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A periodic system of polycyclic aromatic hydrocarbons for predictive molecular growth processes

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Radical–radical reactions of resonantly stabilized species such as propargyl ($C_3H_3^{\cdot}$) and benzyl ($C_7H_7^{\cdot}$) efficiently generate polycyclic aromatic hydrocarbons (PAHs). Key mechanisms—propargyl addition–benzannulation (PABA), methyl addition–ring expansion (MARE), and cyclopentadienyl addition–naphthylization (CPAN)—govern early-stage aromatic growth, but transforming these mechanisms to larger PAHs is computationally challenging due to combinatorial intermediates and reactions on excited state triplet surfaces. Here, we introduce a “periodic system” of PAHs that organizes aromatic growth according to transferable radical–radical motifs, enabling prediction of molecular evolution across the size regime. Using (2-naphthyl)-methyl ($2-C_{11}H_9^{\cdot}$) and benzyl ($C_7H_7^{\cdot}$) radicals as benchmarks, we experimentally demonstrate the predicted gas-phase formation of four- and five-ring PAHs, including (1) $C_{18}H_{12}$ isomers: tetracene, benz[a]anthracene, and [4]helicene; (2) $C_{22}H_{14}$ isomers: benzo[a]tetracene, benzo[a]tetraphene, and [5]helicene. Secondary hydrogen-loss and successive reactions produce even larger 2D and 3D aromatics, such as nanobowls and fullerenes, and their building blocks (corannulene and coronene). This framework provides a unifying and predictive description of PAH growth across combustion and circumstellar environments such as carbon-rich envelopes of late-type Asymptotic Giant Branch (AGB) stars and planetary nebulae.

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Introduction

Polycyclic aromatic hydrocarbons (PAHs)—organic molecules composed of fused benzene rings—play a central role in the evolution of carbon across the universe.^{1–3} They serve as key molecular building blocks in bottom-up processes that generate carbonaceous nanostructures under both low- and high-temperature conditions. In astrophysical environments, these nanostructures appear as interstellar and circumstellar grains in molecular clouds such as the Taurus Molecular Cloud-1 (TMC-1, 10 K),⁴ in carbon-rich envelopes of evolved asymptotic giant branch (AGB) stars such as IRC+10216 (1000–4000 K),⁵ and in planetary nebulae as their evolutionary descendants.^{6,7} On Earth, analogous structures are formed as soot particles during incomplete combustion at temperatures of 1000–2000 K.^{8,9}

In the interstellar medium (ISM), PAHs and their derivatives—including ions, radicals, and substituted aromatics—may

account for up to 30% of the cosmic carbon budget.^{10,11} They are widely considered as carriers of the unidentified infrared bands (UIRs),^{12–14} a family of strong mid-infrared emission features observed throughout galaxies, spanning 3–20 μm and arising from vibrational relaxation of ultraviolet-excited aromatic molecules.^{15,16} Polycyclic aromatic hydrocarbons and related species are also proposed contributors to diffuse interstellar bands (DIBs),^{17–19} a set of over 500 absorption features extending across the visible spectrum (200–400 nm), whose molecular carriers remain only partially identified. Direct detections of aromatic species in TMC-1, including indene (C_9H_8),^{20,21} phenalene ($C_{13}H_{10}$),²² cyclopent(cd)indene ($C_{11}H_8$),²³ and cyano-substituted PAHs such as cyanocoronene,⁴ provide compelling evidence of their ubiquity. Laboratory analyses of extraterrestrial materials, including the Murchison meteorite²⁴ and samples returned by OSIRIS-REx from Bennu²⁵ and Hayabusa2 from Ryugu,²⁶ further confirm the presence of PAHs such as chrysene ($C_{18}H_{12}$) and triphenylene ($C_{18}H_{12}$). Altogether, these observations establish PAHs as key tracers of the chemical evolution of carbon, linking molecular growth in the ISM to the organic inventory of planetary bodies, including Earth.

Radical–radical reactions involving resonantly stabilized free radicals (RSFRs), such as propargyl ($C_3H_3^{\cdot}$) and aryl radicals including phenyl ($C_6H_5^{\cdot}$) and benzyl ($C_7H_7^{\cdot}$), have emerged as efficient pathways to PAH formation at elevated temperatures.^{2,9} Experiments in chemical microreactors, supported by high-level

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electronic structure calculations, have revealed that these radicals can generate PAHs containing up to three fused six-membered rings, such as in anthracene and phenanthrene.^{2,27–30} Mechanistic studies have identified key pathways—propargyl addition–benzannulation (PABA),²⁸ methyl addition–ring expansion (MARE),^{30,31} and cyclopentadienyl addition–naphthylization (CPAN)³²—which rationalize early-stage aromatic growth.^{2,9} Extending these pathways to larger PAHs beyond three benzene rings, however, remains computationally challenging: the number of intermediates and transition states grows combinatorially, and even advanced machine-learning tools are limited to singlet ground-state surfaces, missing reactions that proceed *via* excited triplet states through cycloaddition.^{27,33,34} Such challenges prevent a systematic, automatic exploration of PAH formation beyond three-ring species.

Here, we introduce a generalized, predictive framework—a “periodic system” of PAHs. This concept organizes aromatic structures according to transferable radical–radical reaction motifs. Inspired by Mendeleev’s periodic table of the elements 150 years ago,³⁵ this approach identifies periodic trends, here in ring connectivities, radical types, and annulation pathways. By encoding established mechanisms (PABA, MARE, and CPAN) into a unified classification, we reduce the dimensionality of the reaction space from an intractable enumeration of individual pathways to a finite set of transferable growth rules. Using the (2-naphthyl)-methyl (2-C₁₁H₉•)–(2-naphthyl)-methyl and (2-naphthyl)-methyl–benzyl (C₇H₇•) systems as experimental benchmarks, we demonstrate that this “periodic system” of PAHs predicts the gas-phase formation of previously uncharacterized four- and five-ring aromatics *via* radical–radical reactions through the PABA mechanism. High-temperature microreactor experiments combined with isomer-selective molecular-beam detection using synchrotron vacuum ultraviolet (VUV) photoionization confirm the formation of four-ring PAHs of tetracene, benz[*a*]anthracene, and [4]helicene (C₁₈H₁₂), as well as five-ring species of [5]helicene, benzo[*a*]tetracene, and benzo[*a*]tetracene (C₂₂H₁₄). Longer reactor residence times facilitate secondary reactions *via* hydrogen loss yielding benzo[*ghi*]fluoranthene (C₁₈H₁₀) and benzo[*ghi*]perylene (C₂₂H₁₂), which can further react *via* the hydrogen abstraction–acetylene addition (HACA) mechanism to form corannulene (C₂₀H₁₀) and coronene (C₂₄H₁₂), respectively. These molecules act as fundamental building blocks for flat (2D) and bent (3D) aromatics, including graphitic nanosheets, nanobowls, and fullerenes (C₆₀, C₇₀). Overall, the “periodic system” of PAHs establishes a scalable, predictive route to guide molecular mass growth across chemical environments, providing a unified framework to understand PAH evolution from the ISM to planetary materials.

