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The Journey for the Synthesis of Large Acenes

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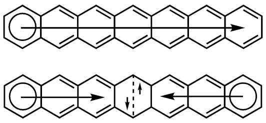
Acenes, the group of polycyclic aromatic hydrocarbons (PAHs) with linearly fused benzene rings, possess distinctive electronic properties with potential applicability in material science. Hexacene was the largest acene obtained and characterized in the last century, followed by heptacene in 2006. Since then, a race for obtaining the largest acene resulted in the development of several members of this family as well as diverse innovative synthetic strategies, from solid-state chemistry to the promising on-surface chemistry. This last technique allows the obtention of large acenes, up to tridecacene, the largest acene so far. This review presents the different methodologies employed for the synthesis of acenes, highlighting the newest studies, to provide a much more thorough understanding of the essence of the electronic structure of this captivating group of organic compounds.

Introduction

Acenes are polycyclic aromatic hydrocarbons (PAHs) consisting of linearly fused benzene rings, forming extended π-conjugated systems.[1] Regarding on the Clar's sextet rule formulated in 1972 for understanding the stability and properties of PAHs, acenes share a distinctive characteristic: they only possess one aromatic π-sextet among all six-membered rings of the entire molecule. There is a correlation between this feature of their aromaticity and reactivity, as it has been reviewed.[2,3] In fact, the presence of open-shell electronic configuration can make acenes to exhibit diradical character due to the delocalization of π-electrons along their backbone (Scheme 1). However, not all acenes have the same behaviour, as the change from closed-shell to open-shell for up to 6-ringed acenes is energetically unfavorable whereas for acenes with 7 or more rings is thermodynamically favourable.[4–7] Some studies have been reported to provide experimental evidences of this diradical character of acenes involving observations of paramagnetic behaviour, electron spin resonance spectroscopy studies and theoretical calculations.[8–10] However, the discussion about the nature of their electronic structure and the electronic configuration of the ground state is still open.[11,12]



Scheme 1. Clar structures for the closed-shell (top) and open shell (bottom) single states of heptacene.[5]

The electronic structure of the acenes not only influence their diradical character but also their HOMO–LUMO gap, which generally decreases as the length of the molecule increases.[13] The acenes with smaller values of HOMO–LUMO gaps tend to exhibit a greater diradical character, which increases with length from diradicaloid to polyradicaloid.[14–16] The narrow energy gap between HOMO and LUMO in acenes results in energetically low-lying triplet states, low ionization potentials (IPs) and high electron affinities (EAs).[17–19] These unique features make acenes of interest for their possible application in organic electronics and material science.[20–23] Readily available tetracene and pentacene, which are semiconductors,[24] are used for the fabrication of organic field-effect transistors (OFETs),[25–31] in organic photovoltaics (OPVs),[32,33] as light-emitting diodes (OLEDs),[34,35] and photodetectors.[36–40]

The synthesis of acenes large than pentacene has been a challenge due to their insolubility and instability leading to dimerization and/or endoperoxide formation. To address these challenges, the "precursor approach" was developed, which involves the synthesis, purification, and characterization of soluble and stable precursors of the desired acenes. These precursors are then processed in solution, and their final conversion into acenes occurs after they are assembled into thin films or crystals, or when adsorbed onto metallic surfaces.[39,41–43] Although the preparation of substituted acenes has been also investigated as a choice for changing their properties and resolve some of their insolubility and instability issues, this review only focus on the development of synthetic strategies to access the unsubstituted large acenes, from the solid state using organic chemistry techniques to innovative on-surface synthesis.

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Organic Synthesis of Acenes

As already mentioned, acenes have so great and unique properties that make them very attractive for their study in different scientific fields, specifically for their application in material science. During last two decades, acenes have been the topic of several reviews.[44–50] The focus here is to show the evolution of strategies for the synthesis of large acenes, from hexacene up to tridecacene, the longest acene obtained and characterized so far.

Hexacene

The first reported syntheses of hexacene (**1**) were based on a catalytic dehydrogenation of different saturated precursors: a) from either 5,16-dihydrohexacene or 6,15-dihydrohexacene using Cu powder at 300–320 °C in an atmosphere of carbon dioxide,[51] b) from docosahydrohexacene using Pd/C at 250–330 °C[52]; c) from 6,15-dihydrohexacene using Cu powder at 325 °C in an atmosphere of CO_2 as well as from 1,2,3,4,7,14-hexahydrohexacene using Pd/C at 345 °C[53]; and d) from 5,16-dihydrohexacene using copper(II) oxide at 270 °C in an atmosphere of carbon dioxide (Scheme 2).[54] In these methodologies, hexacene was finally purified by sublimation in vacuum yielding the acene as dark green crystals, whose structure was determined in a crystallographic study reported in 1962.[55]

However, the quality of the obtained crystals was not good enough for X-ray diffraction analysis. In addition, these early synthetic routes were difficult to reproduce, what made a detailed study of hexacene no possible until 2007, almost 40 years later, when Neckers[56] reported a new strategy based on the Strating-Zwanenberg photodecarbonylation of the α-diketone precursor **2**, which was reported by that group for the synthesis of heptacene only a year before.[57] The preparation of the α-diketone **2**, precursor for the synthesis of hexacene, started by two consecutive Diels-Alder reactions between bicyclo[2,2,2]oct-2,3,5,6,7-pentacene (**7**) and benzyne or 2-naphthyne, followed by the aromatization of the resulting compound using chloranil (Scheme 3). Then, dihydroxylation of the ethene bridge was performed with OsO_4/NMO, followed by the double Swern oxidation of the hydroxy groups with DMSO/TFAA. Hexacene (**1**) rapidly undergoes dimerization in solution, even at very low concentrations, and endoperoxides such as **8** were formed when **1** was generated in an oxygen saturated solution. However, the stability of **1** considerably increased when it was produced in a poly(methyl methacrylate) matrix, remaining stable for more than 12 h. Substituents such as phenyl, *p-tert*-butylphenyl, and mesityl groups were introduced at the 6 and 15 positions at **1**, which did not significantly increase the stability.

Since then, other synthesis of hexacene (**1**) were developed. Thus, the group of Chow used monoketone **3**, synthesized in six steps from the Diels-Alder adduct of 2-benzyne with 6,6-dimethylfulvene via intermediate **9**, as precursor of hexacene

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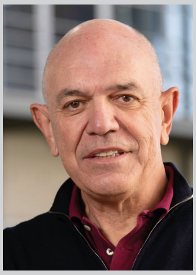
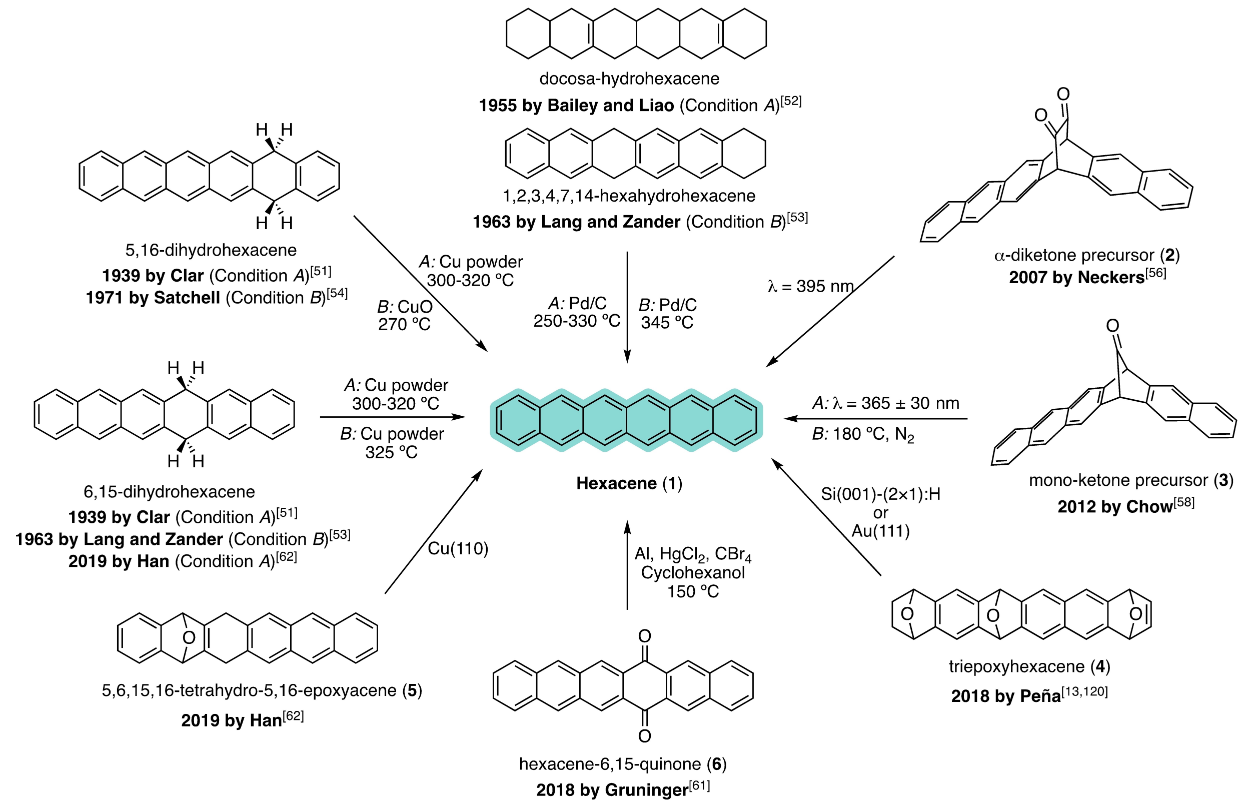
Rafal Zuzak works as a researcher at the Jagiellonian University in Kraków. In 2019, he earned his PhD in physics. The investigation of atomic and molecular systems has been his primary area of interest since the start of his career. Now he is focused on on-surface synthesis experiments, which involve directly initiating chemical processes and forming novel organic structures on crystalline substrates. His research mostly concentrates on creating novel reaction schemes on semiconducting and insulating substrates and integrating molecular nanostructures with low-dimensional devices.

