On-Surface Synthesis and Characterization of Long Acenes

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Acenes represent a unique class of polycyclic aromatic hydrocarbons that have fascinated chemists and physicists due to their exceptional potential for use in organic electronic applications. The comprehensive understanding of their fundamental properties necessitates the expansion of the homologous series towards longer acenes. Here, we demonstrate the on-surface synthesis of tridecacene (**13ac**) and pentadecacene (**15ac**), via atom-manipulation-induced dissociation of trietheno-bridged precursors on Au(111) surface under ultra-high vacuum conditions. The geometric and electronic structures of the generated acenes have been investigated by combined scanning tunnelling microscopy/spectroscopy. We observe that the STS transport gap for **13ac** (1.09 eV)[1] and **15ac** (1.11 eV) shrink again following the gap reopening of dodecacene (12ac)(1.4 eV)[2]. The antiferromagnetic open-shell ground state electron configurations for **13ac** and **15ac** are confirmed from spin-polarized density functional theory calculations, while their open-shell character are significantly reduced upon interaction with the Au(111) surface despite being only physisorbed. For 15ac, a spin-excitation feature at low bias was determined, giving a singlet-triplet gap of around 124 meV. Alternatively, upon a thermal cracking of the trietheno-bridges at higher temperature, **15ac** can be also generated and spontaneously forms complex structure with up to 6 gold atoms on Au(111) surface, suggesting a considerable polyradical character contribution to its electronic ground state[3].

References

[1] Ruan, Z., Schramm, J., Bauer, J. B., Naumann, T., Bettinger, H. F., Tonner-Zech, R., & Gottfried, J. M. J. Am. Chem. Soc. 146 (2024) 3700–3709.
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Figures

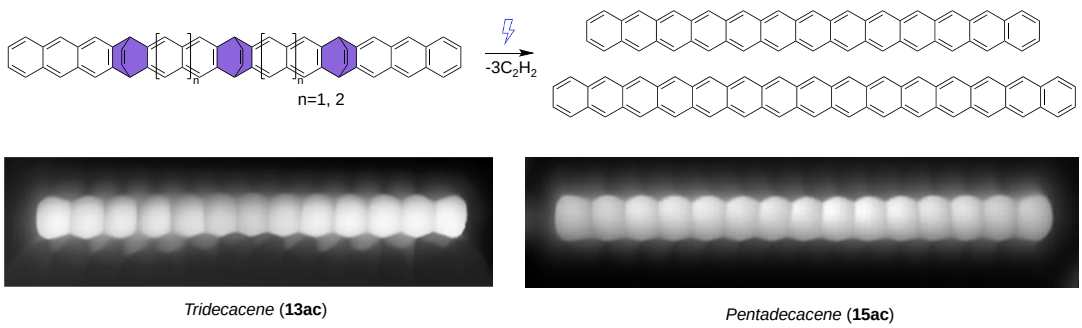

Figure 1: Scheme of the synthetic routs towards **13ac** and **15ac** and their corresponding high resolution bond-resolved STM images.