Results & discussion

(2-Naphthyl)-methyl (2-C₁₁H₉•)–(2-naphthyl)-methyl (2-C₁₁H₉•)–microreactor: mass spectra

The self-recombination of the (2-naphthyl)-methyl radical (2-C₁₁H₉•) was investigated in a chemical microreactor (Fig. S1–S4 and Tables S1 and S2). Mass spectra recorded at a photon

energy of 9.00 eV for the self-reaction of the (2-naphthyl)-methyl (2-C₁₁H₉•) radical are depicted in Fig. 1. At 373 K (Fig. 1a), the helium-seeded 2-chloromethylnaphthalene (2-C₁₁H₉Cl) precursor stays intact. No carbon–chlorine bond cleavage occurred; ion signals were observed at mass-to-charge ratios (*m/z*) of 176 (C₁₁H₉³⁵Cl⁺), 177 (¹³CC₁₀H₉³⁵Cl⁺), 178 (C₁₁H₉³⁷Cl⁺), and 179 (¹³CC₁₀H₉³⁷Cl⁺) (Fig. 1a and S5), which can all be linked to the 2-chloromethylnaphthalene precursor. As the temperature increased to 1123 K (Fig. 1b), the ion counts connected to 2-chloromethylnaphthalene decreased significantly by a factor of about 4. In tandem, ion counts at *m/z* = 141 (2-C₁₁H₉•) arose, indicating efficient carbon–chlorine bond cleavage (Fig. S6). Signals at *m/z* = 140 and 142 can be associated with ionized C₁₁H₈⁺ and C₁₁H₁₀⁺, respectively (Fig. S5). Molecular mass growth processes of *in situ* generated (2-naphthyl)-methyl radicals (2-C₁₁H₉•; 141 amu) resulted in ion counts at higher mass-to-charge ratios of 278, 280, and 282. The signal at *m/z* = 282, *i.e.* twice *m/z* = 141, can be linked to the molecular formula C₂₂H₁₈ and hence likely arose from the self-recombination of two (2-naphthyl)-methyl (2-C₁₁H₉•) radicals. Ion counts at *m/z* = 278 and 280 can be associated with the molecular formulae C₂₂H₁₄ and C₂₂H₁₆, respectively, generated *via* successive hydrogen atom losses of C₂₂H₁₈. Weak ion counts were also collected at *m/z* = 279 (¹³CC₂₁H₁₄⁺), 281 (¹³CC₂₁H₁₆⁺), and 283 (¹³CC₂₁H₁₈⁺), which primarily originate from ¹³C isotopes of ions at *m/z* = 278 (C₂₂H₁₄⁺), 280 (C₂₂H₁₆⁺), and 282 (C₂₂H₁₈⁺), respectively (Fig. S7). To explicitly identify the nature of the isomers formed, photoionization efficiency (PIE) curves, which report the intensities of an ion at a well-defined mass-to-charge ratio *versus* the photon energy, had to be collected between 6.50 and 9.00 eV in an interval of 0.10 eV. These experimentally recorded PIE curves were fitted with a linear combination of known PIE calibration curves of distinct structural isomers to identify which isomer(s) is(are) synthesized.

(2-Naphthyl)-methyl (2-C₁₁H₉•)–(2-naphthyl)-methyl (2-C₁₁H₉•)–microreactor: PIE curves

The analysis of the mass spectra alone reveals molecular mass growth processes leading to hydrocarbons with the molecular formula C₂₂H₁₈ (282 amu) *via* reaction of two (2-naphthyl)-methyl radicals (2-C₁₁H₉•, 141 amu) through reaction (1), followed by loss of up to two hydrogen atoms (C₂₂H₁₆, 280 amu) and eventually four hydrogen atoms (C₂₂H₁₄, 278 amu) schematically *via* reactions (2) and (3), respectively; the corresponding PIE curves are compiled in Fig. 2 (*m/z* = 278) and Fig. S7b (*m/z* = 280) and S7d (*m/z* = 282).

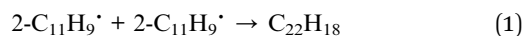


Fig. 2 exhibits the experimental PIE curves collected at *m/z* = 278 (C₂₂H₁₄⁺), along with the reference PIE curves of [5]helicene, benzo[*a*]tetracene, and benzo[*a*]tetracene. These data

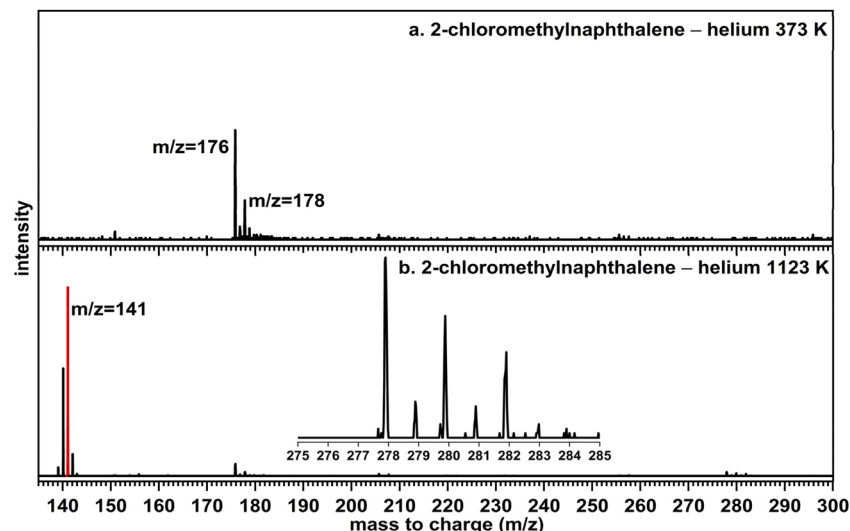


Fig. 1 Representative mass spectra recorded at a photoionization energy of 9.00 eV for the 2-chloromethylnaphthalene–helium system at (a) 373 K and (b) 1123 K.