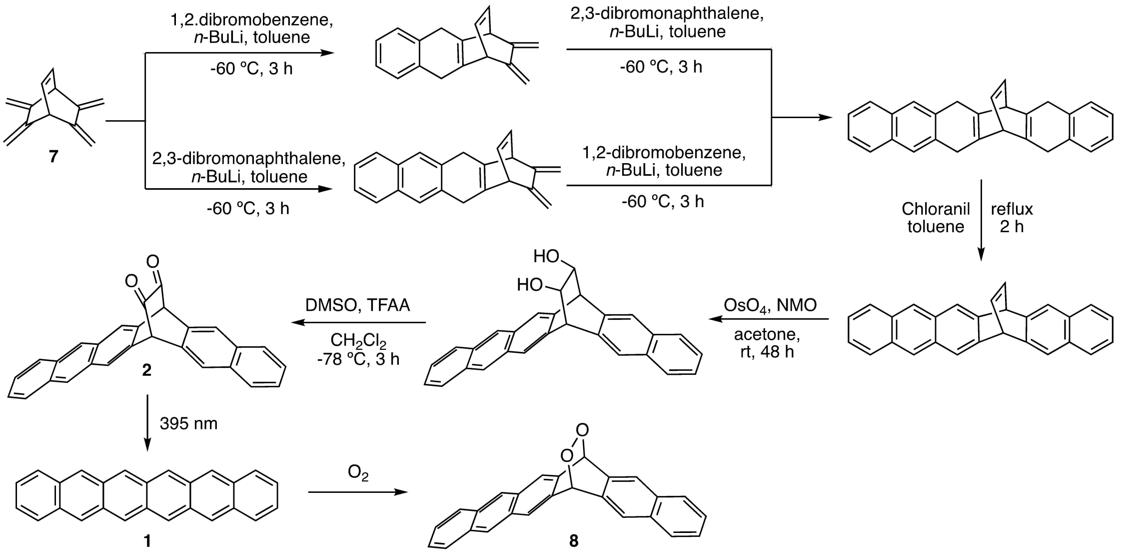
Szymon Godlewski is a Professor at the Jagiellonian University in Kraków. He obtained his PhD in physics in 2011, followed by the degree of habilitated doctor in 2019. From the beginning of his career, his research interests have centered on constructing atomic and molecular systems. In recent years he has focused his attention on the so-called on-surface synthesis approach to initiate chemical reactions and create new organic structures directly on crystalline substrates. In addition to his interest in the synthesis of the longest acenes, the research focuses on the development of new reaction schemes on semiconducting and insulating substrates.



Antonio M. Echavarren got his PhD in Chemistry from the Universidad Autónoma de Madrid (UAM, 1982). He started his independent career at the Institute of Organic Chemistry of the CSIC in Madrid and in 1992 he returned to the UAM as a Professor of Organic Chemistry. From 2004 he is a Group Leader at the Institute of Chemical Research of Catalonia (ICIQ) in Tarragona. He received the National Award in Chemical Science and Technology (2022), the 2023 Rei Jaume I Award in Basic Research, and is the President of the Spanish Royal Society of Chemistry. His work focuses on the development of synthetic methodology for the synthesis of natural and non-natural products.



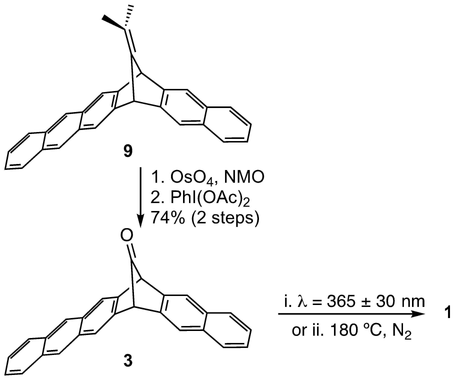
Scheme 2. Summary of reported synthesis of hexacene.



Scheme 3. Synthesis of hexacene (**1**) from diketone precursor **2**.[56]

(**1**).[58] Hexacene (**1**) could be generated from **3** by photodecarbonylation (Scheme 4), although its rapid degradation was observed due to dimerization, as found in the previous work of Neckers.[56] Alternative heating the precursor in solid state at ~180 °C in a nitrogen atmosphere in the dark to avoid the formation of biradical intermediates led to **1**, as confirmed by MALDI-MS. Hexacene (**1**) was found to be stable in the dark under ambient conditions for several days[59] and thermally stable under these conditions up to ~330 °C, according to the thermal gravimetric analysis. This thermal methodology also allowed the formation of hexacene films, which were stable for more than one month at ambient conditions in the dark. Moreover, the crystal structure of **1** was obtained for the first time by X-ray diffraction analysis, confirming its structure.

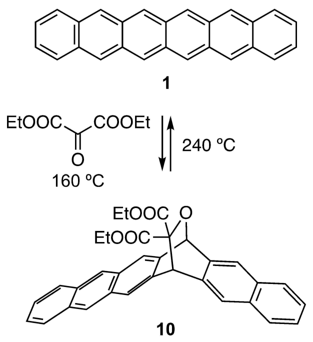
In 2013, the same group synthesized adduct **10** by cycloaddition of **1** and diethyl malonate at 160 °C as a soluble and



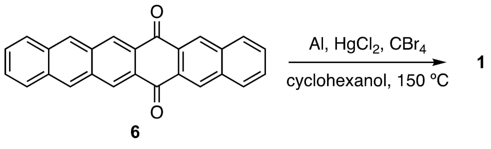
Scheme 4. Synthesis of monoketone **3** as precursor of hexacene (**1**).[58]

stable precursor of **1** (Scheme 5). Adduct **10** showed both thermal and photochemical stability and could be stored in ambient conditions for several months.[60]

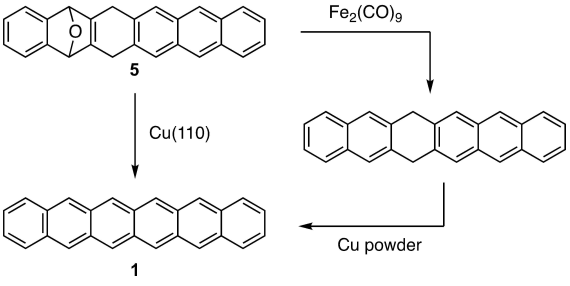
More recently, hexacene was synthesized through a modified Meerwein-Ponndorf-Verley reduction of hexacene-6,15-quinone (**6**) (Scheme 6) and purified by a gradient sublimation obtaining a blue solid in an overall isolated yield of 5 %.[61]



Scheme 5. Synthesis of a new precursor of hexacene and its conversion to the corresponding acene by thermal annealing.[60]



Scheme 6. Synthesis of hexacene (**1**) by Meerwein-Ponndorf-Verley reduction of hexacene-6,15-quinone (**6**).[61]



Scheme 7. Synthesis of hexacene (**1**) by direct on-surface dehydration on Cu(110) or indirectly via copper powder-catalyzed dehydrogenation.[62]

Shortly after, Han et al.[62] synthesized new precursor **5** that was converted into hexacene (**1**) by dehydrogenation and deoxygenation on Cu(110) surface or in a two steps procedure by deoxygenation to form 6,15-dihydrohexacene followed by the catalytic dehydrogenation using Cu powder (Scheme 7).

