Inception of carbonaceous nanostructures via hydrogen-abstraction phenylacetylene-addition mechanism

Hanfeng Jin,1 Lili Ye,2* Jiuzhong Yang,3 Yu Jiang,4 Long Zhao,3 Aamir Farooq1*

1 King Abdullah University of Science and Technology (KAUST), Clean Combustion Research Center, Physical Sciences and Engineering Division, Thuwal 23955-6900, Saudi Arabia.
2 Dalian University of Technology, School of Chemical Engineering, Dalian, Liaoning 116024, China.
3 National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, China.
4 Key Laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education & Hubei Key Laboratory of Catalysis and Materials Science, Hubei R&D Center of Hyperbranched Polymers Synthesis and Applications, South-Central University for Nationalities, Wuhan 430074, China.

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ABSTRACT: Sufficient experimental evidence has suggested polycyclic aromatic hydrocarbons (PAH) to be the building blocks of carbonaceous nanostructures in combustion and circumstellar envelopes of carbon-rich stars, but their fundamental formation mechanisms remain elusive. By exploring the reaction kinetics of phenylacetylene with 1-naphthyl / 4-phenanthryl radicals, we provide compelling theoretical and experimental evidence for a novel and self-consistent hydrogen-abstraction phenylacetylene addition (HAPA) mechanism. HAPA operates efficiently at both low and high temperatures, leading to the formation, expansion and nucleation of peri-condensed aromatic hydrocarbons (PCAH), which are otherwise difficult to synthesis via traditional hydrogen-abstraction acetylene/vinylacetylene addition (HACA / HAVA) pathways. HAPA mechanism can be generalized to other α-alkynyl PCAHs, and thus provides an alternative covalent bond bridge for PCAH combination via an acetylene linker. The proposed HAPA mechanism may contribute towards a comprehensive understanding of soot formation, carbonaceous nanomaterials synthesis, and the origin and evolution of carbon in our galaxy.

Introduction

In the past few decades, polycyclic aromatic hydrocarbons (PAHs) have been at the center of attention as prospective candidates to soot inception, nanoparticle material synthesis and interstellar evolution. The combination of high-resolution atomic force microscopy (AFM) and scanning tunneling microscopy (STM) provided the first glimpse of the molecular building blocks of soot, and provided experimental evidence for the correlation between different PAHs and particle nucleation. Graphene nanocarbon essentially comprises of large PAHs, and it is considered to be a promising material for future capacitors, sensors, and transistors. PAHs are also potential candidates as molecular carriers of undefined infrared emissions and diffuse interstellar bands.

A number of mechanisms were proposed to explain the formation and growth of PAHs starting from small hydrocarbons. Hydrogen-abstraction acetylene-addition (HACA) mechanism is widely suggested as an important formation pathway of PAHs in the combustion of hydrocarbons and in the circumstellar envelopes of carbon rich stars. A repetitive sequence of hydrogen abstraction from an aromatic hydrocarbon followed by acetylene addition, cyclization and aromatization leads to PAHs with multiple fused benzene rings. Similarly, hydrogen-abstraction vinylacetylene-addition (HAVA) mechanism has been invoked since naphthalene, phenanthrene, and anthracene were shown to be synthesized via barrier-less collisions of phenyl (C6H5) and naphthyl (C10H7) radicals with vinylacetylene. Phenyl addition-dehydrocyclization (PAC) mechanism hypothesizes the addition of phenyl to an aromatic hydrocarbon followed by hydrogen abstraction, cyclization and dehydrogenation processes. Two prototype PAHs – fluoranthene and triphenylene – were synthesized by the reactions of phenyl with naphthalene and biphenyl, respectively, at high temperatures, which provided a systematic elucidation of the validity of the PAC mechanism. Recent studies revealed a PAH formation mechanism involving resonance-stabilized radicals (RSRs). The dimerization of RSRs with other large hydrocarbons stabilizes to covalently-bonded clusters at high temperatures through a rapid radical-driven hydrocarbon clustering, and thus bypassing the stepwise addition of small hydrocarbon species; this process leads to a quick inception of oligomers of aromatic compounds.

