}$) and local ESP minima ($V_{S,min}$), respectively.

3.7. Reactivity

In this section, $C_{12}-(CO)_n$ ($n = 2, 4, 6$) are designated as substrates. To explore their reactivity, LEAE [64] and OWDD [65] (Text S3) were combined to characterize the local electronic reactivity (Figures 6 and S15). The dominant nucleophilic sites for all three $C_{12}-(CO)_n$ ($n = 2, 4, 6$) are invariably located on both sides of the molecular surface plane of the longest C–C bonds of the C_{12} ring. These sites possess the most negative LEAE values and the most extensive positive OWDD isosurfaces in each system, demonstrating superior electron-accepting affinity and predominant nucleophilic reactivity. Restricted by molecular symmetry, symmetry-equivalent reactive sites exhibit identical electronic characteristics.

The overall nucleophilic susceptibility of the system is gradually enhanced with increasing $-CO$ groups. The most negative LEAE values of the dominant active sites decrease progressively from -1.53 eV for $n = 2$ to -1.84 eV for $n = 4$, and further to -1.96 eV for $n = 6$. This trend is primarily attributed to the cumulative electron-withdrawing effect of $-CO$ groups. Hence, the final reactivity order follows $C_{12}-(CO)_6 > C_{12}-(CO)_4 > C_{12}-(CO)_2$. As the number of $-CO$ groups increases from $n = 2$ to $n = 6$, both HOMO and LUMO energies shift toward more negative values, accompanied by a gradual reduction in the HOMO–

LUMO gap (Table 4). Meanwhile, the molecular symmetry evolves from C_{2v} via D_{2h} to D_{3h} , which governs the count of equivalent reactive sites within the series. The decreasing LUMO energy qualitatively aligns with the trend toward more negative LEAE values at major active sites, although LEAE additionally accounts for electronic relaxation upon electron attachment. As presented in Figures 6 and S15, additional secondary nucleophilic reaction sites are different for the three species. These sites are situated on the exterior face of the C_{12} ring at the intermediate C–C bonds (1.37 Å) for $C_{12}-(CO)_2$, both faces of the C_{12} ring at the intermediate C–C bonds (1.37 Å) for $C_{12}-(CO)_4$, and both faces of the C_{12} ring at the C–C bonds of OCCO units for $C_{12}-(CO)_6$. And the corresponding values are -1.19 eV, -1.24 eV, and -1.38 eV, respectively. It is noteworthy that the OWDD isosurfaces of these positions are positive for the former two, and negative for the latter. Although both faces of the C_{12} ring at the C–C bonds of OCCO units for the three species exhibit certain nucleophilic reactivity, the negative OWDD isosurfaces indicate these sites are more susceptible to electrophilic reactivity.

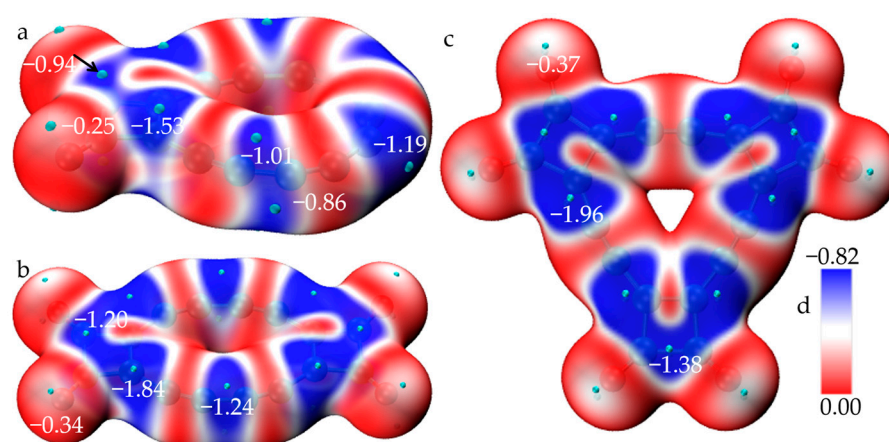


Figure 6. The LEAE (local electron attachment energy) on the molecular surface defined by an electron density of 0.004 a.u. ((a): $C_{12}-(CO)_2$; (b): $C_{12}-(CO)_4$; (c): $C_{12}-(CO)_6$; (d): color bar). All values are in eV.

Table 4. Frontier-orbital energies (eV) for $C_{12}-(CO)_n$ ($n = 2, 4, 6$).