Heptacene

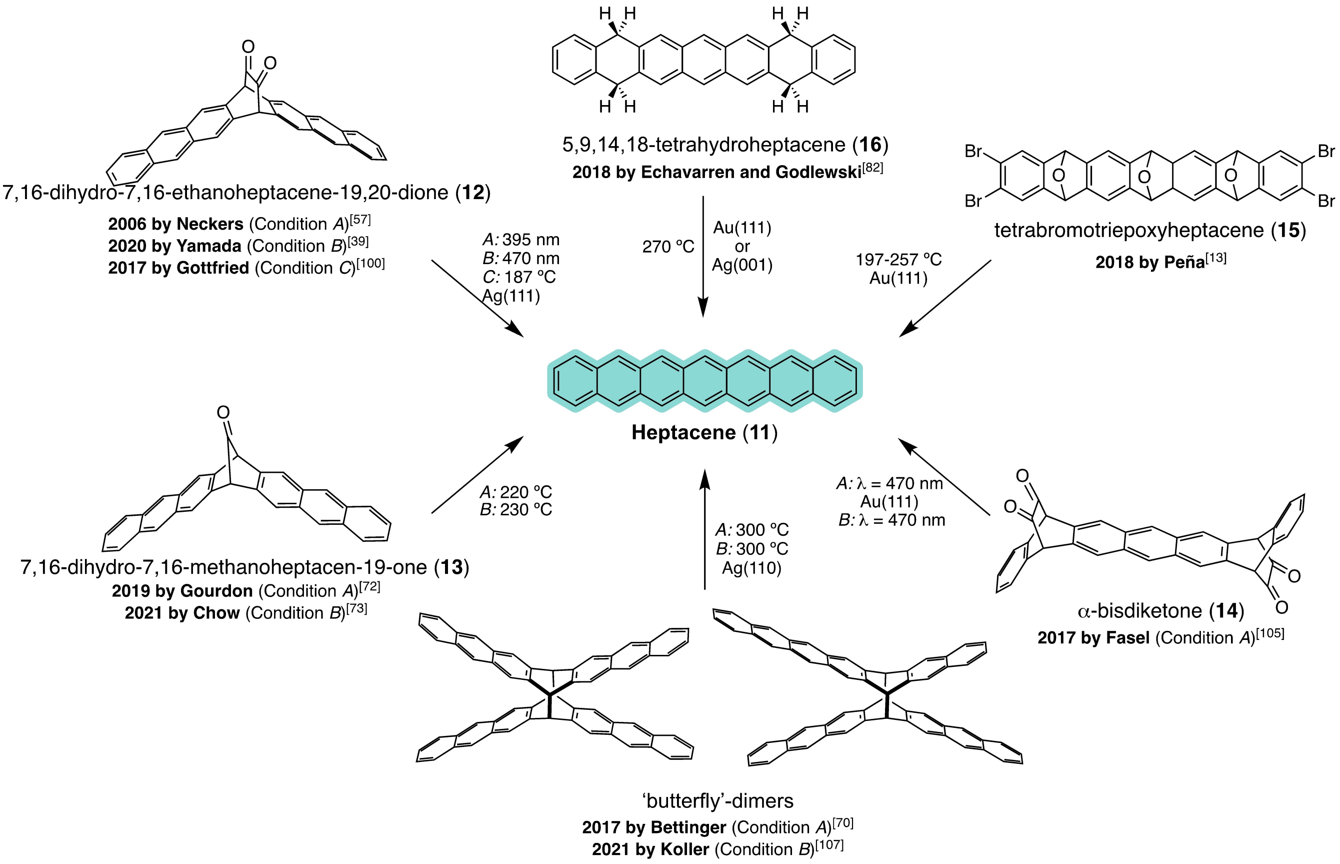
Synthetic approaches towards heptacene (**11**) are summarized in Scheme 8. Clar and co-workers first attempted the synthesis of **11** in 1942 by a catalytic dehydrogenation of a partially saturated precursor with copper bronze at 310 °C in a carbon dioxide atmosphere.[63] In the next years, there were some reports with crossed arguments about the nature of the synthesized acene and its precursors.[52,64,65]

It was not until 2006 when an unequivocal synthesis was reported by Neckers through a Strating-Zwanenburg photodecarbonylation[66] of α-diketone precursor **12**.[57] Diketone **12** was synthesized by a double Diels-Alder reaction of **7** (Scheme 9), essentially as shown before in Scheme 3. Reaction of **11** with O_2 leads to endoperoxide **17**. The mechanism of the formation of heptacene (**11**) from **12** was investigated through time-resolved nanosecond laser flash photolysis (LFP) and femtosecond pump-probe UV-vis spectrometric techniques by the same group. Both the singlet and the triplet states of the diketones precursors seems to be involved in the decarbonylation process.[67] Some years later, this group performed a computational mechanistic study of this transformation for the formation of anthracene, the smallest acene, whose results confirmed the previous experimental studies.[68]

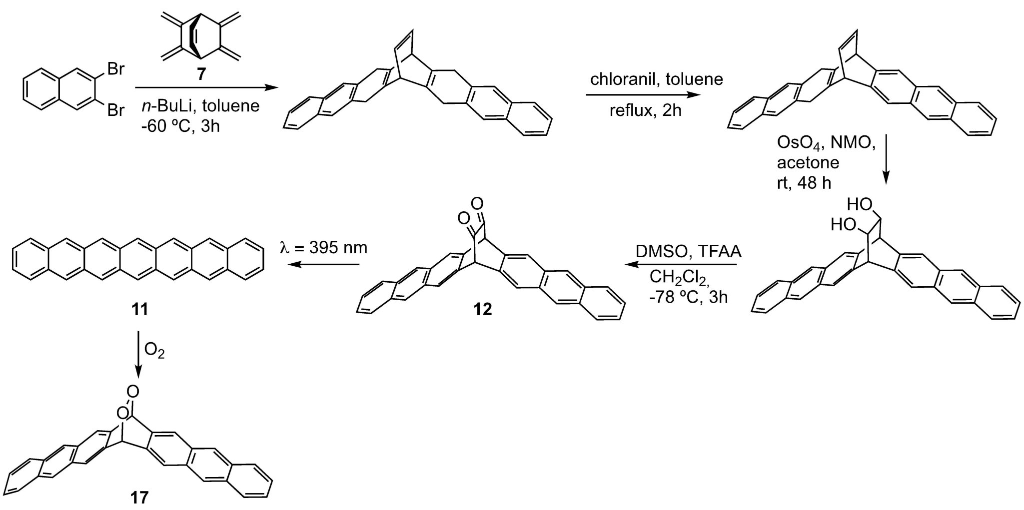
This strategy was also used for the synthesis of pentacene, hexacene and heptacene through matrix isolation conditions, which allows the study of spectral properties and thermal stabilities of these acenes.[69]

Conversion into heptacene (**11**) was also reported from diheptacenes as precursors (Scheme 10), which could be obtained through two different strategies: photodecarbonylation of α-diketone precursor **12** or through a Meerwein-Ponndorf-Verley reduction of heptacene-7,16-quinone (**18**).[70] In both cases, a mixture of two diheptacenes along with two dihydroheptacenes as byproducts was obtained. Heptacene (**11**) was obtained after heating the solid sample to 300 °C for 12 min, following the conversion by solid state ^{13}C CP-MAS NMR spectroscopy. Acene **11** could also be obtained in thin films through the thermal cycloreversion of these dimers. This thermal technique has been widely used since 1996 for the synthesis of pentacene in a film after deposition of tetrachlorobenzene-pentacene adduct as the precursor.[71] Heptacene was found to be stable in both solid state and in film at room temperature for several weeks.[70]

This stability of solid heptacene (**11**) was also confirmed by the group of Gourdon[72] who synthesized this acene by decarbonylation of **13** at 105–220 °C (Scheme 11). Monoketone precursor **13** was synthesized by double Diels-Alder reaction of



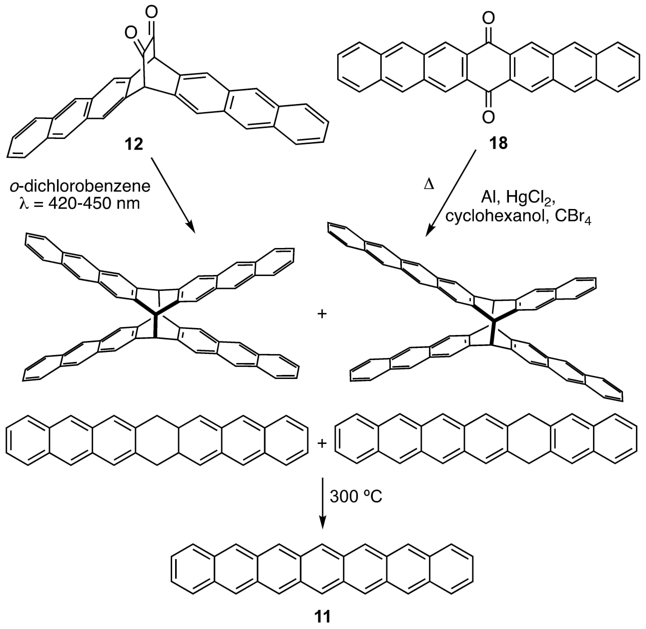
Scheme 8. Summary of reported synthesis of heptacene.