Peri-condensed aromatic hydrocarbons (PCAHs), with only π bonds between C atoms, can be present in large amounts in flames; however, their nucleation mechanism to carbonaceous nanoparticles remains unclear. Both HACA and HAVA mechanisms have come under scrutiny, despite their potential in synthesizing PAHs in extreme environments, as modelling investigations indicate slow efficiency of stepwise acety-
lène/vinylacetylene addition to reproduce the observed PAH concentrations in flame experiments. Meanwhile, density functional theory studies demonstrated the importance of aliphatic chain to cross link closed shell PAHs in the nucleation process when reaction temperature is higher than 1000 K. Phenylacetylene (C6H=C=H) is the simplest representative of alkynyl PAH with an unsaturated aliphatic substituent. H-abstraction reactions of PAHs produce aryl radicals, where phenyl is the simplest aryl radical. Literature PAH models postulated the formation of phenanthrene by the reaction of phenyl and phenylacetylene according to the quantum chemical investigations. However, a crossed molecular beam experiment at a relatively high collision energy did not observe phenanthrene from this reaction. Elementary reaction experiments and complementary quantum chemical calculations further revealed 1,2-diphenylvinyl radical to be the dominant intermediate in the reaction of phenyl and phenylacetylene. Direct H-elimination of 1,2-diphenylvinyl leading to diphenylacetylene is more favorable than its isomerization to form phenanthrene.

![Figure 1. Schematic reaction pathways in HAPaA mechanism.](image)

(A) different aryl periphery types are labelled by different colors; (B) HAPaA reaction pathways for “zigzag” and “armchair”; (C) ring-closure reactions for “cove” and “fjord”.

Aryl radical position is not limited to the “free” periphery (e.g., phenyl); phenylacetylene can combine with aryls at different PCAH periphery types (see Fig. 1A). Here, we report the results of elementary reaction experiments of 1-naphthyl (“zigzag”) and 4-phenanthryl (“armchair”) with phenylacetylene, where speciation was carried out by synchrotron vacuum ultra-violet photoionization molecular beam mass spectrometry (SVUV-PMBMS). By combining these data with quantum chemical calculations, we present barrierless formation routes to PAHs that are applicable in low-temperature interstellar and high-temperature combustion. With the addition of phenylacetylene to “zigzag” and “armchair” aryl radicals, the adducts fuse new aromatic ring by laying the C=C double bond over these periphery (Fig. 1B). Such alternative channels are different from the previously proposed H-elimination channel, which transform “zigzag” and “armchair” to other periphery types. In Fig. 1C, “cove” and “fjord” are easy to aromatize via ring closure, and are thus rarely observed in large PAHs at high temperatures. As summarized in Fig. 1, initial aryl radicals obtained from H-abstraction reaction combine with phenylacetylene to form covalent-bonded compounds yielding resonantly stabilized radicals (RSRs) which promote further tautomerization over low energy barriers. All periphery types alternate to each other in this process, to generate a self-consistent mechanism named as H-abstraction Phenylacetylene-Addition (HAPaA). This facile mechanism towards higher order PAHs, in low and high temperature environments, illustrates the formation of cold molecular clouds, such as carbon chain rich cores of TMC-1 and OMC-1, as potential “molecular nurseries” of PAH synthesis. This mechanism also shows acetylene to be a potential linker for soot inception from PCAHs in the post-flame zone.