document an excellent match of the experimentally recorded PIE curve at $m/z = 278$ with a linear combination of the reference curves of three $C_{22}H_{14}$ isomers. In detail, the onset of the experimental ion counts at 7.00 ± 0.03 eV agrees well with the ionization energy (IE) of benzo[*a*]tetracene (6.97 ± 0.02 eV (ref. 36)). However, the experimental PIE data could only be satisfactorily fitted to the reference PIE curve of benzo[*a*]tetracene within the range of 6.50 to 7.20 eV (Fig. S8a); the experiments reveal additional ion counts beyond 7.30 ± 0.03 eV. Considering the IE of benzo[*a*]tetracene (7.30 ± 0.05 eV (ref. 37)), the

reference PIE curve is added to the fit (Fig. S8b) to reproduce the experimental data from 6.50 to 7.50 eV. Furthermore, the notable contribution of [5]helicene (IE = 7.51 ± 0.02 eV (ref. 37)) is taken into account, enabling the entire experimental PIE dataset to be satisfactorily matched by a linear combination of the reference curves of the aforementioned three $C_{22}H_{14}$ isomers (Fig. 2). By linear fitting of these calibration PIE curves to the experimentally measured data, the branching ratios of the ions of [5]helicene, benzo[*a*]tetracene, and benzo[*a*]tetracene are extracted to be $70.3 \pm 4.9 : 22.8 \pm 1.6 : 6.9 \pm 0.5\%$ at

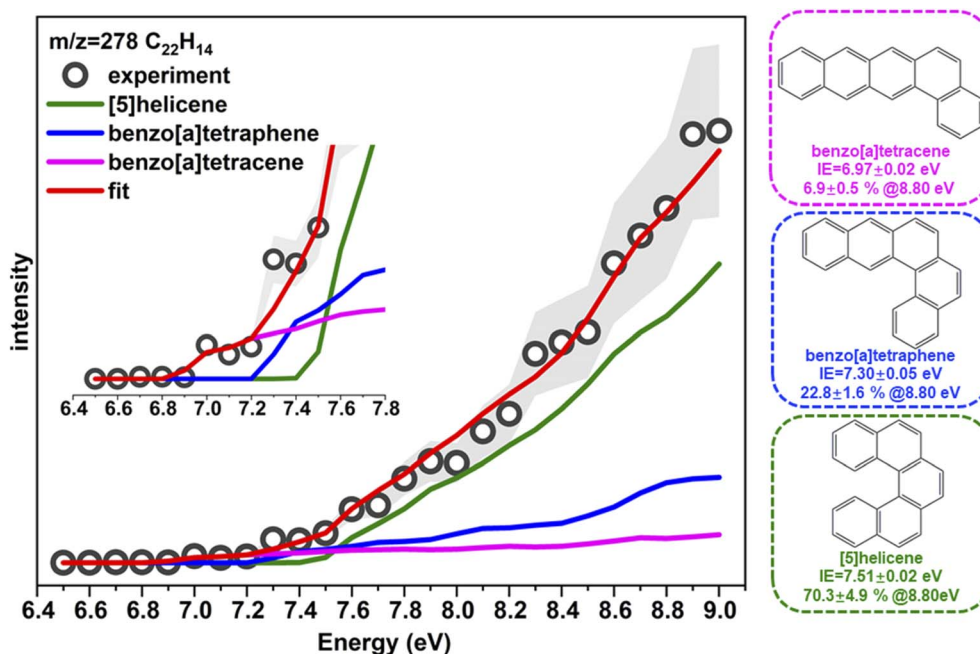


Fig. 2 Experimental and reference PIE curves for $m/z = 278$. The black circles refer to the normalized experimental data with 1σ error limits defined in the shaded area. The colored lines refer to reference PIE curves.

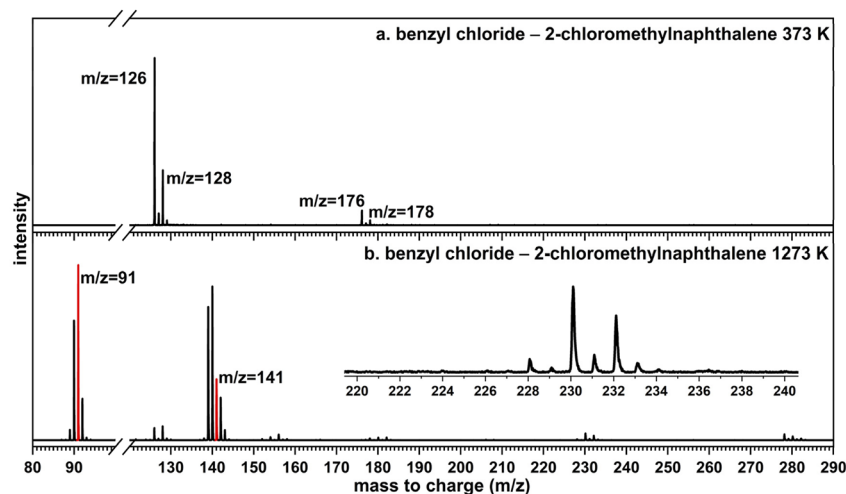


Fig. 3 Representative mass spectra recorded at a photoionization energy of 9.00 eV for the benzyl chloride–2-chloromethylnaphthalene/helium system at (a) 373 K and (b) 1273 K in the chemical microreactor.

8.80 eV, taking 7% uncertainty of the experimental PIE data into consideration. In addition, three additional $C_{22}H_{14}$ isomers, pentaphene, dibenz[*a,h*]anthracene, and pentacene, are also taken into consideration; these can be added at a level of up to 3% without changing the fits of the PIE curve (Fig. S9). In summary, based on PIE analysis, at least three $C_{22}H_{14}$ isomers are detected: [5]helicene, benzo[*a*]tetraphene, and benzo[*a*]tetracene.

