



[Schmidt, B. V.K.J.](#) (2023) MOF-made polyacenes. *Nature Synthesis*, 2, pp. 813-814. (doi: [10.1038/s44160-023-00340-4](https://doi.org/10.1038/s44160-023-00340-4))

There may be differences between this version and the published version.
You are advised to consult the published version if you wish to cite from it.

<https://eprints.gla.ac.uk/301117/>

Deposited on 20 June 2023

Enlighten – Research publications by members of the University of Glasgow

<http://eprints.gla.ac.uk>

CONFINED POLYMERIZATION

MOF-made polyacenes

The synthesis of polyacene is hampered by low solubility and instability of the product as well as side-reactions. Now, polyacene is synthesized by polymerizing monomers confined in a metal-organic framework.

Bernhard V. K. J. Schmidt

School of Chemistry, University of Glasgow, Glasgow, UK.

bernhard.schmidt@glasgow.ac.uk

@schmidtpolylab

Conjugated polymers are an intriguing class of polymer which have found applications owing to their conductive properties, for example, in batteries or organic light emitting diodes^{1,2}. New types of conjugated polymers are thus sought after to improve such devices and to attain unprecedented properties and applications. A promising group of conjugated polymers are polyacenes that consist of chains of linearly fused benzene rings. However, research is limited owing to their challenging synthesis and low yield. So far to the researcher's knowledge, chains of up to twelve benzene rings have been reported and promising physical properties observed. Now, writing in *Nature Synthesis*, Uemura and co-workers describe a method to obtain polyacenes consisting of chains of approximately 18 benzene rings – in quantities of around 20 milligram and potentially more³.

Pentacene was first reported in 1912⁴ and over the past decades more and more acenes were synthesized, showing intriguing physical properties, for example, charge carrier mobility⁵. The goal of achieving polyacenes was on the mind of chemists ever since. Nevertheless, synthesis in solution remains a challenge as a consequence of the low solubility and chemical instability of acenes as well as side-reactions⁶.

Furthermore, high regioselectivity of the coupling reactions of acene building blocks is required to obtain a linear molecule instead of a branching or zig-zag addition. A way to overcome solubility and instability by the introduction of solubilizing and stabilizing groups attached to the acenes. In this way, the synthesis of acenes containing up to nine benzene rings, namely nonacene, was achieved⁷. Another approach towards longer acenes has been on-surface synthesis, which facilitated synthesis of acenes with twelve benzene rings, dodecacene⁸. On-surface synthesis shows that spatial restriction may be a possible direction for polyacene synthesis. This observation suggests that increasing the spatial restriction still further by performing the synthesis in a confined 3D environment is a potential strategy to higher acenes. This type of confined synthesis is referred to by some researchers as 'ship-in-a-bottle'. The 'ship-in-a-bottle' synthetic method reported by Uemura and coworkers uses the confined space of a porous 3D metal-organic frameworks (MOFs). Within the MOF or 'bottle', the coupling of benzene rings occurs with few side reactions. These MOFs feature well-defined pores perfectly suited as confinement for polymerization reactions⁹. Unlike previous synthesis routes, this synthesis of polyacenes – the 'ship' - introduces the building blocks into the MOF at the start of the synthesis (Fig. 1a). As such, polyacene chains can grow without interference from neighbouring chains or free monomers in the environment. Furthermore, the spatial restriction forces the monomers into an alignment that leads to linear growth without the introduction of zig-zag addition.

To achieve the goal of polyacene synthesis, a simple two step-procedure is used (Fig. 1b). At first, the monomer 2,6-bis(bromomethyl)naphthalene or 2,6-bis(bromomethyl)anthracene is introduced into the porous MOF via sublimation, leading to a chain-like alignment of monomers inside of the MOF channel. Next, the MOF with the monomers encased within is heated to 250 °C to induce bond formation. As such, linear polymers consisting of naphthalene or anthracenes units connected by two methylene units are obtained – the so called hydroacenes. After removal of the MOF template, the hydroacene precursor polymer is reacted by heating to 300 °C under air to perform the dehydro-aromatization revealing the final polyacene with an average of around 18 benzene units along the chain.

The polyacenes formed have low solubility, yet the molecular properties of the materials can be analyzed by absorption spectroscopy and mass spectrometry. Spectroscopic analysis revealed substantial absorption from the visible to the near infrared region and bandgaps around 1.30 eV, which are close to the theoretical value (1.23 eV) for acenes with infinite chain length¹⁰.