**Results**

**Quantum Chemical Calculations and Reaction Mechanism.** Energy barriers and rate coefficients reported in previous studies indicate that the combination of phenyl and β-C-atom of phenylacetylene at 1000 K is about 50 times faster than that of α-C-atom. Since naphthyl and phenanthryl have similar reaction kinetics as phenyl, the addition of phenylacetylene to naphthyl or phenanthryl may also predominantly occur at the β (terminal) C-atom. Figure 2A presents the major reaction channels of phenylacetylene addition to 1-naphthyl, illustrating the prototypical HAPaA route for “zigzag”. RSR [1] is formed via the barrierless addition of 1-naphthyl radical to phenylacetylene, the β-C-atom of phenylacetylene is the dominant site for aryl addition. Intramolecular H-transfer across “zigzag” has a much lower energy barrier than other reaction channels (Supporting Information, Fig. S1), yielding intermediate [2] which readily cyclizes to intermediate [3]. Acenaphthylene and phenyl-acenaphthylene are the promising products of this reaction channel. Direct cyclization of RSR [1] is also favorable over a low energy barrier of 18.70 kcal/mol. Phenyl-acenaphthylene is then formed via H-elimination from intermediate [4]. The HAPaA route for “zigzag” creates “armchair” and “cove”, or maintains “zigzag” by eliminating a phenyl radical.

Figure 2B presents the major reaction channels of phenylacetylene addition to 4-phenanthryl radical, illustrating the prototypical HAPaA route for “armchair”. RSR [5] is formed by a barrierless addition of 4-phenanthryl radical to phenylacetylene. It further cyclizes to intermediate [8] over a very low energy barrier of about 6 kcal/mol, then eliminates an H-atom to form 4-phenyl-pyrene. New “zigzag”, “armchair” and “cove” sites are created in this process. Moreover, H-transfer of RSR [5] via a hepta-ring transition state overcomes a barrier of about 8 kcal/mol to form intermediate [6], which further cyclizes to intermediate [7]. Beside 4-phenyl-pyrene, pyrene is also derived from intermediate [7] via phenyl elimination, which evolves the periphery of “armchair” to “zigzag”. The reaction channels where the C=C double bond sidechain of phenylacetylene lays over “zigzag” and “armchair” peripheries are the dominant HAPaA routes according to these theoretical calculations. The HAPaA route for “zigzag” fuses new penta-ring, while that for “armchair” fuses new benzene ring. Other unimolecular isomerization of [1] and [5] have energy barriers in excess of 20 kcal/mol (Supporting Information, Figs. S1 and S2), and thus have weak competition to the routes...
naphthyl and 4-iodo-phenanthrene (Fig. S12), respectively. Normal and italic numbers label relative energies of intermediates and transition states, respectively. (A) “zigzag”: reactants are 1-naphthyl and phenylethynyl; (B) “armchair”: reactants are 4-phenanthryl and phenylethynyl.

depicted in Fig. 2.

Besides cyclization channels, entropy driven H-elimination reactions of [1] and [5] form 1-phenylethynyl-naphthalene and 4-phenylethynyl-phenanthrene (Q1 and Q2 in Fig. 2), respectively; however, these products may not be very relevant due to their high energy barriers. Pressure- and temperature-dependent reaction rate coefficients, calculated by solving RRKM and master equations, support the dominance of the two cyclization channels over Q1 or Q2 channels in 1-naphthyl / phenylethynyl or 4-phenanthryl / phenylethynyl reactions (Supporting Information, Fig. S12). The Q1 channel is comparable to the cyclization channels at T > 2000 K; the Q2 channel is much slower than the cyclization channels in the temperature range of 500 – 2500 K at various pressures.

Phenylethynyl addition to “cove” has an energy barrier of 3.36 kcal/mol which is different from the barrierless addition steps of “zigzag” and “armchair” (Supporting Information, Fig. S3). Further isomerization of its initially formed adduct is also very difficult due to the steric hindrance. The steric hindrance at “fjord” is generally similar or stronger than “cove”. Meanwhile, “cove” and “fjord” radicals have a tendency for unimolecular ring closure reactions with energy barriers of about 20 and 3 kcal/mol, respectively (Supporting Information, Fig. S4). Therefore, these two periphery types prefer ring closure reactions as compared to the phenylethynyl addition, as shown in Fig. 1C.