(2-Naphthyl)-methyl (2- $C_{11}H_9^{\cdot}$)-benzyl ($C_7H_7^{\cdot}$)-microreactor: mass spectra

The reaction of the (2-naphthyl)-methyl radical (2- $C_{11}H_9^{\cdot}$) with the benzyl radical ($C_7H_7^{\cdot}$) was also investigated in the chemical microreactor (Fig. S1–S4 and Tables S1 and S2). Fig. 3a reveals a representative mass spectrum collected at 9.00 eV of the benzyl chloride–2-chloromethylnaphthalene system at 373 K; only ion signals corresponding to precursors of benzyl chloride and 2-chloromethylnaphthalene were observed at $m/z = 126$ ($C_7H_7^{35}Cl^+$), 127 ($^{13}CC_6H_7^{35}Cl^+$), 128 ($C_7H_7^{37}Cl^+$), 129 ($^{13}CC_6H_7^{37}Cl^+$), 176 ($C_{11}H_9^{35}Cl^+$), 177 ($^{13}CC_{10}H_9^{35}Cl^+$), 178 ($C_{11}H_9^{37}Cl^+$) and 179 ($^{13}CC_{10}H_9^{37}Cl^+$). At 1273 K, the intensities of the aforementioned ion signals decreased significantly by a factor of about 3.5, while prominent ion peaks emerged at $m/z = 91$ and 141 (Fig. 3b and S10). These can be unambiguously assigned to the benzyl ($C_7H_7^{\cdot}$) and (2-naphthyl)-methyl (2- $C_{11}H_9^{\cdot}$) radicals, respectively, generated *via* carbon–chlorine bond rupture in the precursors at elevated temperature.^{38–40} Additional ion counts at $m/z = 89, 90, 92, 139, 140,$ and 142 are related to the hydrogen atom elimination/addition of benzyl and (2-naphthyl)-methyl at 1273 K (Fig. 3b and S11). Most importantly, the adduct of the radical–radical recombination of (2-naphthyl)-methyl with benzyl is evident at $m/z = 232$; concomitant signals were also observed at $m/z = 230$ and 228 (Fig. 3b), along with ion counts at $m/z = 154, 156, 178, 180, 182, 278, 280,$ and 282 . Ion signals at $m/z = 154$ and 156 are proposed to be ascribed to ethenylnaphthalene ($C_{12}H_{10}$) and

ethylnaphthalene ($C_{12}H_{12}$), respectively (Fig. S12a and b). Their formation proceeds *via* the recombination of (2-naphthyl)-methyl (2- $C_{11}H_9^{\cdot}$) with methyl ($CH_3^{\cdot}$), followed by hydrogen eliminations.^{28,38} Previous work reported the benzyl self-reaction yielding $C_{14}H_{10}$ (178 amu), $C_{14}H_{12}$ (180 amu) and $C_{14}H_{14}$ (182 amu) (Fig. S12c–e).²⁷ Further, signals at $m/z = 278, 280,$ and 282 can be linked to the self-reaction of the (2-naphthyl)-methyl radical as demonstrated above (Fig. S12f–h). Overall, a comparison of ion counts for the (2-naphthyl)-methyl radical (2- $C_{11}H_9^{\cdot}$)-benzyl radical ($C_7H_7^{\cdot}$) system (Fig. 3b) with the corresponding blank experiment and self-reactions of benzyl²⁷ and (2-naphthyl)-methyl (Fig. 1b) provides compelling evidence for the formation of species with the molecular formula $C_{18}H_{16}$ (232 amu), $C_{18}H_{14}$ (230 amu), and $C_{18}H_{12}$ (228 amu). Accounting for the molecular weights of reactants and products, $C_{18}H_{16}$ (232 amu) isomer(s) likely originate(s) from the formation of the adduct formed *via* carbon–carbon bond coupling of two resonantly stabilized radicals: benzyl ($C_7H_7^{\cdot}$, 91 amu) and (2-naphthyl)-methyl (2- $C_{11}H_9^{\cdot}$, 141 amu). The hydrocarbons $C_{18}H_{14}$ (230 amu) and $C_{18}H_{12}$ (228 amu) are likely generated through hydrogen elimination from $C_{18}H_{16}$ (232 amu). Additionally, low-intensity signals were also detected at $m/z = 229$ ($^{13}CC_{17}H_{12}^+$), 231 ($^{13}CC_{17}H_{14}^+$), and 233 ($^{13}CC_{17}H_{16}^+$); these can be predominantly attributed to ^{13}C counterparts of $C_{18}H_{12}$ (228 amu), $C_{18}H_{14}$ (230 amu), and $C_{18}H_{16}$ (232 amu), respectively (Fig. S13a, c and e).

(2-Naphthyl)-methyl (2- $C_{11}H_9^{\cdot}$)-benzyl ($C_7H_7^{\cdot}$)-microreactor: PIE curves of products

To identify the molecular structures of the $C_{18}H_{12}$ (228 amu), $C_{18}H_{14}$ (230 amu), and $C_{18}H_{16}$ (232 amu) isomers formed in the (2-naphthyl)-methyl radical (2- $C_{11}H_9^{\cdot}$) with the benzyl radical ($C_7H_7^{\cdot}$) system, PIE curves are acquired from 6.90 to 9.00 eV in steps of 0.10 eV at 1273 K. Fig. S13b and d exhibit PIE data for $m/z = 230$ ($C_{18}H_{14}^+$) and 232 ($C_{18}H_{16}^+$), respectively, along with detailed analyses in the SI. A close look at the PIE curve of $m/z =$

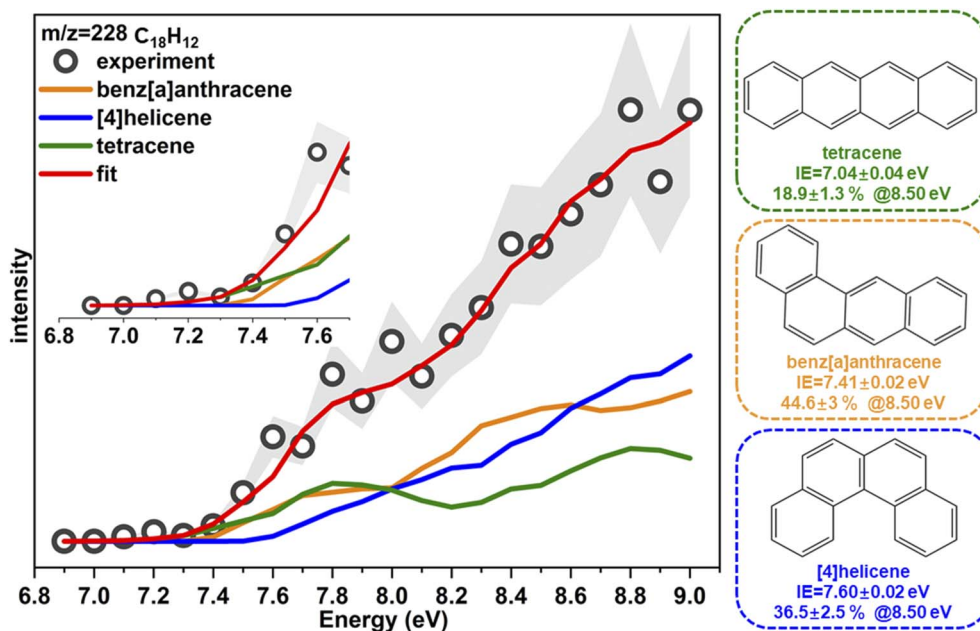


Fig. 4 Experimental and reference PIE curves for $m/z = 228$. The black circles refer to the normalized experimental data with 1σ error limits defined in the shaded area. The colored lines refer to reference standard PIE curves.