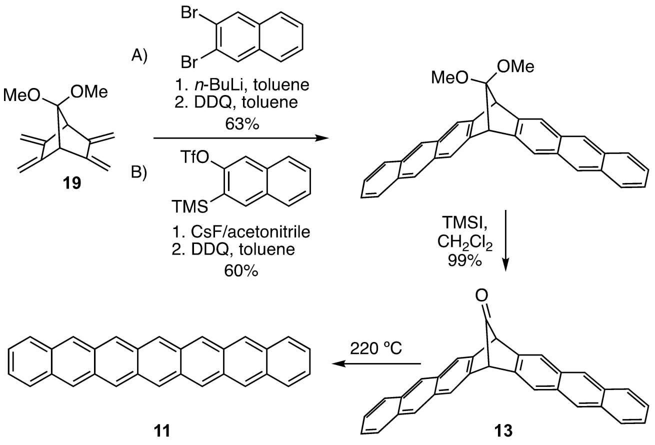
Scheme 9. Synthesis of heptacene (**11**) through the photodecarbonylation of 7,16-dihydro-7,16-ethanoheptacene-19,20-dione (**12**) in a polymer matrix using a UV-LED lamp (395 ± 25 nm) and its oxidation to form endoperoxide 17.[57]

19 with 2-naphthyne. In this study, acene **11** was shown to be stable up to 420 °C by FTIR and solid-state cross-polarization magic angle spinning (CP-MAS) NMR spectroscopy. Soon after, a variation of this route for the synthesis of **11** was reported by the group of Chow from **20**, that also proceeds by decarbonylation of ketone **13** (Scheme 12).[73] This synthesis allowed the fabrication of organic field-effect transistor devices composed of a top-contact thin film of **11** on a HMDS/SiO_2/Si substrate to evaluate its hole-transfer property, which resulted in a value of 2.2 $cm^2\,V^{-1}\,s^{-1}$, being higher than that found for in hexacene (0.076 $cm^2\,V^{-1}\,s^{-1}$).

Visible-light-induced photodecarbonylation of **22** in the interior of single-crystal led to **11**, whereas the decarbonylation of **14** only led to intermediate **21** (Scheme 13).[74]

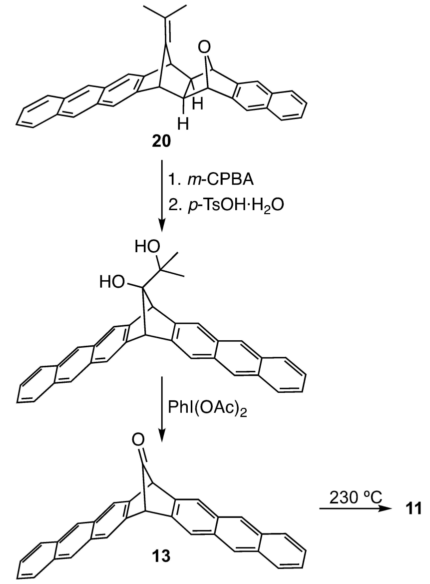


Scheme 10. Photochemical and reductive Meerwein – Ponndorf – Verley synthesis of diheptacenes from α-diketone **12** and heptacene-7,16-quinone (18).[70]

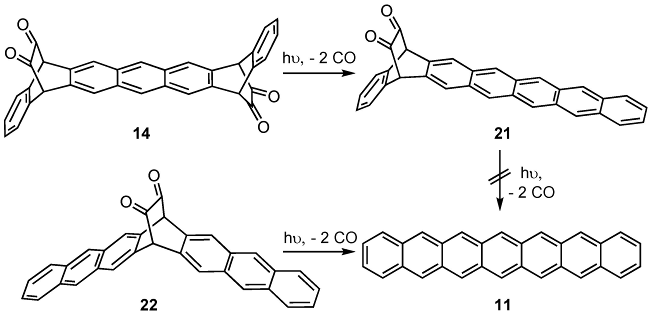


Scheme 11. Synthesis of heptacene (**11**) from ketone 13.[72]

A recent study on the adiabatic ionization energies of heptacene and shorter acenes shows that the energy decreases as the number of rings increases.[75]



Scheme 12. Synthesis of heptacene (**11**) from **20** via ketone 13.[73]



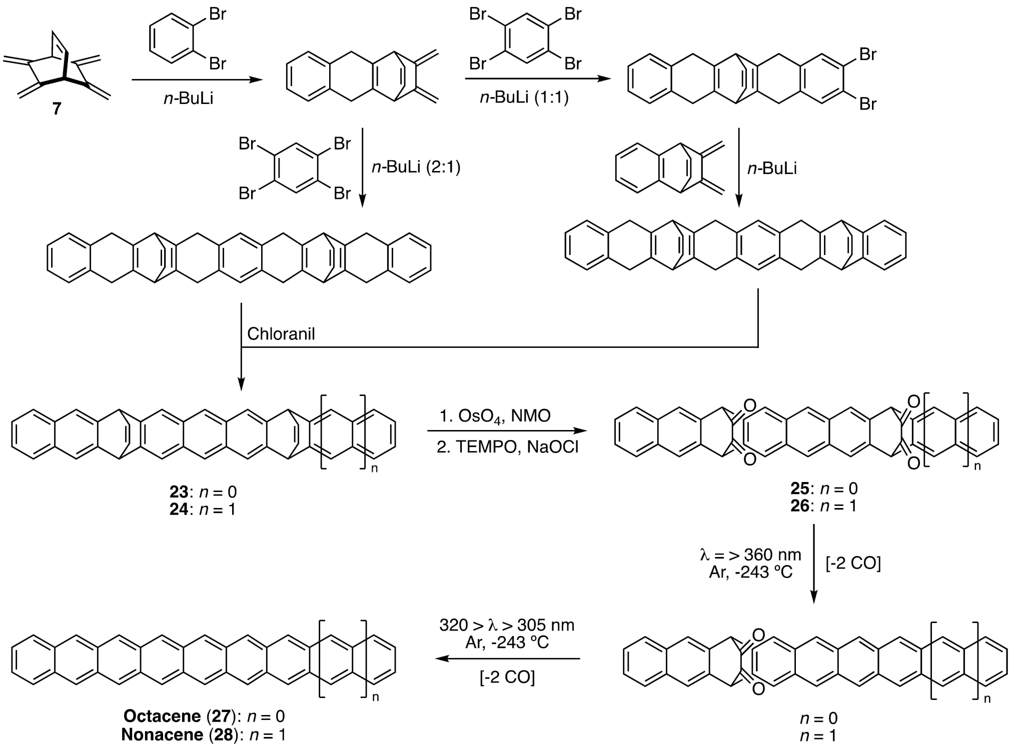
Scheme 13. Synthesis of heptacene (**11**) through a visible-light-induced photodecarbonylation of **14** or **22**.[74]

Large Acenes

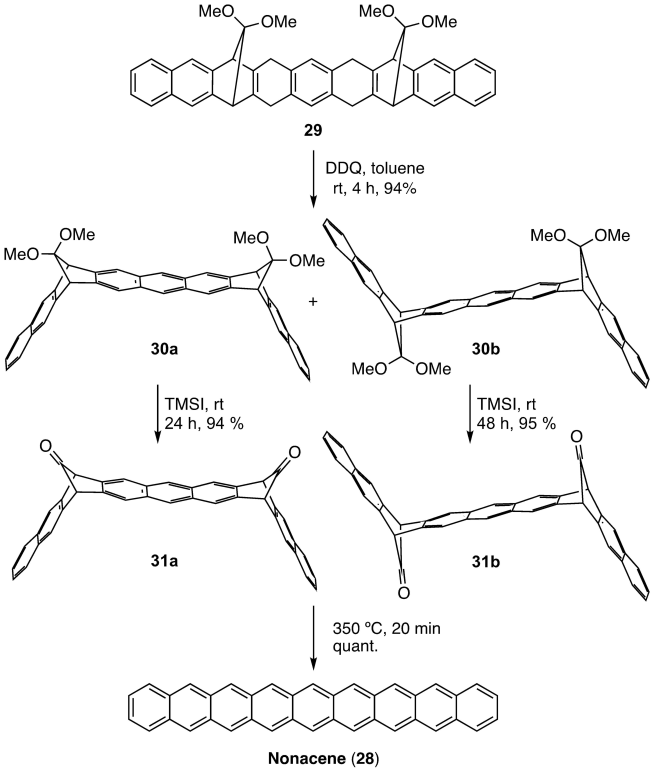
The group of Bettinger reported a photochemical synthesis of octacene and nonacene in 2010 taken advantage of the cryogenic matrix-isolation technique for the stabilization of more reactive acenes.[76] For the synthesis of octacene (**27**) and nonacene (**28**), a double α-diketone bridge needs to be installed in the precursors. To achieve this, successive Diels-Alder reactions of in situ-generated benzynes with 5,6,7,8-tetramethylenebicyclo[2.2.2]oct-2-ene (**7**) were performed, followed by aromatization using chloranil to form **23** and **24** (Scheme 14). Subsequently, dihydroxylation using OsO_4/NMO and oxidation of the diols with TEMPO/NaOCl led to **25** and **26**, respectively, which underwent photodecarbonylation at −243 °C within an argon matrix to finally give rise to octacene (**27**) and nonacene (**28**). During the irradiation process, intermediates containing a diketone were observed.

