Synthesis of Polyacene Utilizing Coordination Nanospaces

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Acenes are a class of aromatic hydrocarbons composed of linearly fused benzene rings. The intriguing feature of acenes—evolution of physical properties with an increase in the benzene ring number—fascinated a wide spectrum of researchers. However, the synthesis of long acenes has been challenging due to their low solubility and inherent chemical instability. Since the first synthesis of pentacene in 1912,¹ the length of acenes has been gradually increased (one benzene ring at a time) via solution and on-surface synthesis, reaching dodecacene (12 rings), the longest acene reported so far.²

Here, we present a new methodology to extend the acene systems, mediated by a metal–organic framework (MOF), achieving the first synthesis of polymeric acenes with numerous benzene rings, namely polyacene.³ The strategy involves two steps: controlled synthesis of a polymeric hydroacene as a precursor within the MOF nanochannels, and the subsequent conversion into polyacene via dehydro-aromatization reaction (**Fig. 1**). The geometrical constraints of the MOF allowed for suppression of unfavorable crosslinking reactions, providing the linearly extended polymeric precursor. A series of characterizations, including solid-state NMR, UV/vis/NIR, and FT-IR spectroscopy measurements, confirmed the formation of polyacene that was overwhelmingly longer than the previously reported ones. The bulk-scale synthesis of polyacene will open up a new avenue toward not only unveiling the unique topological properties of the acene series but also its future applications in organic electronics and spintronics.



Fig. 1 Synthetic procedure of polyacene using a MOF.

REFERENCES

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