$228\text{ (C}_{18}\text{H}_{12}^+)$ reveals that the experimental data can be nicely replicated with a linear combination of reference PIE curves of benz[a]anthracene, [4]helicene, and tetracene (Fig. 4, S14 and S15). In detail, the onset of the ion counts appears at 7.10 ± 0.03 eV. This onset along with the data points up to 7.40 eV can be replicated nicely by the reference PIE curve of tetracene ($\text{C}_{18}\text{H}_{12}$, IE = 7.04 ± 0.04 eV (ref. 41)) (Fig. S14a). Beyond this range, a contribution from additional isomer(s) is required. This pronounced enhancement could be fitted with the reference curve of benz[a]anthracene (IE = 7.41 ± 0.02 eV⁴¹) up to 7.60 eV (Fig. S14b). Finally, contributions from a third isomer – [4]helicene (IE = 7.60 ± 0.02 eV (ref. 41 and 42)) – are required to replicate the overall experimental PIE curve. Overall, ion branching ratios of benz[a]anthracene, [4]helicene, and tetracene are extracted to be $44.6 \pm 3.0 : 36.5 \pm 2.5 : 18.9 \pm 1.3\%$ at 8.50 eV, taking 7% uncertainty of the experimental PIE data into consideration. In summary, the formation of the major products of benz[a]anthracene, [4]helicene, and tetracene in experiment 2 can be confirmed through the PIE analysis methods.

(2-Naphthyl)-methyl (2-C₁₁H₉[•])-benzyl (C₇H₇[•])-flow tube reactor: mass spectra

The reaction of the (2-naphthyl)-methyl radical (2-C₁₁H₉[•]) with the benzyl radical (C₇H₇[•]) (Fig. S16 and S17) was also investigated in the flow tube reactor (Fig. S1–S4 and Tables S1 and S2) to explore the effect of the longer residence time of 6×10^3 μs in the flow reactor *versus* 10^2 μs in the chemical microreactor. Fig. 5a displays the expanded view of the representative mass spectrum in the m/z range of 225 to 235 and 275 to 284. Ion signals at $m/z = 278$ (C₂₂H₁₄⁺), 280 (C₂₂H₁₆⁺), 282 (C₂₂H₁₈⁺) ((2-naphthyl)-methyl (2-C₁₁H₉[•])-(2-naphthyl)-methyl (2-C₁₁H₉[•]) system) and $m/z = 228$ (C₁₈H₁₂⁺), 230 (C₁₈H₁₄⁺), 232 (C₁₈H₁₆⁺)

((2-naphthyl)-methyl (2-C₁₁H₉[•])-benzyl (C₇H₇[•]) system) were also observed in the present flow tube reactor study, along with the corresponding ¹³C peaks at $m/z = 229$ (¹³CC₁₇H₁₂⁺), 231 (¹³CC₁₇H₁₄⁺), 233 (¹³CC₁₇H₁₆⁺), 279 (¹³CC₂₁H₁₄⁺), 281 (¹³CC₂₁H₁₆⁺), and 283 (¹³CC₂₁H₁₈⁺). Most importantly, ion signals at $m/z = 226$ and 276, which are absent in both experiments exploiting a chemical microreactor, are also observable. These two signals can be attributed to C₁₈H₁₀ and C₂₂H₁₂ isomers, respectively. Their formations likely proceed *via* respective dehydrogenation of C₁₈H₁₂ and C₂₂H₁₄—a process facilitated by the high temperature (1273 K) and longer residence time (6×10^3 μs) in the flow tube reactor. This extended residence time facilitates higher order reactions, resulting in the increasing complexity of the product spectra (Fig. S16 and S18–S23). Notably, in the (2-naphthyl)-methyl-benzyl reaction system studied with the flow tube reactor, signals were also detected at $m/z = 250$ and 300 (Fig. 5b); these signals were absent in the corresponding experiments exploiting the chemical microreactor. These signals can be attributed to isomers with the molecular formulae C₂₀H₁₀ and C₂₄H₁₂, respectively.

(2-Naphthyl)-methyl (2-C₁₁H₉[•])-benzyl (C₇H₇[•])-flow tube reactor: PIE curves

To identify the isomers, PIE curves were collected from 6.90 to 9.00 eV to determine the nature of the C₁₈H₁₀ and C₂₂H₁₂ isomer(s) formed. Fig. 6a presents the experimental PIE data for $m/z = 226$ (C₁₈H₁₀⁺) along with the reference PIE curve of benzo[ghi]fluoranthene. The onset of the experimental PIE curve emerged at 7.40 ± 0.03 eV, which is consistent with the IE (7.40 ± 0.05 eV (ref. 41 and 42)) of benzo[ghi]fluoranthene. Effectively, the experimental PIE curve of $m/z = 226$ can be nicely replicated with the reference PIE curve of benzo[ghi]fluoranthene.