	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)
$C_{12}-(CO)_2$	−8.69	−2.69	6.00
$C_{12}-(CO)_4$	−9.23	−3.26	5.97
$C_{12}-(CO)_6$	−9.47	−3.69	5.78

It is noteworthy that the present conclusions only reflect intrinsic electronically controlled reactivity tendencies. Factors including solvent effects, steric hindrance, and kinetic reaction barriers are not considered, and thus the predicted reactivity trend cannot be directly equated to experimental reaction observations.

4. Conclusions

In this work, the structural, electronic, and reactive properties of planar $C_{12}-(CO)_n$ ($n = 2, 4, 6$) were systematically characterized via multi-descriptor analyses.

First, the C_{12} skeleton exhibits pronounced bond-length alternation, with π -electrons localized at short bonds rather than delocalized over the macrocyclic ring. The decrease in AV1245 from 1.04 ($n = 2$) to 0.40 ($n = 6$), the increase in FLU- π from 0.498 to 0.773, and persistently negative HOMA values, consistently exclude global aromaticity. OCCO fusion suppresses π_{in} delocalization (AV1245- π_{in} : 0.60 $\rightarrow$ 0.09) far more strongly than π_{out}

(0.44 $\rightarrow$ 0.31), confirming that a single aromaticity index is insufficient for this class of functionalized π -macrocycles.

Second, simulated UV-Vis spectra show that increasing OCCO content shifts the dominant absorption bands toward the ultraviolet region; the strongest band for $n = 6$ appears at 280.7 nm. Hole–electron analyses verify that low-energy excitations are local excitations dominated by intra-ring charge redistribution. UFF-based vdW potential reveals an anomalous He > Ne adsorption strength sequence, and it differs from the BSSE-corrected DFT binding energy results obtained on fully optimized geometries.

Third, LEAE and OWDDs jointly establish the intrinsic electron-accepting reactivity order $C_{12}-(CO)_6 > C_{12}-(CO)_4 > C_{12}-(CO)_2$. The most negative LEAE values decrease progressively from -1.53 eV ($n = 2$) to -1.84 eV ($n = 4$) and -1.96 eV ($n = 6$). This trend arises from the cumulative electron-withdrawing effect of $-CO$ groups. Molecular symmetry evolves from C_{2v} through D_{2h} to D_{3h} with increasing n , governing the number of equivalent reactive sites.