**Elementary Reaction Experiments.** The reaction systems of 1-naphthyl / phenylethynyl and 4-phenanthryl / phenylethynyl were measured at 1173 K and 3 Torr in a flow reactor coupled to SVUV-PI-MBMS.\(^{33,34}\) We initiated these two reaction sequences in excess of phenylethynyl by producing 1-naphthyl and 4-phenanthryl radicals via rapid thermal decomposition of 1-iodo-naphthalene and 4-bromo-phenanthrene, respectively. In the control experiment, phenylethynyl, 1-iodo-naphthalene and 4-bromo-phenanthrene were separately injected to the flow reactor at the same experimental condition. Under the reaction conditions of 1173 K and 3 Torr, the adducts from the reactions of 1-naphthyl / phenylethynyl and 4-phenanthryl / phenylethynyl are not easy to stabilize to the intermediates in the potential energy wells of Fig. 2 (Supporting Information, Fig. S12). Chemical-activation channels are important in such a reaction environment, and these channels directly lead to the products.\(^{6,37}\) SVUV-PI-MBMS experiments identified the products of these elementary reactions instead of reaction intermediates.

Figure 3A shows measured mass peaks from m/z = 70 to 260 for 1-naphthyl / phenylethynyl reaction at a photon energy of 9.5 eV. Mass peak of m/z = 254 is 1-iodo-naphthalene which decomposes to 1-naphthyl radical. Iodide atom (m/z = 127) ionizes at 10.45 eV\(^{38}\), and it has no interference to the detection of 1-naphthyl; however, the expected signal of m/z = 127 from 1-naphthyl is not observed in Fig. 3A. Mass peaks of m/z = 128 and 129 are naphthalene and its \(^{13}\)C-isotope, derived from 1-naphthyl, according to the photoionization efficiency (PIE) curves in Fig. 4B. A previous study using a similar molecular beam sampling system at the outlet of a flow reactor also did not detect aryl radicals.\(^{39}\) We hypothesize that these very reactive aryl radicals may combine with free H-radicals within the residence time of our reactor or abstract H-atoms via wall reaction at the pinhole of the quartz nozzle.\(^{40}\) Therefore, the detection of benzene, naphthalene, and phenanthrene instead of phenyl, 1-naphthyl, and 4-phenanthryl in Fig. 3 is an artefact of our reactor and sampling system (Supporting Information). Mass peaks m/z = 78, 152, 228 and 229 in Fig. 3A are absent in the control experiment (Supporting Information, Fig. S11), suggesting that signals at these mass-to-charge ratios originate from the reaction of 1-naphthyl and phenylethynyl. Mass peak m/z = 228 (C\(_{18}\)H\(_{22}\)) corresponds to the products of 1-naphthyl and phenylethynyl with an H-atom loss; these products are phenyl-acenaphthylene and/or 1-phenylethynyl-naphthalene. Mass peak m/z = 229 could be [1] and/or \(^{13}\)CC\(_{17}\)H\(_{12}\). Figure 4E presents the PIE curve of m/z = 228 measured in the reaction, reproduced by the reference
curves of phenyl-acenaphthylene and 1-phenylethynyl-naphthalene. The branching ratio is evaluated to be 93% and 7% by the photoionization cross sections (PICSs) of both molecules (Supporting Information, PICS measurement and PIE curve fitting method). The best fitting result of the PIE curve indicates the majority of the signal to be from phenyl-acenaphthylene, which agrees with theoretically predicted branching ratios (Supporting Information, Fig. S12).

Figure 3. Mass spectra recorded at a photoionization energy of 9.5 eV. (A) 1-naphthyl / phenylacetylene reaction; (B) 4-phenanthyl / phenylacetylene reaction. Weak ion peaks (red) are multiplied by a factor of 10 or 50 for clarity.