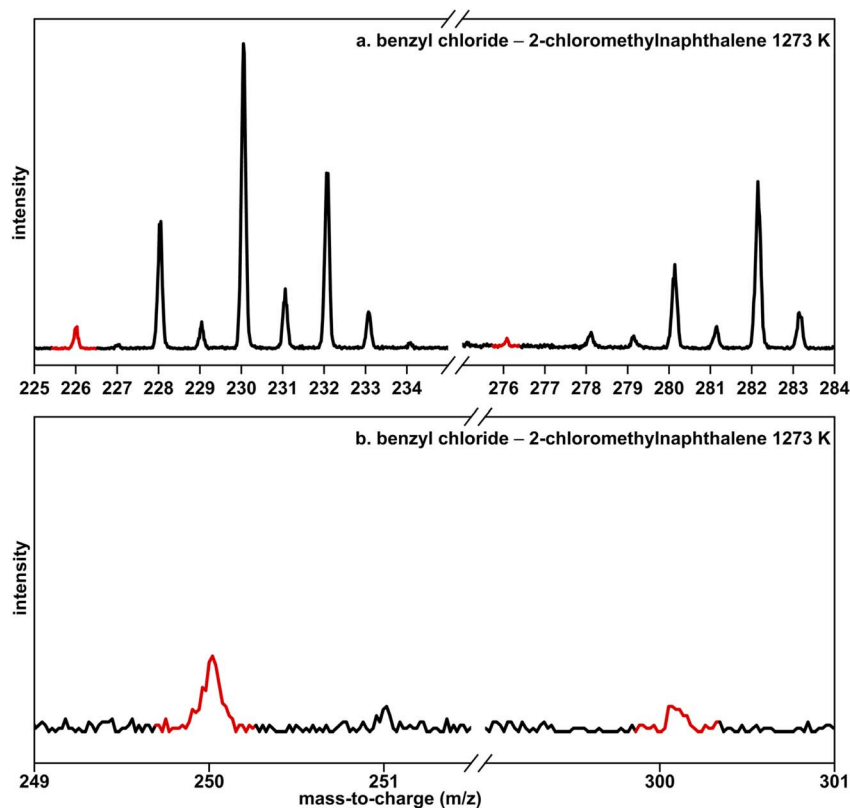


Fig. 5 Representative mass spectrum recorded at a photoionization energy of 9.00 eV and 1273 K for the benzyl chloride–2-chloromethylnaphthalene/helium system in the flow tube reactor. Enlarged mass spectra are shown in panel (a) $m/z = 225$ – 235 and 275 – 284 ; (b) $m/z = 249$ – 301 .

Likewise, the experimental PIE data of $m/z = 276$ ($C_{22}H_{12}^+$) (Fig. 6d) can be fitted to the reference PIE curve of benzo[ghi]perylene.⁴³ Here, the onset (7.20 ± 0.03 eV) of $m/z = 276$ closely

matches the reported IE (7.19 ± 0.01 eV (ref. 43)) of benzo[ghi]perylene. Overall, this analysis provides strong evidence of the formation of benzo[ghi]fluoranthene ($C_{18}H_{10}$) and benzo[ghi]

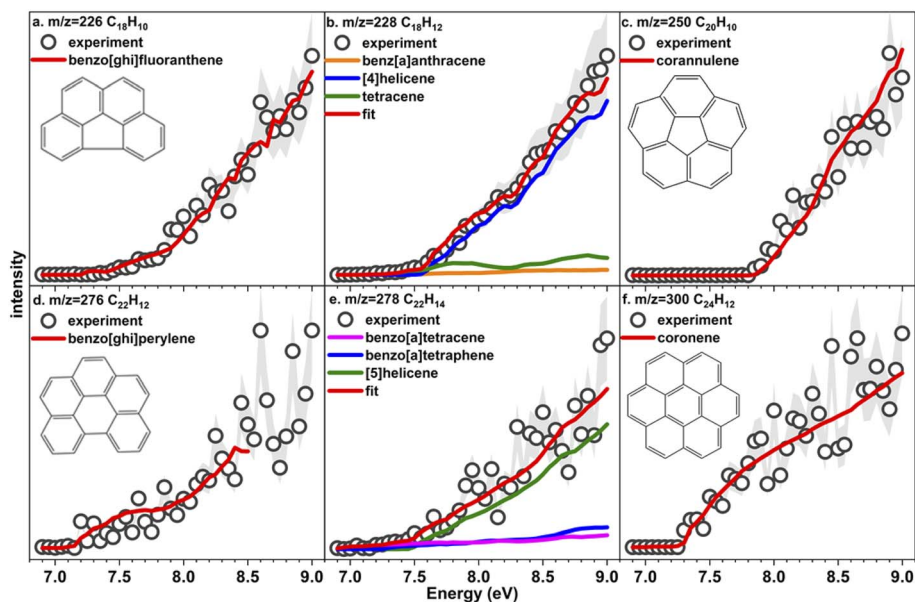


Fig. 6 Experimental and reference PIE curves for (a) $m/z = 226$, (b) $m/z = 228$, (c) $m/z = 250$, (d) $m/z = 276$, (e) $m/z = 278$ and (f) $m/z = 300$. The black circles refer to the normalized experimental data with 1σ error limits defined in the shaded area. The colored lines refer to reference standard PIE curves.

Table 1 “Periodic System” of PAHs incorporating molecular mass growth processes *via* radical–radical reactions through the propargyl addition–benzannulation (PABA), methyl addition–ring expansion (MARE), and cyclopentadienyl addition–naphthylization (CPAN) mechanisms. Systems in bold leading up to three–ringed PAHs have been studied experimentally;^{27,28,30–32,46–48} the systems in *italics* are the topic of the present study. C1: methyl ($\text{CH}_3^\bullet$), C3: propargyl ($\text{C}_3\text{H}_3^\bullet$), C5: cyclopentadienyl ($\text{C}_5\text{H}_5^\bullet$), C7: benzyl ($\text{C}_7\text{H}_7^\bullet$), C9: indenyl ($\text{C}_9\text{H}_7^\bullet$), C11: naphthyl–methyl ($\text{C}_{11}\text{H}_9^\bullet$), C13: fluorenyl ($\text{C}_{13}\text{H}_9^\bullet$), and C15: anthracenylmethyl/phenanthrenylmethyl ($\text{C}_{15}\text{H}_{11}^\bullet$)

	C1	C3	C5	C7	C9	C11	C13	C15
C1			MARE		MARE		MARE	
C3		PABA		PABA		PABA		PABA
C5			CPAN		CPAN		CPAN	
C7				PABA		<i>PABA</i>		PABA
C9					CPAN		CPAN	
C11						<i>PABA</i>		PABA
C13							CPAN	
C15								PABA