Nonacene (**28**) was synthesized in solid state via a thermal bisdecarbonylation process (Scheme 15).[77] The precursors for nonacene were synthesized via a novel synthetic route involving the in situ generation of bis(aryne) that undergoes a double Diels-Alder reaction to give rise to **29**, whose aromatization with 2,3-dichloro-5,6-dicyanoquinone (DDQ) leads to a mixture of the *syn* and *anti* isomers **30 a,b**. Cleavage of the acetals was achieved with trimethylsilyl iodide to form **31 a,b**. Final thermal decarbonylation led to **28**, which exhibited thermal stability up to 450 °C, and showed no signs of decomposition after being stored for two months in an argon-filled glovebox at room temperature.

The same methodology employed for the synthesis of octacene (**27**) and nonacene (**28**) by the group of Bettinger



Scheme 14. Synthesis of octacene and nonacene.[76]

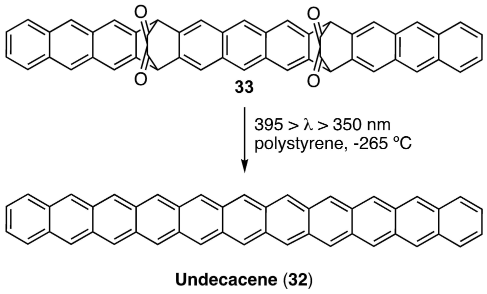


Scheme 15. Synthesis of nonacene (**28**) through a thermal decarbonylation.[77]

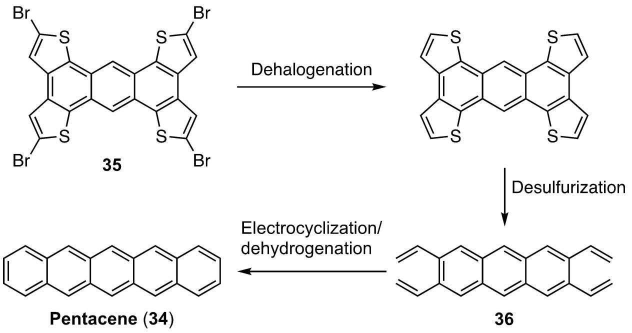
(Scheme 14) was extended for the preparation of undecacene (**32**) (Scheme 16).[78] The synthesis of the precursor **33** closely resembled the previous procedure, involving a Diels–Alder reaction, aromatization, dihydroxylation using OsO_4, and oxidation with TEMPO/NaOCl. During the photodecarbonylation, the corresponding intermediate with only one decarbonylated bridge was also observed until undecacene was formed through prolonged irradiation.

On-Surface Synthesis

On-surface synthesis has emerged as a tool for the formation of novel organic and inorganic nanostructures and molecular assemblies directly on a solid surface under ultra-high vacuum (UHV) conditions. This approach enables control on the spatial arrangement and chemical composition of the synthesized materials at the atomic or molecular scale and has led to the discovery of new reaction pathways.[79] The synthesized nanostructures can be then characterized using a variety of surface sensitive techniques, including scanning tunneling microscopy (STM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermal gravimetric analysis (TGA), near edge X-ray absorption fine structure spectroscopy (NEXAFS), angle-resolved photoemission spectroscopy (ARPES), as well as infrared or Raman spectroscopy. These techniques provide insights into the structure, morphology, composition, and electronic properties of the synthesized materials.[80] A remarkable step forward in atomic-scale identification of the synthesized compounds was achieved in 2009, when Leo Gross and co-workers demonstrated the bond-resolved visualization



Scheme 16. Synthesis of undecacene (**32**) by photodecarbonylation of tetraketone 33.[78]

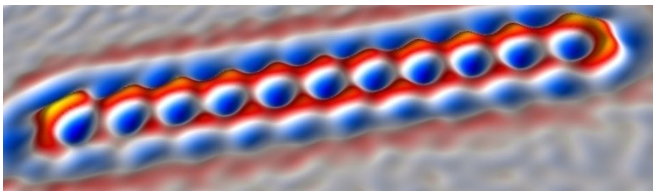


Scheme 18. Synthesis of pentacene (**34**) from tetrathienoanthracene **35** on Ni(111) surface.[97]

of organic species by non-contact AFM measurements performed with a functionalized tip.[81] Since that time the bond-resolved AFM imaging has gained popularity as an excellent technique for the ultimate level of structural characterization in surface assisted experiments providing doubtless identification of synthesized compounds, illustrated below on the example of undecacene with clearly discernible eleven linearly fused rings (Scheme 17).

While the majority of surface assisted experiments is based on the thermally driven initiation of reactions, light induced transformations and atom manipulation approaches may serve as alternatives.[83] The first on-surface reaction driven by atom manipulation with STM was performed in 2000 by Hla et al. for the conversion of iodobenzene into biphenyl.[84] Since then, several reactions were performed on surfaces, such as Ullmann-like polymerization,[85] cyclodehydrogenation,[86] polymerization of diacetylenes,[87] C–H activation of linear alkanes,[88] formation of fullerene hemispheres,[89] synthesis of vinylene groups,[90] formation of double bonds by a non-reductive approach[91] and the Bergman cyclizations,[92,93] among others.[94] Thanks to the ultra-high vacuum conditions the surface assisted chemical reactions create an ideal playground for the generation of intrinsically instable and reactive compounds, such as acenes, triangulenes[95] or cyclocarbon.[96] Therefore, application of on-surface methods for the synthesis of large acenes would overcome solubility and stability issues posed by these group of molecules.

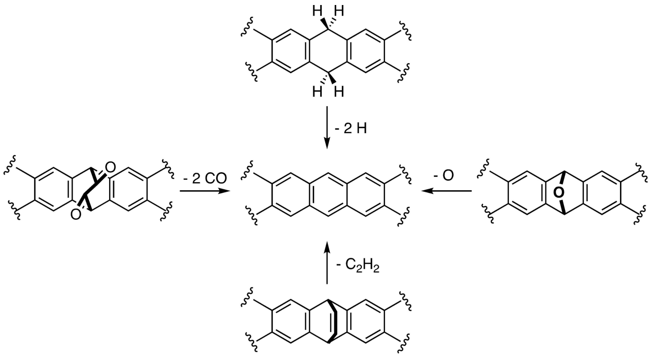
The first on-surface example was reported in 2013 by the groups MacLeod, Perepichka, and Rose in which pentacene was formed on a Ni(111) surface from tetrabrominated tetrathienoanthracene **35** by dehalogenation, desulfurization, and a remarkable double electrocyclization of 2,3,6,7-tetravinylanthracene (**36**), followed by dehydrogenation (Scheme 18).[97]



Scheme 17. 3D non-contact AFM image of on-surface synthesized undecacene.[82]

The on-surface chemistry has been later applied to the formation of large acenes by depositing a strategic precursor on a metal surface to perform the last step in the synthesis, which could be decarbonylation, dehydrogenation, deoxygenation, or the extrusion of an etheno bridge as acetylene in a formal retro-Diels-Alder reaction (Scheme 19).

Actually, the whole series of acenes, up to tridecacene, whose synthesis has been reported independently in 2024 by two groups,[98,99] has been obtained and characterized on surfaces, being gold and silver the most used metal surfaces. Assessment of substrate properties, including composition and symmetry, has been thoroughly reviewed in conjunction with various other parameters relevant to on-surface synthesis.[83] In broad terms, molecular layers tend to exhibit weaker physisorption onto gold surfaces, while their chemisorption onto silver and copper surfaces is usually stronger. In terms of symmetry, hexagonal (111)-oriented surfaces are known for their high density and inertness, contrasting with the lower density and heightened reactivity of rectangular (110)-oriented surfaces.[83] In this context, among noble metal substrates, the Au(111) surface has been most often applied for the synthesis of large acenes. This could be understood in terms of a compromise between providing the required catalytical activity for on-surface chemical transformations leading to the target parent acenes and the idea to retain as much as possible the original (gas phase) electronic properties of the synthesized system upon adsorption on the substrate surface. The detailed analysis



Scheme 19. Four alternative strategies for the on-surface synthesis of acenes.

