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Supporting Information

Gas-Phase Preparation of the 14π Hückel Polycyclic Aromatic Anthracene and Phenanthrene Isomers ($C_{14}H_{10}$) via the Propargyl Addition–BenzAnnulation (PABA) Mechanism

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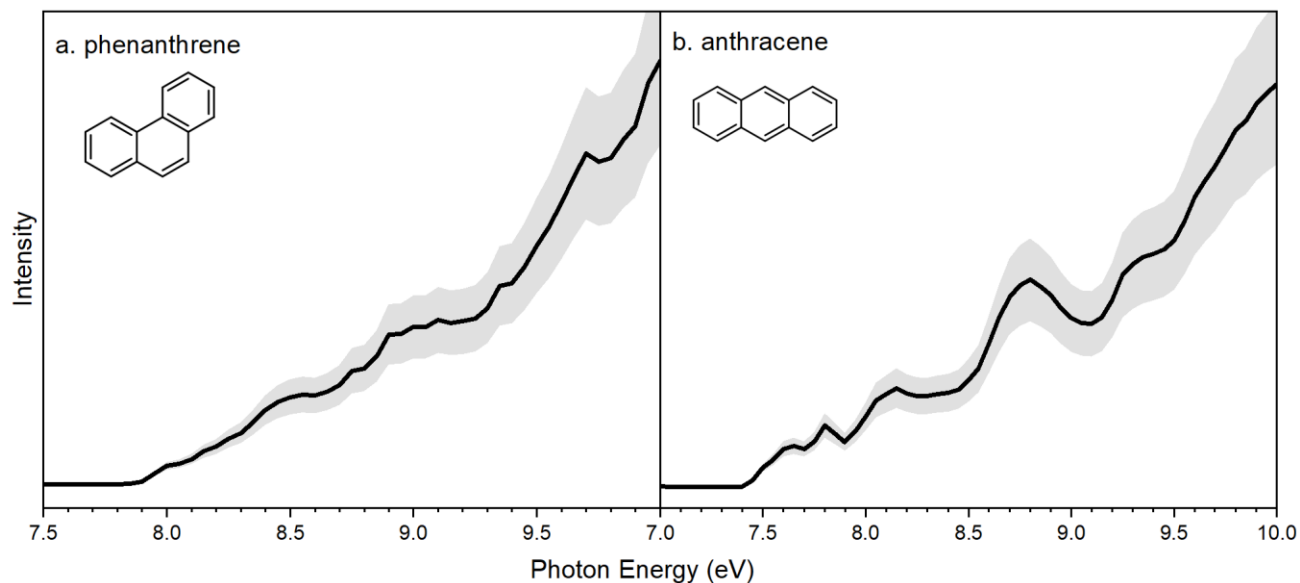


Figure S1. PIE calibration curves for distinct $C_{14}H_{10}$ isomers: phenanthrene, anthracene^[1]. The overall error bars (grey area) consist of two parts: $\pm 15\%$ based on the accuracy of the photodiode and a 1σ error of the PIE curve averaged over the individual scans. The photoionization cross sections (PICSSs) were determined from the Photoionization Cross Section Database.

We also inspect the PIE curves at $m/z = 139, 140, 141, 142, 143$ and 180 (Figs. S2 and S3) to provide additional information of the underlying reaction mechanism(s). In 1'-naphthylmethyl/propargyl system, the signal at $m/z = 141$ is attributed to the 1'-naphthylmethyl ($C_{11}H_9^+$) from the C-Cl bond dissociation of the precursors 1'-chloromethylnaphthalene. The experimental PIE curve of 1'-naphthylmethyl ($C_{11}H_9^+$) at $m/z=141$ is presented in Fig. S2c. Unfortunately, the onset of PIE curve is not exhibited due to the low photoionization energy. The complete PIE curve of 1'-naphthylmethyl can be referred to the previous investigation^[2]. The H-loss of 1'-naphthylmethyl leads to the formation of the species at $m/z = 139$ ($C_{11}H_7$, Fig. S2a) and 140 ($C_{11}H_8$, Fig. S2b). However, no corresponding PIE reference data for $m/z=139$ and 140 are available. Figure S2d exhibits the experimental PIE curve at $m/z=142$ with the fit based on the reference data of 1'-methylnaphthalene ($C_{11}H_{10}$) and the 1'-naphthylmethyl isotope ($^{13}C_{10}H_9$). 1'-Methylnaphthalene is generated from the H-addition of 1'-naphthylmethyl radical. For PIE curves at $m/z = 143$, it is attributed to the ^{13}C -isotopic of 1'-methylnaphthalene ($^{13}C_{10}H_{10}$, Fig. S2e). Similarly, the signals in 2'-naphthylmethyl/propargyl system could be analogous to those in 1'-naphthylmethyl/propargyl system, and will not be discussed in details here.