	C1	C3	C5	C7	C9	C11	C13	C15
C1	0		1		2		3	
C3		1		2		3		4
C5			2		3		4	
C7				3		4		5
C9					4		5	
C11						5		6
C13							6	
C15								7

perylene ($\text{C}_{22}\text{H}_{12}$), likely originating from dehydrogenation of $\text{C}_{18}\text{H}_{12}$ and $\text{C}_{22}\text{H}_{14}$ isomers, respectively. As a matter of fact, these isomers were also detected *via* ion signals at $m/z = 228$ ($\text{C}_{18}\text{H}_{12}^+$, Fig. 6b) and $m/z = 278$ ($\text{C}_{22}\text{H}_{14}^+$, Fig. 6e). As in the chemical microreactor study, three contributions were required to fit each PIE curve acquired from experiments using the flow tube reactor. For $m/z = 228$, these are benz[*a*]anthracene, [4] helicene, and tetracene with ion branching ratios of $3.8 \pm 0.3\%$, $86.5 \pm 6.1\%$, and $9.7 \pm 0.7\%$, respectively. For $m/z = 278$, these are [5]helicene, benzo[*a*]tetracene and benzo[*a*]tetracene with an ion branching ratio of $76.2 \pm 5.3 : 14.9 \pm 1.0 : 8.9 \pm 0.6\%$. The experimental differences, using the flow tube reactor and chemical microreactor in branching ratios of $\text{C}_{18}\text{H}_{12}$ and $\text{C}_{22}\text{H}_{14}$ isomers, have been comparatively analyzed in the SI (Fig. S24). Fig. 6c displays the experimental PIE curve recorded at $m/z = 250$ ($\text{C}_{20}\text{H}_{10}^+$), alongside the reference PIE spectrum of corannulene. The experimental onset of 7.85 ± 0.03 eV agrees well with the reported IE of corannulene (7.85 ± 0.05 eV (ref. 44)). Moreover, the experimental PIE profile for $m/z = 250$ within 6.90–9.00 eV closely matches the reference data of corannulene.⁴⁴ Despite the noticeable jitter in the experimental PIE profile of $m/z = 300$ due to low signal intensity, the overall shape can be reproduced by the reference data of coronene.⁴³ Importantly, the onset value of ion counts of 7.30 ± 0.03 eV is consistent with the IE of coronene (7.30 ± 0.05 eV (ref. 43)). This evidence supports the identification of corannulene and coronene, respectively. Corannulene ($\text{C}_{20}\text{H}_{10}$, 250 amu) and coronene ($\text{C}_{24}\text{H}_{12}$, 300 amu) are likely generated through hydrogen abstraction–acetylene addition (HACA) of benzo[*ghi*]

fluoranthene ($\text{C}_{18}\text{H}_{10}$) and benzo[*ghi*]perylene ($\text{C}_{22}\text{H}_{12}$), respectively, at elevated temperatures.^{43,44}

Discussion & conclusion

Radical–radical reactions involving resonantly stabilized free radicals (RSFRs) and aryl (AR) radicals provide a highly efficient pathway for the formation of polycyclic aromatic hydrocarbons (PAHs) in high-temperature gas-phase environments. Chemical microreactor studies identify three dominant growth mechanisms involving C1 to C9 radicals—methyl ($\text{CH}_3^\bullet$), propargyl ($\text{C}_3\text{H}_3^\bullet$), cyclopentadienyl ($\text{C}_5\text{H}_5^\bullet$), benzyl ($\text{C}_7\text{H}_7^\bullet$), indenyl ($\text{C}_9\text{H}_7^\bullet$), and fluorenyl ($\text{C}_{13}\text{H}_9^\bullet$)—which enable sequential formation of multi-ring aromatics *via* propargyl addition–benzannulation (PABA),²⁸ methyl addition–ring expansion (MARE),³¹ and cyclopentadienyl addition–naphthylization (CPAN)⁴⁵ (Table 1). Within the “Periodic System” of PAHs, these mechanisms define a unified growth progression toward increasingly complex benzenoid structures, extending to species containing up to seven fused rings.

The PABA mechanism, exemplified by the self-reaction of benzyl ($\text{C}_7\text{H}_7^\bullet$) radicals, yields phenanthrene and anthracene ($\text{C}_{14}\text{H}_{10}$).²⁷ Phenanthrene forms on the singlet ground-state surface *via* barrierless radical recombination, whereas anthracene arises through an alternative pathway on the excited-state triplet surface *via* cycloaddition dynamics (Fig. S25). This dual-surface reactivity challenges the conventional assumption that PAH growth is confined to ground-state chemistry and establishes excited-state radical–radical reactions as a parallel and

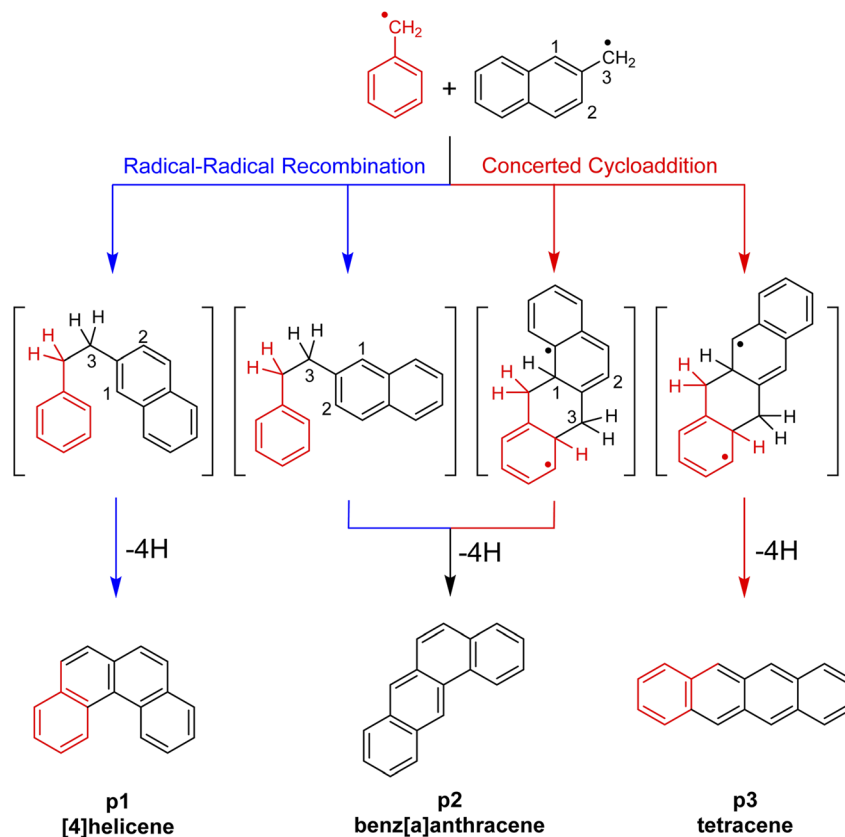


Fig. 7 Schematic mechanism. PAHs carrying four benzene rings are predicted to be formed *via* PABA in the (2-naphthyl)-methyl (2-C₁₁H₉^{*})-benzyl (C₇H₇^{*}) system involving classical radical–radical recombination and concerted cycloadditions on ground state singlet and excited triplet surfaces, respectively.