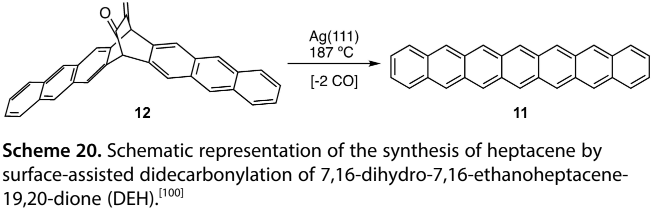
of the acenes on Ag(111) by STM revealed slight deformation with the central ring approaching the surface and combination of NEXAFS and DFT (density functional theory) indicated hybridization of the molecule states with the substrate.[100] In contrast, bond-resolved non-contact AFM images of large acenes on Au(111) indicated on almost planar adsorption[82] and DFT calculations pointed on the dominant contribution of the dispersive interactions,[99] which shall limit the hybridization and influence of the substrate on the electronic structure. Nevertheless, screening resulting in the gap renormalization of physisorbed molecules has to be taken into account.[101] The application of the scanning tunneling spectroscopy (STS) measurements provides the opportunity to monitor the electronic properties, e.g., the dependence of the transport gap on the number of annulated rings. Additionally, recent advances in the analysis of the π-magnetism of the hydrocarbon molecules based on the inelastic excitations by tunneling electrons[102,103] may also provide a deeper insight into the theoretically predicted open-shell contribution to the overall electronic structure of large acenes.

Synthesis by Decarbonylation

As it has been showed throughout this review, both thermal and photochemical decarbonylation processes of relatively strained bridged 1,2-dicarbonyl precursors are useful strategies for the synthesis of acenes. However, it was not until 2017 when the decarbonylation was demonstrated on-surface in this context. Thus, heptacene (**11**) was produced on a Ag(111) surface after annealing the metal substrate at 187 °C.[100] The α-diketone precursor **12** was obtained using a modified synthetic route[104] based on the methodology developed by Neckers[57] (Scheme 20).

The research group of Fasel reported the formation of gold surface-directed heptacene organometallic complexes **37** via thermal activation on Au(111) substrate under ultrahigh vacuum (UHV) conditions (Scheme 21).[105] To achieve this, precursor **38** was synthesized in six steps from heptacenequinone **18**. Annealing of **38** at 162 °C, followed by bisdecarbonylation at 262 °C led to **37**.

The group of Fasel also reported the on-surface synthesis of heptacene (**11**) and nonacene (**28**) via visible-light-induced photo-dissociation of α-bisdiketones **14** and **26**, respectively, on Au(111) under UHV conditions by photoirradiationconducted at 470 nm (Scheme 22).[106] Precursors **14** and **26** for these syntheses were prepared by modification of previously reported strategies.[76,105]



Scheme 20. Schematic representation of the synthesis of heptacene by surface-assisted didecarbonylation of 7,16-dihydro-7,16-ethanoheptacene-19,20-dione (DEH).[100]

The group of Koller used the thermal cycloreversion of diheptacenes (see Scheme 10) to form highly oriented monolayers of heptacene on Ag(110) under UHV conditions (Scheme 23).[107] The electronic and structural properties of these monolayers were examined in detail using ARPES and DFT calculations. The findings were then compared with those of pentacene, revealing notable differences in their geometrical orientation and electronic structure. For instance, whereas pentacene adsorbs preferentially across Ag substrate rows, heptacene preferred orientation is along the [110] direction, following the surface rows. Additionally, the research revealed full occupation of LUMO electronic level of heptacene, in contrast to only partial filling reported previously for pentacene.

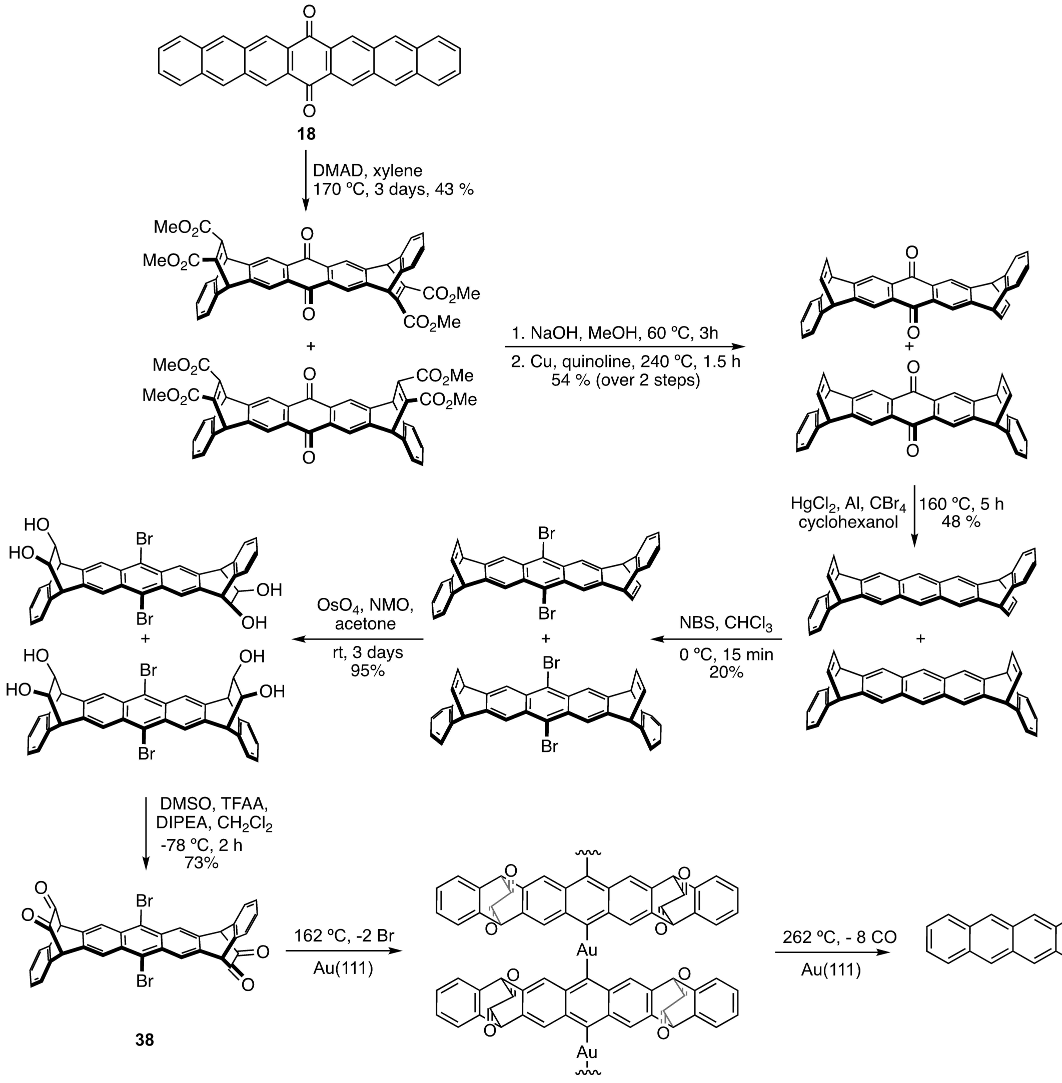
Synthesis by Acetylene Extrusion

Undecacene (**32**) was also synthesized on an Au(111) surface as as part of a study on the synthesis and characterization of substituted analogs of undecacene, as the 6,12,19,25-tetraazaundecacene.[108] Thus, **32** was obtained by annealing the dietheno-bridge precursor **39** (Scheme 24), prepared through solution chemistry in 10 steps from bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride. Interestingly the nitrogen substituted analog of undecacene was generated from the similar precursor molecules by tip induced atom manipulation. By combining experimental and computational data, it was concluded that the ground state of both undecacene (**32**), as well as tetraazaundecacene exhibit considerable open-hell character when absorbed on Au(111). In fact, after annealing of precursors to 220 °C the authors found on a surface a whole family of acenes from anthracene up to undecacene, with predominant abundance of anthracenes, tetracenes and pentacenes.

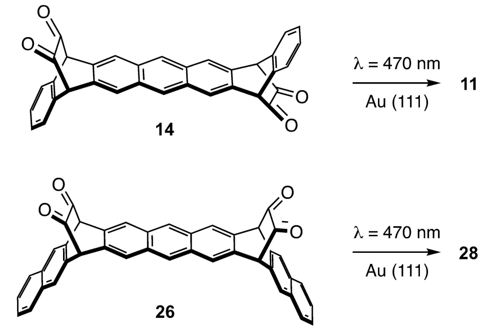
Following this strategy, recently the on-surface production of tridecacene (**40**) on Au(111) was achieved. In this study the parent tridecacene was generated through a tip-induced atom manipulation including a conformational transition from the edge-on adsorbed to the stretched linear conformer followed by a series of three etheno-bridges removals (Scheme 25).[99] Precursor **41** was obtained as a mixture of three stereoisomers by a Diels-Alder reaction between diene **42** and an in-situ generated bisbenzyne, followed by dehydrogenation with DDQ. In this study the authors concluded based on spin-polarized DFT calculations that upon adsorption on Au(111) the open-shell character of tridecacene is reduced and the antiferromagnetic state is only 2 kJ/mol lower in energy compared to the non-magnetic closed-shell configuration, which makes these state almost isoenergetic.