In summary, $-CO$ substitution modulates reactivity intensity and the multiplicity of equivalent reactive sites in OCCO-fused macrocycles. This regulatory mechanism may be qualitatively transferable to analogous fused-ring systems, though further validation is required. This work may provide a helpful reference for synthesizing the C_{12} ring using $C_{12}-(CO)_n$ ($n = 2, 4, 6$) as precursors.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/nano16191254/s1>, Table S1: Optimized Cartesian coordinates for $C_{12}-(CO)_n$ ($n = 2, 4$, and 6) at the ω B97XD/def2-TZVP level; Figure S1: Cavity of $C_{12}-(CO)_n$; Figure S2: Numbering of chemical bonds of $C_{12}-(CO)_n$; Table S2: Bond orders of chemical bonds for $C_{12}-(CO)_n$ calculated at the ω B97XD/def2-TZVP level; Figure S3: Optimized structures and related structural parameters of $C_{12}-(CO)_n$ ($n = 2, 4$ and 6) at the CAM-B3LYP/def2-TZVP and PBE1PBE/def2-TZVP levels; Table S3: Comparison of bond lengths and bond angles of $C_{12}-(CO)_n$ ($n = 2, 4$, and 6) calculated with the three functionals ω B97XD, CAM-B3LYP, and PBE1PBE using the def2-TZVP basis set; Table S4: Comparison of bond orders of $C_{12}-(CO)_n$ ($n = 2, 4$, and 6) calculated with the three functionals ω B97XD, CAM-B3LYP, and PBE1PBE using the def2-TZVP basis set; Figure S4: IRI color bar; Figure S5: STM image of $C_{12}-(CO)_n$; Figure S6: Electron density difference and Gaussian-smoothed C^+/C^- function isosurfaces for $C_{12}-(CO)_n$; Figure S7: Orbital interaction diagram of $C_{12}-(CO)_n$; Table S5: Contributions of fragment orbitals to frontier molecular orbitals of $C_{12}-(CO)_n$; Figure S8: Isosurface map of occupied π_{in} and π_{out} molecular orbitals of $C_{12}-(CO)_n$; Text S1. Physical meaning, thresholds, and limitations of the aromaticity descriptors; Figure S9: Isosurface contour of ELF- π_{in} , ELF- π_{out} , and ELF- π of $C_{12}-(CO)_n$; Figure S10: Simulated absorption spectra and charge-transfer spectra of $C_{12}-(CO)_2$ (200–715 nm and 200–425 nm); Table S6: Excited energy, excited wavelength, oscillator strength and main molecular orbital transitions of 20 excited states of $C_{12}-(CO)_n$ at TD- ω B97XD/def2-TZVP level (based on the optimized structure at the level of ω B97XD/def2-TZVP); Table S7: Excited energy, excited wavelength, oscillator strength and main molecular orbital transitions of 20 excited states of $C_{12}-(CO)_n$ at TD-CAM-B3LYP/def2-TZVP level (based on the optimized structure at the level of ω B97XD/def2-TZVP); Figure S11. Comparison of the simulated UV-Vis spectra of $C_{12}-(CO)_n$ calculated at TD-CAM-B3LYP/def2-TZVP and TD- ω B97XD/def2-TZVP levels based on the same structure optimized at the ω B97XD/def2-TZVP level; Table S8: Excited energy, excited wavelength, oscillator strength and main molecular orbital transitions of low-lying excited states of $C_{12}-(CO)_n$ obtained from TD-CAM-B3LYP/def2-TZVP and TD- ω B97XD/def2-TZVP levels; Figure S12: NTO pair for low-lying excited states of $C_{12}-(CO)_n$; Figure S13: Excited-state hole-electron analyses for $C_{12}-(CO)_n$; Text S2: Hole-electron analysis and assignment of locally excited states; Figure S14: Isosurface of the vdW potential of $C_{12}-(CO)_n$ with various probes; Table S9: The van der Waals potential minima and vertical distances between noble gas atom and molecular plane for noble-gas probes over $C_{12}-(CO)_n$ substrates; Table S10: SAPT0 energy decomposition results for the $C_{12}-(CO)_n@He/Ne$ complex at the SAPT0/juncc-pVDZ level; Table S11: Raw interaction energies

ΔE_{raw} , counterpoise-corrected interaction energies ΔE_{CP} , and BSSE values for $\text{C}_{12}-(\text{CO})_n@ \text{He}/\text{Ne}$ ($n = 2, 4, 6$) calculated using different methods; Table S12: Vertical distances ($\text{\AA}$) between the noble-gas atom and the C_{12} ring for $\text{C}_{12}-(\text{CO})_n@ \text{He}/\text{Ne}$ ($n = 2, 4, 6$); Table S13: Optimized Cartesian coordinates for $\text{C}_{12}-(\text{CO})_n@ \text{He}/\text{Ne}$ ($n = 2, 4, 6$) at the $\omega\text{B97XD}/\text{def2-TZVP}$ level; Figure S15: Isosurface maps of the orbital-weighted dual descriptor (OWDD) for $\text{C}_{12}-(\text{CO})_n$; Text S3: Additional information on LEAE and OWDD.

Author Contributions: Conceptualization, X.C.; methodology, P.-P.L.; validation, G.-N.X.; formal analysis, P.-P.L.; investigation, G.-N.X.; resources, G.-N.X.; data curation, P.-P.L.; writing—original draft preparation, X.C.; writing—review and editing, P.-P.L.; visualization, X.C.; supervision, G.-N.X.; project administration, G.-N.X.; funding acquisition, P.-P.L. All authors have read and agreed to the published version of the manuscript.

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Abbreviations

The following abbreviations are used in this manuscript:

IRI	Interaction region indicator
LOL	Localized orbital locator
EDD	Electron density difference
ECDA	Extended charge decomposition analyses
HOMA	Harmonic oscillator measure of aromaticity
ELF	Electron localization function
FLU	Aromatic fluctuation index
CTS	Charge-transfer spectra
vdW	van der Waals
ESP	Electrostatic potential
OWDD	Orbital-weighted dual descriptor
LEAE	Local electron attachment energy
HOMO	The highest occupied orbital
LUMO	The lowest unoccupied orbital
UFF	Universal force field
SAPT	Symmetry adapted perturbation theory
BSSE	Basis set superposition error

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