efficient channel for aromatic ring expansion. The C7–C11 (Fig. 7) and C11–C11 (Fig. 8) reaction networks provide direct experimental validation of this framework. In the C7–C11 system, three four-ring PAHs are both predicted and observed:

[4]helicene (p1), benz[a]anthracene (p2), and tetracene (p3) (C₁₈H₁₂). Among these, tetracene forms exclusively *via* triplet-surface cycloaddition, whereas [4]helicene arises from singlet-state radical–radical recombination at sp² centers. In the C11–

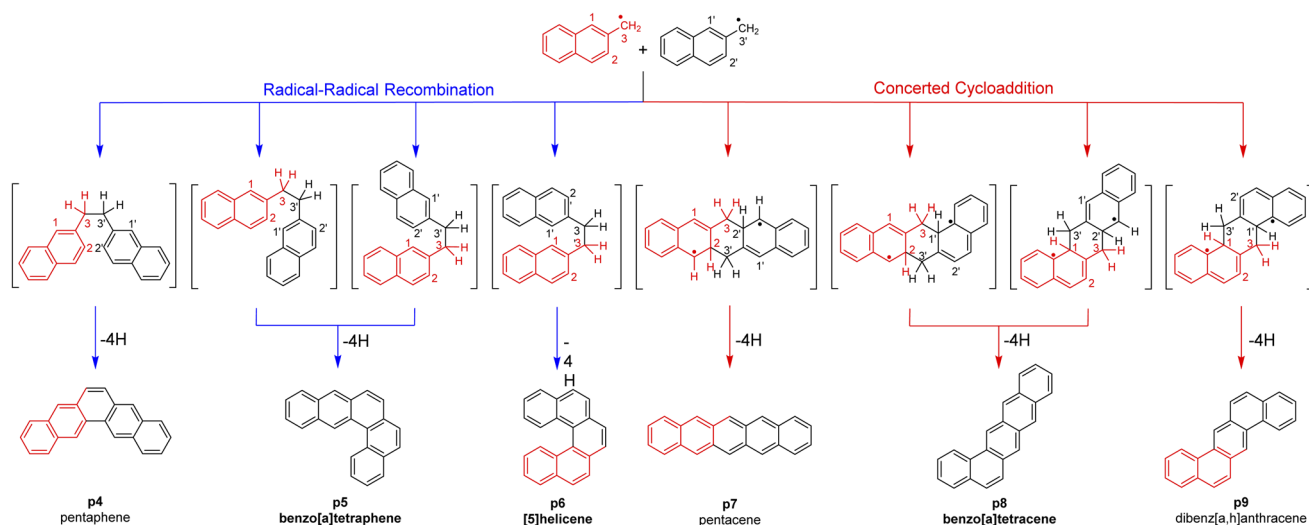


Fig. 8 Schematic mechanism. PAHs carrying five benzene rings are predicted to be formed *via* PABA in the (2-naphthyl)-methyl (2-C₁₁H₉^{*})-(2-naphthyl)-methyl (2-C₁₁H₉^{*}) system involving classical radical–radical recombination and concerted cycloadditions on ground state singlet and excited triplet surfaces, respectively.

C11 system, five-ring PAHs including benzo[*a*]tetraphene (p5), [5]helicene (p6), and benzo[*a*]tetracene (p8) (C₂₂H₁₄) are observed, again reflecting a clear mechanistic separation between singlet-driven recombination and triplet-mediated cycloaddition pathways. Additional low-abundance species, including pentaphene (p4), pentacene (p7), and dibenz[*a,h*]anthracene (p9), are consistent with photoionization efficiency (PIE) signals at $m/z = 278$ (C₂₂H₁₄⁺) (Fig. S9), indicating a broader product manifold.

[4]Helicene and [5]helicene act as key branching intermediates that extend PAH growth beyond planar aromatics. Subsequent hydrogen loss and secondary reactions yield benzo[ghi]fluoranthene (C₁₈H₁₀) and benzo[ghi]perylene (C₂₂H₁₂) (Fig. 6a and d), while further growth *via* hydrogen abstraction–acetylene addition (HACA) produces corannulene (C₂₀H₁₀, 250 amu) and coronene (C₂₄H₁₂, 300 amu) (Fig. 6c and f). These species represent fundamental precursors to both planar graphene fragments and curved carbon architectures, including nanobowls and fullerene-like structures (C₆₀, C₇₀).

In conclusion, the agreement between the “Periodic System” predictions and experimental observations across both singlet and triplet channels establishes radical–radical chemistry as a unified and predictive framework for PAH growth. Rather than isolated reaction pathways, these systems define a continuous growth cascade in which small aromatic radicals evolve into progressively fused structures through successive recombination, cycloaddition, and dehydrogenation events. Extending this framework, the C7–C11 and C11–C11 networks naturally evolve toward PAHs containing some 50–100 carbon atoms, corresponding to graphene-like fragments on the order of 1 nm. Under high-temperature conditions, this radical-driven growth provides a direct molecular pathway from discrete PAHs to incipient soot nuclei, bridging gas-phase chemistry and condensed carbon formation. This mechanism supports soot inception and interstellar grain formation as emergent outcomes of hierarchical radical–radical assembly governed by the “Periodic System” of PAHs. Therefore, this framework unifies PAH formation across combustion and astrochemical environments and establishes radical–radical reactions as a central organizing principle for aromatic carbon growth. Beyond predictive capability, the “Periodic System” of PAHs provides a mechanistic basis for reactivity trends among key radicals and a foundation for rational design and control of higher-order carbon nanostructures in our universe.

Author contributions

R. I. K. conceptualized the experiments, W. L., H. J. and M. X. conducted the experiments. L. Z. and J. Y. supervised the experiments. W. L., L. Z., S. G. and R. I. K. performed the data analysis and wrote the paper. All authors discussed the data and approved the manuscript for submission.

Conflicts of interest

The authors declare no competing interest.

Data availability

Essential data are provided in the main text and the supplementary information (SI). Additional data can be available from the corresponding author upon reasonable request. Supplementary information: Experimental data (Fig. S1–S4, Tables S1 and S2); additional mass spectra (Fig. S5–S23); simplified reaction pathways for the benzyl radical self-reaction (Fig. S24). See DOI: <https://doi.org/10.1039/d6sc05859k>.

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