Figure 3B shows measured mass peaks from m/z = 70 to 285 for 4-phenanthyl / phenylacetylene reaction at a photon energy of 9.5 eV. Mass peaks of m/z = 256 and 258 are the two isotomers of 4-bromo-phenanthrene which decomposes to 4-phenanthryl radical. Mass peaks m/z = 78, 202 and 278 in Fig. 3B are absent in the control experiment (Supporting Information, Fig. S11), suggesting that signals at these mass-to-charge ratios originate from the reaction of 4-phenanthryl and phenylacetylene. Mass peak m/z = 278 (C_{22}H_{14}) corresponds to the products of 4-phenanthryl and phenylacetylene with an H-atom loss; these products are 4-phenyl-pyrene and/or 4-phenylethynyl-phenanthrene. Figure 4H presents the PIE curve of m/z = 278 measured in this reaction, which can be perfectly reproduced by the reference curve of 4-phenylpyrene. The contribution of 4-phenylethynyl-phenanthrene is negligible (Supporting Information, Fig. S13). Therefore, 4-phenyl-pyrene is identified to be the dominant product, in agreement with the predicted branching ratios (Supporting Information, Fig. S12).

Mass peaks m/z = 152 (C_{12}H_{8}) in Fig. 3A and m/z = 202 (C_{16}H_{10}) in Fig. 3B correspond to the products of the HAPaA routes for “zigzag” and “armchair”, respectively. 1-Naphthyl and 4-phenanthryl, respectively, add to phenylacetylene and subsequently eliminate phenyl radical, which then transforms to benzene (m/z = 78, C_{6}H_{6}). As shown in Figs. 4A, C and G, PIE curves of m/z = 78, 152 and 202 measured in the reactions agree with the reference curves of benzene, acenaphthylene, and pyrene, respectively (Supporting Information). Altogether, the experiments illustrate that phenylacenaphthylene and acenaphthylene are formed in 1-naphthyl / phenylacetylene reaction, while 4-phenyl-pyrene and pyrene

Figure 4. PIE curves of critical products. A-E) 1-naphthyl / phenylacetylene reaction; F-H) 4-phenanthyl / phenylacetylene reaction. Black/blue dots: experimental data; green/purple lines: reference PIE curves; red lines: the overall fit.

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are formed in 4-phenanthryl / phenylacetylene reaction.

Mass peak m/z = 178 observed in 1-naphthyl / phenylacetylene reaction (Fig. 3A) is absent in the control experiment of phenylacetylene or 1-iodo-naphthalene, and the signal of m/z = 178 in 4-phenanthryl / phenylacetylene reaction (Fig. 3B) is much stronger than that in the control experiment of 4-bromo-phenanthrene (Supporting Information, Fig. S11). These results suggest a C$_{16}$H$_{10}$ byproduct other than 4-phenanthryl derived phenanthrene in these reaction systems. PIE curve of m/z = 178 in Fig. 4D perfectly agrees with the reference curve of diphenylacetylene$^{42}$, and the PIE curve in Fig. 4F is fit by a linear combination of the reference curves of diphenylacetylene and phenanthrene (evaluated branching ratios: 74% and 26%, respectively). Because of the formation of phenyl radical in the reaction systems of 1-naphthyl / phenylacetylene and 4-phenanthryl / phenylacetylene, mass peak m/z = 178 (C$_{16}$H$_{10}$) may be diphenylacetylene formed via the combination of phenyl and phenylacetylene$^{31}$.

Discussion

As summarized in Fig. 1, theoretical and experimental results demonstrate the selectivity of aryl periphery type to the HAPaA product: i. adduct on “free” periphery eliminates an H-atom to regain triple bond$^{31}$; ii. adduct on “zigzag” cyclizes to create “zigzag” and/or “armchair” via dehydrogenation or phenyl elimination; iii. adduct on “armchair” cyclizes to create “zigzag” “armchair”, and/or “cove” via dehydrogenation or phenyl elimination; iv. and v. the closure reactions of “cove” and “fjord” create “armchair”. Both benzene and acetylene are crucial intermediates in astrochemistry$^{13, 42-44}$ and combustion chemistry$^{1}$. Subsequent to the H-abstraction of benzene, phenylacetylene is one of the primary products from the reaction of phenyl and acetylene at PAH forming conditions$^{31}$. The conversion among different peripheries and sufficient amount of phenylacetylene make HAPaA a self-consistent mechanism for PAH growth.