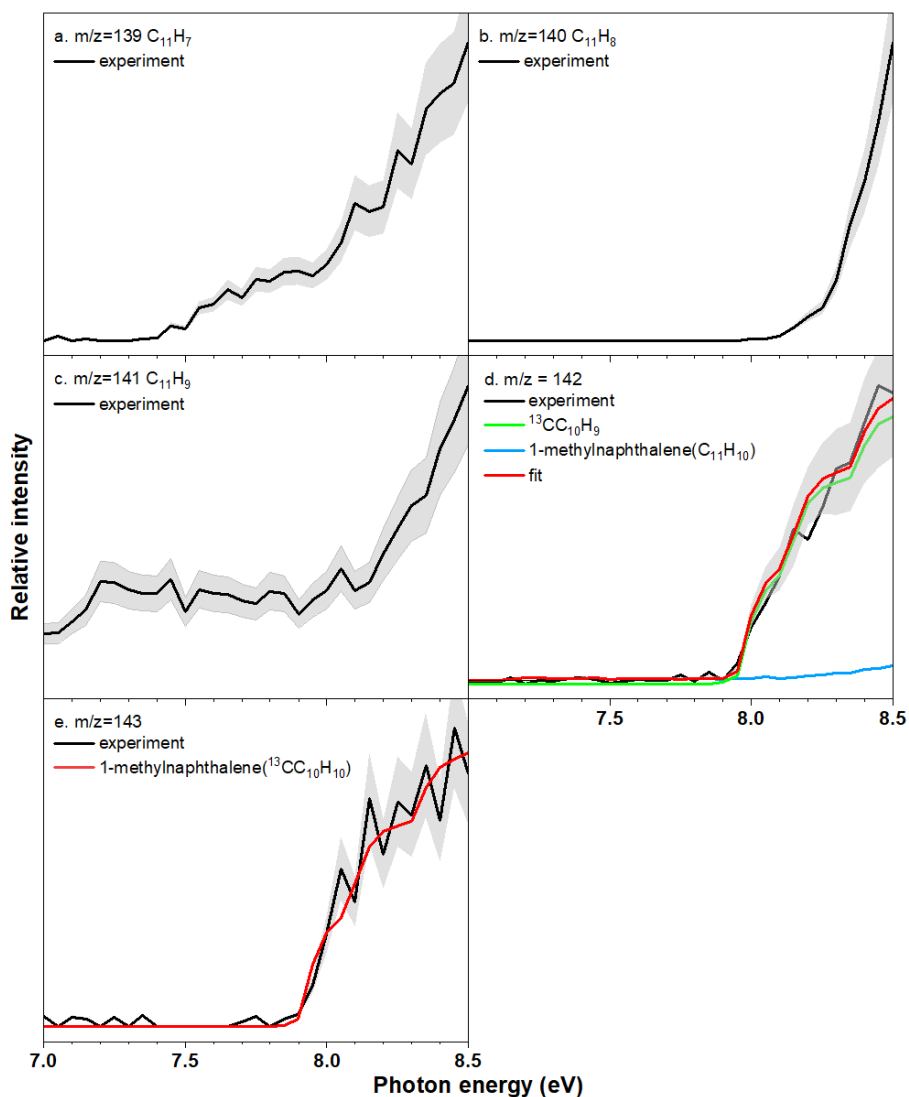


Figure S2. PIE curves along with the fits for additional species ($m/z = 139, 140, 141, 142$ and 143) in the 1'-naphthylmethyl ($C_{11}H_9^+$)/propargyl ($C_3H_3^+$) system. The black line refers to the normalized experimental data. The colored lines refer to the reference PIE curves of isomers. The red line shows the overall fit via the linear combination of the reference curves. The overall error bars consist of two parts: $\pm 15\%$ based on the accuracy of the photodiode and a 1σ error of the PIE curve averaged over the individual scans. Signal at $m/z = 141$ can be connected to the 1'-naphthyl-methyl ($C_{11}H_9^+$) prepared via the pyrolysis of 1'-chloromethylnaphthalene ($C_{11}H_9Cl$, $m/z = 176$ and 178). The H-loss (139 amu., 140 amu.) and H-addition products (142 amu., 143 amu.) to 1'-naphthylmethyl can be detected via signal at $m/z = 139$ ($C_{11}H_7$), 140 ($C_{11}H_8$), 142 ($^{13}CC_{10}H_9/C_{11}H_{10}$) and 143 ($^{13}CC_{10}H_{10}$).