Dehydrogenation of Hydroacenes

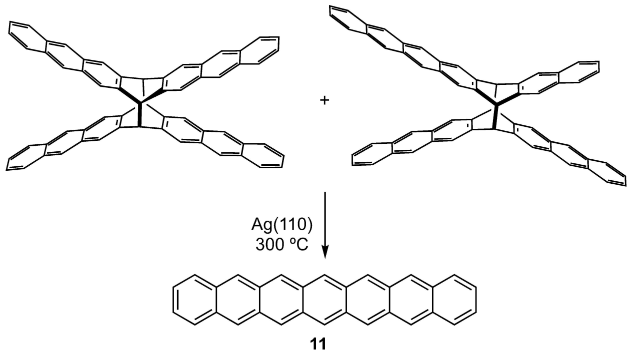
The groups of Echavarren and Godlewski developed a synthesis of acenes based on a new approach for the synthesis of hydroacenes by combination of the Pd(0)-catalyzed Sonogashira coupling with a gold(I)-catalyzed [4+2] intramolecular



Scheme 21. On-surface synthesis of heptacene organometallic complexes **37** from dibromo-heptacene precursor **38**.[105]

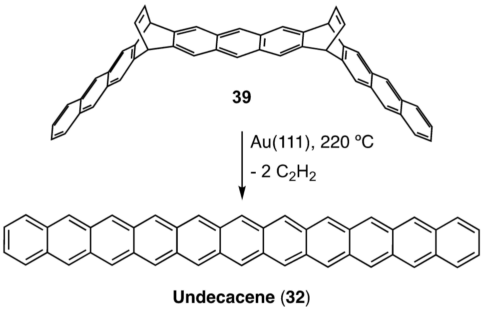


Scheme 22. Photodecarbolylation of **14** and **26** for the on-surface synthesis of heptacene (**11**) and nonacene (**28**).[106]

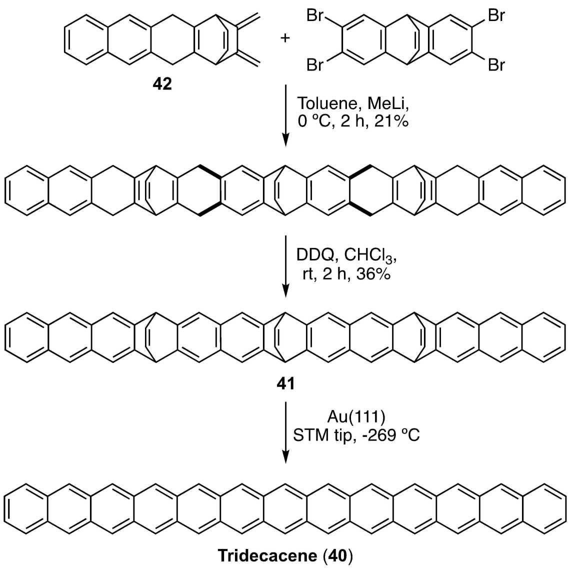


Scheme 23. Synthesis of heptacene (**11**) by thermal cycloreversion of diheptacenes on Ag(110).[107]

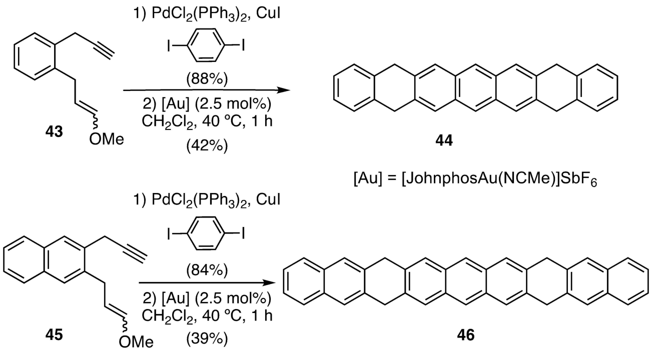
cycloaddition.[82,109,110] Firstly, the Sonogashira coupling is used to build a linear framework by connecting aromatic units through alkyne linkages. Subsequently, the gold(I)-catalyzed [4 +2] cycloaddition is employed to cyclize the linear precursor into the desired polycyclic acene structure. This combination enables the efficient and selective formation of complex acene structures in fewer steps. Thus, for example, tetrahydroacenes **44** and **46** were synthesized from 1,7-enynes **43** and **45**, respectively, and *p*-diiodobenzene (Scheme 26).[109] These and



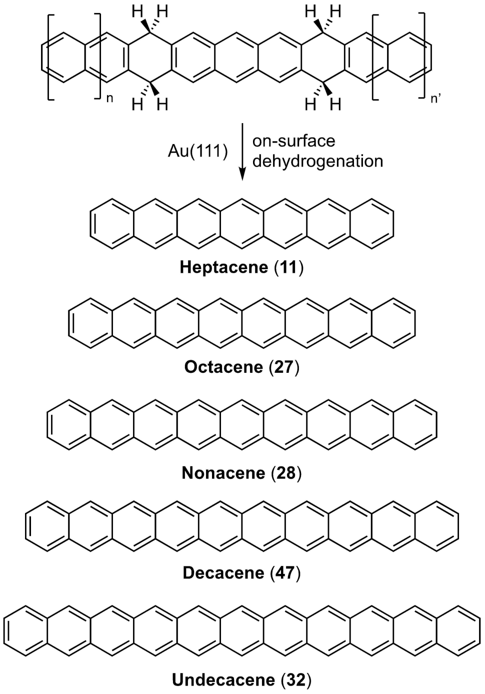
Scheme 24. Schematic representation of the synthesis of undecacene (**32**) from **39**.[107]



Scheme 25. On-Surface synthesis of tridecacene and its precursors.[99]



Scheme 26. Synthesis of tetrahydroacenes **44** and **46** by Sonogashira coupling and gold(I)-catalyzed [4+2] intramolecular cycloaddition.[109]



Scheme 27. Synthesis of large acenes by on-surface dehydrogenation of hydroacenes.[82]

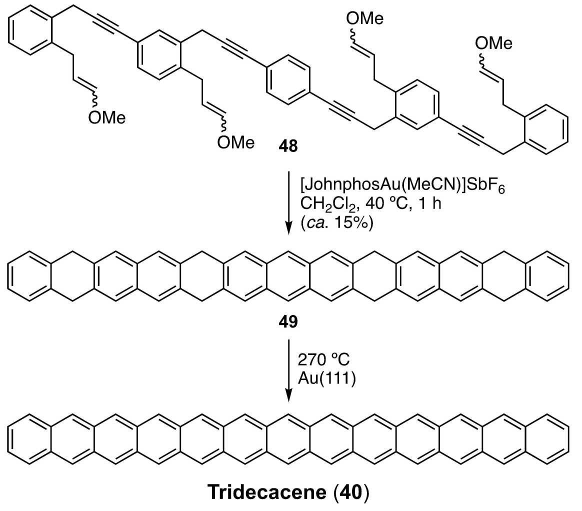
other hydroacenes were then converted into acenes by dehydrogenation on a Au(111) surface (Scheme 27).[82,110] Successful synthesis of a series of acenes from heptacene (**11**) to undecacene (**32**) allowed for the tracking of the transport gap evolution with increased number of fused rings. The recorded dependence could be well fitted with the exponential decay with some deviation observed for undecacene, which may originate from the increased contribution of the open-shell character.[82] Furthermore, a brominated tetrahydroheptacene was also used for synthesis of heptacene on Ag(001) surface.[111] Tetrahydroheptacenes were also used to generate the dihydroheptacenes, in which the remaining two methylene groups served as a spacer limiting the influence of the substrate on the electronic structure of the molecule on Ag(001).[112]

The approach based on the application of a hydrogenated precursor was recently applied for the synthesis of tridecacene (**40**), the largest acene synthesized up to date. This was achieved by a four-fold gold(I)-catalyzed [4+2] intramolecular cycloaddition of tetra-1,7-enyne **48** to form octahydrotridecacene **49**, followed by on-surface dehydrogenation on Au(111) (Scheme 28).[98] The properties of tridecacenes were thoroughly examined by a combination of STS, inelastic electron tunneling spectroscopy and many body calculations revealing the single-triplet spin excitation and providing the first experimental confirmation of the acene magnetic character.[98]

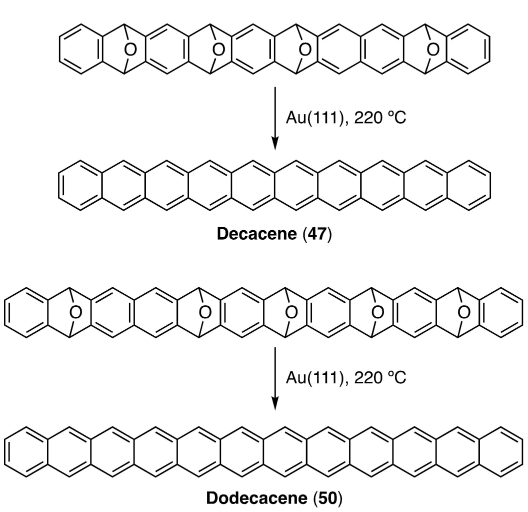
Indacenoditetracenes, which are antiaromatic analogues of undecacene[113] and other polyarenes[114,115] were also synthesized by Sonogashira coupling, gold(I)-catalyzed [4+2] cycloaddition, and on-surface dehydrogenation.