HAPaA mechanism is not limited to phenylacetylene addition. The key structure is the triple bond neighboring the benzene ring. A RSR is thus formed in its addition to aryl, which benefits further isomerization. A double bond is maintained in the molecular structure of reaction intermediate to fuse new aromatic rings. Other PCAHs with α-alkynyl substitution are potential candidates for HAPaA mechanism, such as ethynyl-naphthalene, ethynyl-pyrene, ethynyl-ovalene, etc., HAPaA mechanism thus may be extended to H-Abstraction PCAH with α-alkynyl substitution Addition. The carbon/hydrogen (C/H) ratio of nascent soot is in a range of 1.2 – 2, while that of moderately-sized or mature soot is 8 – 20$^{45}$. Soot inception is accompanied by continuous molecular weight increase and hydrogen release, which is promoted by the addition of higher C/H ratio molecules. The reactants of HACA, HAVA, PAC and HAPaA mechanisms are acetylene, vinylacetylene, phenyl, and phenylacetylene (α-alkynyl PCAHs), which have C/H ratios of 1.0, 1.0, 1.2, and 1.3 (ethynyl-naphthalene: 1.5, ethynyl-pyrene: 1.8), respectively. HAPaA thus has a clear advantage among these mechanisms for PAH growth and particle surface growth due to its larger increment of C/H ratio. Moreover, “cove” and “fjord” created in the HAPaA routes further promote the dehydrogenation efficiency. Soot inception likely takes place by the clustering process of large precursor molecules. Direct dimerization of two PCAHs is kinetically unstable, especially at the high temperatures of soot nucleation$^{1}$. HAPaA mechanism provides an alternative C-C covalent bond bridge for the combination of two PCAHs, in which acetylene plays as a linker of large PCAHs. In the first step, the high concentration of acetylene in both low-temperature astrochemistry$^{13, 43}$ and high-temperature combustion conditions$^{1}$ benefits its addition to PCAHs. Abundant α-alkynyl PCAHs are produced, e.g., the concentration of phenylacetylene approaches 200 ppm in premixed ethylene sooting flames, which is comparable to that of benzene$^{46}$. In the second step, α-alkynyl PCAHs react with aryl radicals of various periphery types via the HAPaA mechanism, which in turn yields larger PCAHs. The continuous loop of these two steps clusters PCAHs to incipient soot particles.

Conclusion

Our theoretical calculations and experimental results identified phenyl-acenaphthylene, acenaphthylene, phenyl-pyrene and pyrene as the key reaction products in 1-naphthyl / phenylacetylene and 4-phenanthryl / phenylacetylene reaction systems, revealing the critical role of the previously elusive HAPaA mechanism. Since the initial addition step of phenylacetylene to aryl radical is barrierless, HAPaA mechanism is efficient in the mass growth of PAHs under low-temperature conditions of circumstellar envelopes of carbon stars and high-temperature conditions of combustion. The aryl periphery type shows high selectivity of the HAPaA product, where “zigzag” and “armchair” have high intensity to fuse new penta- and hexa-aromatic rings, respectively. The evolution of different periphery types to each other, including “armchair” derived from the ring closure reactions of “cove” and “fjord”, makes HAPaA a self-consistent mechanism. The formation chemistry of both planar and curved aromatic nanostructures may be explained by this mechanism, such as buckminsterfullerene which has been detected in combustion and planetary nebula.

Kinetic findings in this work also suggest PCAHs with α-alkynyl substitution to be potential building blocks of carbonaceous nanostructures. With the assistance of abundant acetylene in combustion and circumstellar envelopes, HAPaA mechanism benefits the bonding of two PCAHs which is difficult to stabilize via direct combination. This discovery has radical implications on our understanding of soot precursor molecular structure and its growth reactions, and it can help to improve the accuracy as well as fidelity of multi-scale kinetic models of soot formation. HAPaA mechanism may also be exploited for the synthesis of 2D and 3D carbonaceous nanomaterials under the effective control of reaction route selectivity.