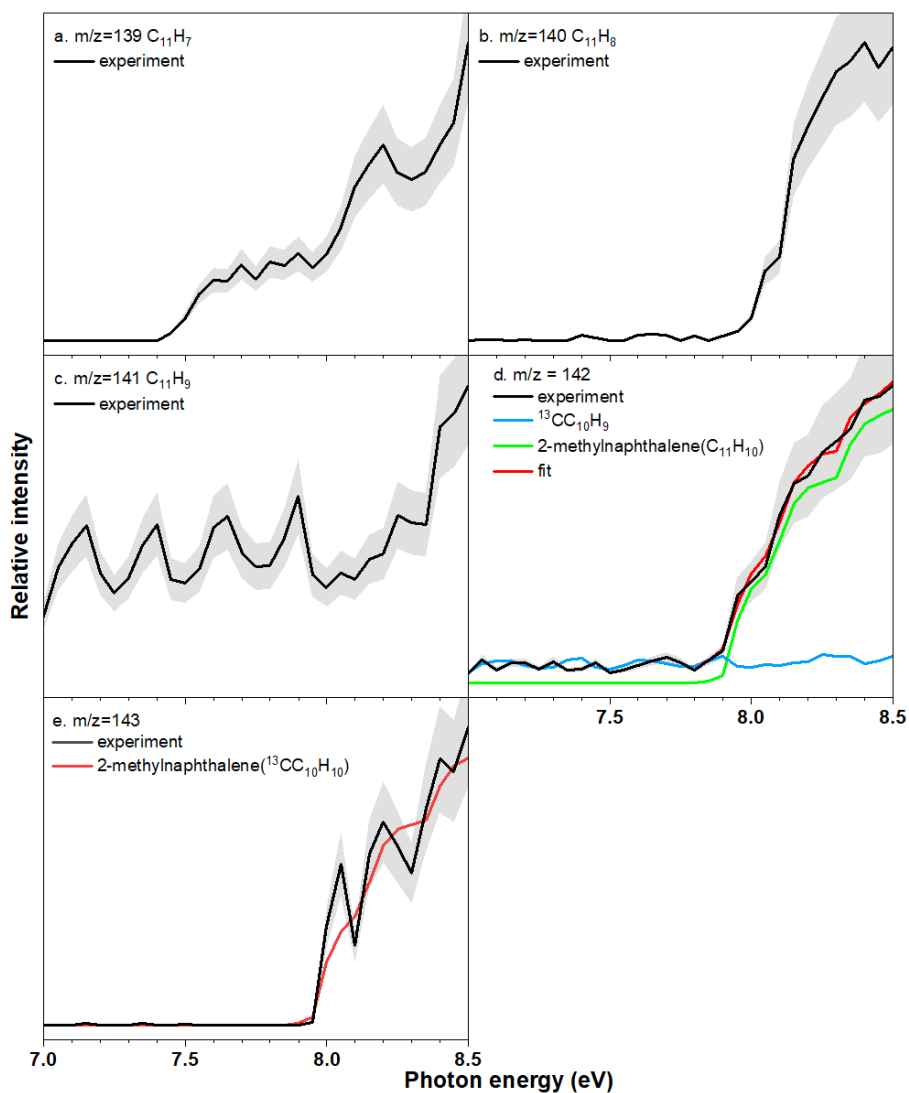


Figure S3. PIE curves along with the fits for additional species ($m/z = 139, 140, 141, 142$ and 143) in the 2'-naphthylmethyl ($C_{11}H_9^+$)/propargyl ($C_3H_3^+$) system. The black line refers to the experimental data. The colored lines refer to the reference PIE curves of isomers. The red line shows the overall fit via the linear combination of the reference curves. The overall error bars consist of two parts: $\pm 15\%$ based on the accuracy of the photodiode and a 1σ error of the PIE curve averaged over the individual scans. Signal at $m/z = 141$ can be connected to the 2'-naphthylmethyl ($C_{11}H_9^+$) prepared via the pyrolysis of 2'-chloromethylnaphthalene ($C_{11}H_9Cl$, $m/z = 176$ and 178). The H-loss (139 amu., 140 amu.) and H addition products (142 amu., 143 amu.) to 2'-naphthylmethyl can be detected via signal at $m/z = 139$ ($C_{11}H_7$), 140 ($C_{11}H_8$), 142 ($^{13}CC_{10}H_9/C_{11}H_{10}$) and 143 ($^{13}CC_{10}H_{10}$).

References

- [1] L. Zhao, R. I. Kaiser, B. Xu, U. Ablikim, M. Ahmed, M. M. Evseev, E. K. Bashkurov, V. N. Azyazov, A. M. Mebel, *Nat. Astron.* **2018**, 2, 973-979.
- [2] W. Li, L. Zhao, R. I. Kaiser, *Phys. Chem. Chem. Phys.* **2023**, 25, 4141-4150.