Deoxygenation of Epoxyacenes

Epoxyacenes have also been used as precursors of acenes, performing the conversion via on-surface deoxygenation. Notably, the groups of Peña and Moresco achieved the synthesis of decacene (**47**)[13,116] and dodecacene (**50**)[117] for the first time using this methodology (Scheme 29), following their



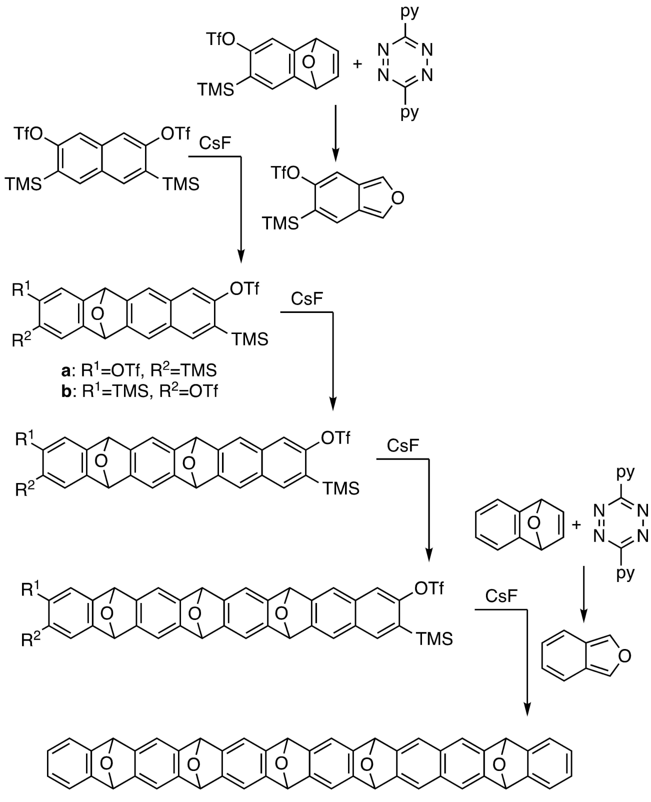
Scheme 28. Synthesis of tridecacene (**40**) from octahydrotridecacene (**49**).[98]



Scheme 29. Synthesis of decacene (**47**) and dodecacene (**50**) by deoxygenation of epoxyacenes.[13,116,117]

synthesis of tetracene on Cu(111)[118] and hexacene on Au(111)[119] surfaces. The STS measurements of dodecacene (**50**) on Au(111) revealed the re-opening of the transport gap, which was interpreted by the authors in terms of the increase of the radical character.

Epoxyacenes were obtained by successive Diels-Alder reactions of arynes with isobenzofurans leading to mixtures of regio- and /or stereoisomers isomers (Scheme 30).



Scheme 30. Synthesis of the epoxyacene precursor of dodecacene (**50**).[117]

While the focus of research on large acenes predominantly revolves around metal surfaces, it is worth mentioning that the groups of Peña and Moresco also obtained hexacene through surface-assisted reduction on a H-passivated Si(001) surface.[120] Moreover, a new methodology for the synthesis of polyacenes based on application of metal organic frameworks has been proposed recently.[121] In this study the authors applied 2,6-bis(bromomethyl)naphthalene and 2,6-bis(bromomethyl)anthracene for the directed 1-D polymerization within the MOF channels followed by dehydrogenation affording polyacenes of different lengths.

Experimental Electronic Properties of the Acenes

The experimental analysis of properties and characteristics of larger parent acenes is scarce due to the challenges in their synthesis and is mostly limited to the investigation of the optical gap for molecules generated in polymer matrices[76,78] or the analysis of the transport gap by STS experiments in case of larger acenes synthesized through the on-surface chemistry concept on metallic surfaces under ultra-high vacuum conditions.[82,106,108,110,116,117,119] The extended analysis of the optical spectra of a series of acenes up to undecacene has been performed by the group of Bettinger leading to the conclusion that the HOMO-LUMO transition associated with the optical gap could be very well described as being proportional to the inverse number of fused rings, as expected for a particle in a box model.[78] The dependence is also comparatively well fitted with the exponential decay of the gap with increasing number of benzene units with a limiting value of approximately 1.2 eV obtained by extrapolation.

The evolution of the transport band gap measured by STS experiments has been followed on surfaces by a series of experiments starting with different precursor molecules and on-surface reaction schemes. Due to the fact that the vast majority of these experiments were performed on the Au(111) surface, it is possible to compare data obtained in independent experiments performed in different research groups and using significantly different molecular precursors. The experimental values of the recorded HOMO-LUMO gap up to undecacene follow a similar trend as in the described above optical measurements with a saturating value extracted from extrapolation being below 1.0 eV.[82] We should, however, emphasize here that the transport band gap is usually renormalized by the proximity of a metallic substrate, as widely discussed in the literature.[101] This renormalization can also affect the resulting value of the recorded band gap in non-linear way for acenes of different lengths. It is worth to note that in contrary to previous reports predicting the emergence of the open-shell character of acenes due to electron correlations already for shorter members of acene family, more recent studies suggest that in the gas phase up to nonacene[122] or decacene[11,98] the acenes are rather on the closed-shell side of the closed to open-shell transition. This agrees with recent experimental reports for larger acenes up to undecacene, where STS measurements have not provided convincing evidence of the dominance of the open-shell character. However, the described trend of exponential decay of the transport gap was disturbed in the experiments probing dodecacene,[117] where a measurable increase of the transport gap to approximately 1.4 eV (originating from the upward shift of the empty state resonance) was reported. This has been explained as a destabilization of the empty state STS electronic resonance through higher molecular empty states since the tunneling involves a combination of electron transfer paths through the virtual quantum occupations of higher levels. Consequently, this may lead to the upward shift of the empty state STS resonance and gap reopening. Recently, the increase of the observed transport gap of dodecacene has also been theoretically suggested to originate from the strong non-dynamic electron correlation assuming that the first empty state STS resonance originates from the maxima of the local density of states of the first excited (S1) state of dodecacene.[123] The slight increase of the transport band gap from undecacene to dodecacene could be also tentatively attributed to the closed-to-open shell transition or renormalization of the band gap due to the proximity of the metallic substrate. Recently the STS measurements of tridecacene revealed the similar value of the transport gap as for dodecacene.[98] Moreover, the studies provided the first convincing fingerprint of the magnetic ground state of larger acenes by the presence of an inelastic signal at 126 meV attributed to the spin excitation from the singlet diradical ground state to the triplet excited state.[98] Another studies of tridecacene molecules generated by atom manipulation from different precursors leading to the contamination of the Au(111) surface by reaction byproducts reported smaller STS gap of approximately and the lack of the open-shell character inelastic tunneling fingerprint,[99] which may suggest that the fine tuning of the interaction with the Au(111) surface may influence the balance of the open and closed-shell contribution to the overall electronic configuration. A recent report on the polyacenes describe their diradical character based on electron spin resonance (ESR) and superconducting quantum interfering device (SQUID) measurements.[121] The stability of the bulk polyacenes was suggested to likely originate from the decreased diradical character due to the interchain antiferromagnetic coupling, which occurs for neighboring polyacenes located in close proximity.

Overview and Outlook

By pushing the boundaries of synthetic methodologies and exploring innovative pathways to access large acenes, researchers have opened new avenues for the development of advanced materials and devices with improved performance and functionality. The synthesis of acenes, particularly through on-surface methods, stands as a significant advancement in the fields of organic chemistry and materials science. This family of polycyclic aromatic hydrocarbons possess distinct electronic and optical properties of interest for a wide range of applications across various industries, from organic electronics to molecular nanotechnology.

On-surface synthesis offers unprecedented precision in controlling the molecular assembly process, facilitating the tailored fabrication of acene structures with customized functionalities and properties. Moreover, this approach yields valuable insights into fundamental chemical processes occurring at surfaces, thereby elucidating reaction mechanisms and surface interactions.

Currently, the on-surface synthesis of the longest acenes requires application of relatively large precursor molecules. This poses new challenges for the synthesis of the next members of the family, e.g., increasing insolubility of precursors, difficulties in purification and further complications in UHV deposition. This forces to seek for alternative deposition methods and the search for new reaction pathways. Among them, a combination of intramolecular and surface directed intermolecular reactions may be an attractive approach for a significant increase in the number of fused rings and the search for a polyradical contribution. Similarly, the development of synthetic strategies based on atom manipulation may pave the way toward synthesis on inert surfaces, which would less affect the magnetic properties of large acenes and enable deeper insight into their character.

Supporting Information Summary

Additional supporting information can be found online in the Supporting Information section at the end of this article.

Acknowledgements

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: Acenes · Electronic properties · HOMO-LUMO gap · On-surface · Semiconductors · Solid-state · Stability · Synthesis

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