Methods

Computational: The potential energy surface (PES) for HAPaA mechanism was calculated with a combination of density functional theory (DFT) hybrid method M062X/6-311+G(d,p)$^{47}$ and double hybrid method B2PLYPD3/def2-TZVPP$^{48,49}$. Results were compared to CCSD(T)/cc-pVnZ (n=D, T, Q) with respect to the energies of two key channels in phenyl / phenylacetylene reaction and to the standard enthalpies of formation for several unsaturated hydrocarbons (Supporting Information, Table S1). Pressure- and temperature-dependent chemical kinetics of key elementary reactions
were computed by solving RRKM/ master equations with MESS code\(^{36}\). Lennard-Jones parameters (\(c, \sigma\)) of reactants were (515.9 cm\(^{-1}\), 8.066 Å) for 1-naphthyl / phenylacetylene and (580.8 cm\(^{-1}\), 8.831 Å) 4-phenanthryl / phenylacetylene systems, respectively\(^{31}\), and those for argon were (79.2 cm\(^{-1}\), 3.47 Å)\(^{22}\). Average energy transferred per collision was assumed with a temperature-dependent expression \(<\Delta E_{\text{down}}> = 400/(T/300)^{0.8}\) in a single-exponential down model.

**Experimental**: The experiments were conducted at an undulator-based synchrotron vacuum ultra-violet beamline (BL03U) of Hefei Light Source (HLS II), China. The elementary reactions of 1-naphthyl / phenylacetylene and 4-phenanthryl / phenylacetylene were performed in a resistively-heated flow reactor. 1-Naphthyl and 4-phenanthryl were prepared in situ via the pyrolysis of 1-iodonaphthalene (Macklin, 98%) and 4-bromophenanthrene (Supporting Information, Synthesis of chemicals), respectively. These precursors were seeded with phenylacetylene (Sigma-Aldrich, 98%) in argon carrier gas (3 Torr). A tungsten–rhenium (W–Re) thermocouple was positioned at the middle region to control the reactor temperature. The reacting species were sampled by a quartz nozzle with an orifice of 1.1 mm, forming a supersonic molecular beam due to the large pressure gradient. The forming molecular beam passed through a skimmer, and was ionized by the tunable SVUV light. Ions were transferred by an ion introducer, and finally detected by a home-made reflection time-of-flight mass spectrometer\(^{33-34}\). Control experiments were conducted by expanding argon carrier gas separately with 1-iodonaphthalene, 4-bromophenanthrene, and phenylacetylene, while keeping the same temperature and pressure as 1-naphthyl / phenylacetylene and 4-phenanthryl / phenylacetylene reactions. SVUV single photon ionization is essentially a fragmentation-free ionization technique and is considered to be a soft ionization method compared to electron impact ionization\(^{34}\). PIE curves at a particular m/z ratio are obtained over a wide photon energy range by integrating the ion counts recorded at the specific mass of species. These scans show the intensity changes of each individual mass peak as a function of the photon energy (step interval 0.03 eV). Reference PIE curves of phenyl-acenaphthylene (Supporting Information, Synthesis of chemicals), 1-phenylethynyl-naphthalene (Supporting Information, Synthesis of chemicals), pyrene (Macklin, 99%), and 4-phenyl-pyrene (Supporting Information, Synthesis of chemicals) were measured using their benzene solutions in this study.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website: Theoretical approach, experimental approach, and appended experimental results (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

* Aamir Farooq, aamir.farooq@kaust.edu.sa
* Lili Ye, yell@dlut.edu.cn

**Author Contributions**

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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H-abstraction phenylacetylene addition mechanism (HAPaA)

"armchair" ↔ "zigzag" ↔ "cove"

"free" ↔ "fjord"

phenyl elimination

H-elimination

H-elimination