Electron spin resonance and superconducting quantum interfering device were used to probe the biradical character of the synthesized polyacenes. It was found that open-shell singlet biradical molecules with carbon-centred radicals were present, yet a quite low concentration of spins was observed. The polyacene material is remarkably stable against oxidation in air, which is attributed to aggregation of the chains in the solid state leading to a reduction in biradical character, limited oxygen access as well as limited chain mobility to undergo oxidation and dimerization reactions.

The work by Uemura and co-workers is intriguing for several reasons. First, polyacenes with these numbers of benzene rings in the chain have not been reported so far. This gives the opportunity to study the properties of this type of conjugated polymers. It also may be possible to synthesize even longer polyacenes. Furthermore, the material is synthesized in good yield and can be scaled up relatively easily to obtain the product in reasonable amounts. The amount of material is crucial to enable further characterization and for integration into devices in the future.

A caveat of these polyacene materials is their challenging processing and improvement on this aspect will be essential to establish applications of polyacenes. To enhance processibility, further molecular design may be one way forward, for example, using monomers with solubilizing groups.

Meanwhile, this 'ship-in-a-bottle' synthesis of polyacenes, in reasonable amounts, opens up possibilities for further developments of polyacene materials and applications of such conjugated polymers in organic electronics.

References

1 Fratini, S. et al. *Nat. Mater.* **19**, 491–502 (2020).

2 Qiu, Z., Hammer, B. A. G. & Müllen, K., *Prog. Polym. Sci.* **100**, 101179 (2020).

3 T. Kitao et al., *Nat. Synth.* **2**, XX-XX (2023).

4. Mills, W. H. & Mills, M., *J. Chem. Soc., Trans.* **101**, 2194-2208 (1912).

5 Watanabe, M. et al. *Nat. Chem.* **4**, 574-578 (2012).

6Tönshoff, C. & Bettinger, H. F., *Chem. Eur. J.* **27**, 3193-3212 (2021).

7 Kaur, I., Jazdyk, M., Stein, N. N., Prusevich, P. & Miller, G. P., *J. Am. Chem. Soc.* **132**, 1261-1263 (2010).

8 Krüger, J. et al., *ACS Nano* **10**, 4538-4542 (2016).

9 Schmidt, B. V. K. J., *Macromol. Rapid Commun.* **41**, 1900333 (2020).

10 Shen, B., Tatchen, J., Sanchez-Garcia, E. & Bettinger, H. F, *Angew. Chem., Int. Ed.* **57**, 10506-10509 (2018).

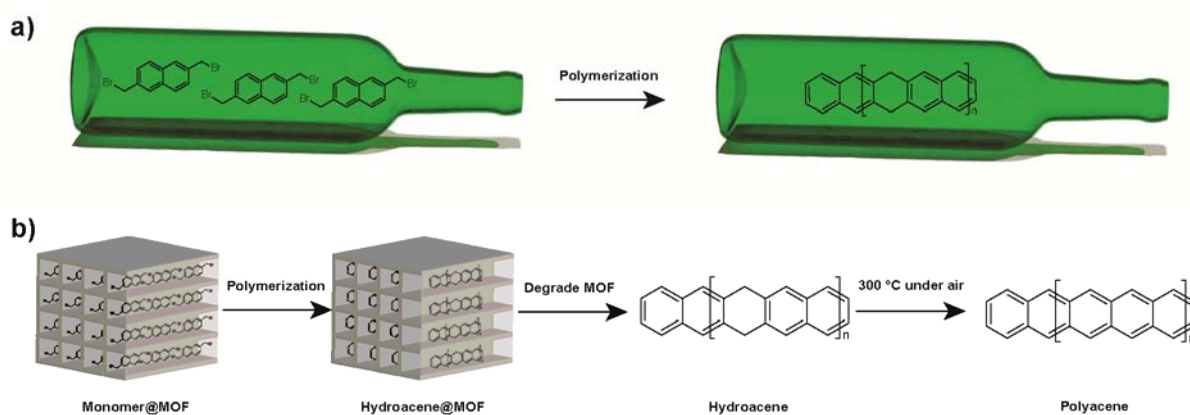


Figure 1 The confined synthesis of polyacenes in metal-organic frameworks (MOFs). a) A schematic of polyacene synthesis prepared by a ship-in-a-bottle approach, from the starting monomer 2,6-bis(bromomethyl)naphthalene. b) The synthetic approach towards polyacenes via the inclusion of monomer (exemplary for 2,6-bis(bromomethyl)naphthalene) into the MOF, followed by polymerization in the MOF channels and MOF degradation, to obtain free hydroacene and finally, conversion of hydroacene to polyacene.

Competing interests

The authors declare no competing interests.