Towards Nanographenes with zigzag periphery
Zu Nanographenen mit Zick-Zack-Peripherie

Dissertation

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Halle-Wittenberg

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Verteidigungsdatum: 07.07.2021

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Date of defence: 07.07.2021.

List of Abbreviations.

2D – Two dimensional

Ac – Acetyl substituent

AFM – Atomic force microscopy

APEX – Annulative π-Extension

Ar – Aryl substituent

DBA – Dibenzylideneacetone

DBATT – 2.3,8.9-dibenzanthanthrene

DCE – Dichloroethane

DCM – Dicholomethane

DDQ – 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

DMF – Dimethylformamide

DMSO – Dimethylsulphoxide

DPEX – dehydrative π-extension

DPPF – 1,1'-Bis(diphenylphosphino)ferrocene

EC – electrocyclization

Et – ethyl substituent

Hex – Hexyl substituent

HOMO – Highest occupied molecular orbital

HLG – HOMO – LUMO gap

HMPA – Hexamethylphosphotriamide

iPr – Isopropyl substituent

LDB – localized double bond

LooP – Ladderization of oligophenylenes

LUMO - Lowest unoccupied molecular orbital

Me – Methyl substituent

NIR – Near-infrared spectroscopy

NBS – N-Bromosuccinimide

NMO – N-Methylmorpholine N-oxide

NMR – Nuclear magnetic resonance

Ox – Oxidation

PAH – Polycyclic Aromatic Hydrocarbon

Ph – Phenyl substituent

PPA – Polyphosphoric acid

p-TSA – *para*-Toluenesulfonic acid

SET – Single electron transfer

S_NAr – Aromatic nucleophilic substitution

STM – Scanning tunnelling microscopy

t-Bu – *tert*-Butyl substituent

TBAF – Tetrabutylammonium fluoride

TEA – Triethylamine

Tf – Trifluoroacetyl substituent

TFFA – Trifluoroacetic anhydride

THF – Tetrahydrofuran

TIPS – Triisopropylsilyl substituent

TMS – Trimethylsilyl

Ts – Tosyl substituent

hv – Light.

Was mich nicht umbringt, macht mich stärker.

Götzendämmerung, Friedrich Nietzsche. 1888.

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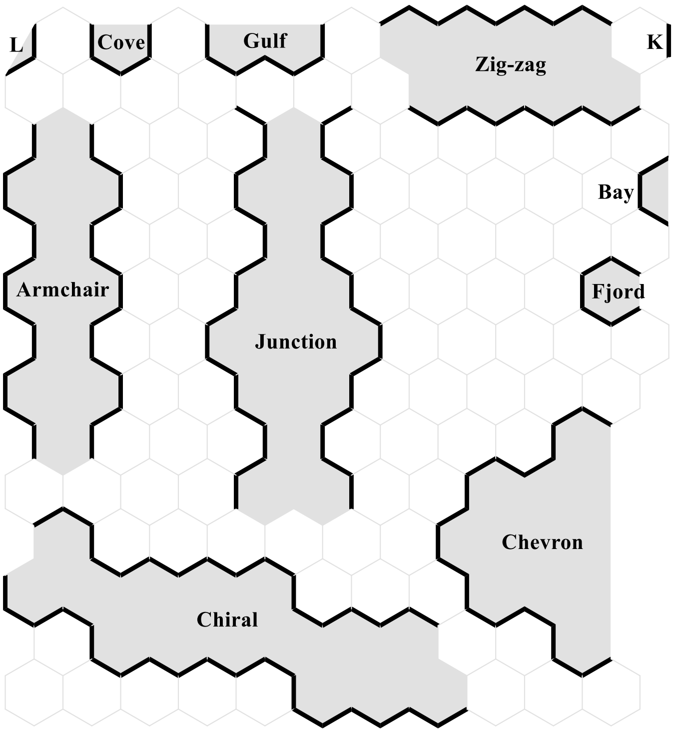
1. Introduction

The unique ability of carbon to create stable chains is the key prerequisite to life diversity on Earth and is the fruitful foundation for unlimited scientific investigations., The discovery of new allotrope forms of carbon such as fullerene C_{60}[1] and graphene [2] (single-atom-thick honeycomb lattice of carbon) marked by Noble prizes in 1996 and 2010 respectively lead to the explosive interest in the field of carbon-rich materials. Nowadays, sp^2 carbon-based materials such as acenes, fullerenes, graphene, single-wall carbon nanotubes (SWCNTs), graphene oxide became the backbone of modern material science[3]. The key to this success lies in the possibility of controlling and tuning of properties of the carbon materials via changing the shape, width, and edge topologies [4].

From the geometrical perspective the ideal hexagonal honeycomb arrangement of carbon atoms observed in graphene can result in two edge topology types: zigzag and armchair periphery (Scheme 1). The simplest fragment of the zigzag periphery is called L-region. The armchair periphery consists of two components: K-region and *bay*-region. Defects in zigzag end up in *cove* and *gulf* regions, while defects in the armchair periphery lead to the *fjord* and *chevron* regions. The combination of armchair and zigzag peripheries could lead to the junction and chiral edge topologies as it is shown in Scheme 1.



Scheme 1. Edge definitions in a graphene sheet.

From the perspective of physical properties, the zigzag periphery is the most interesting because it leads to the decreased HOMO-LUMO gap (HLG) resulting in strong absorptions in visible and NIR regions. This fact allows to use PAHs with zigzag periphery as organic semiconductors with high charge mobilities[5–10], materials for non-linear optics[11–14], photovoltaics[15–17], organic light-emitting diodes[18–20], liquid crystals[21], singlet fission[22–24], single-molecule spectroscopy[25,26] and molecular magnetism[27,28]. Also, open-shell PAHs and graphenes nanoribbons are promising materials for the next-generation quantum computers because eliminated hyperfine interactions in graphene hold great potential for electron spin qubits[29,30].

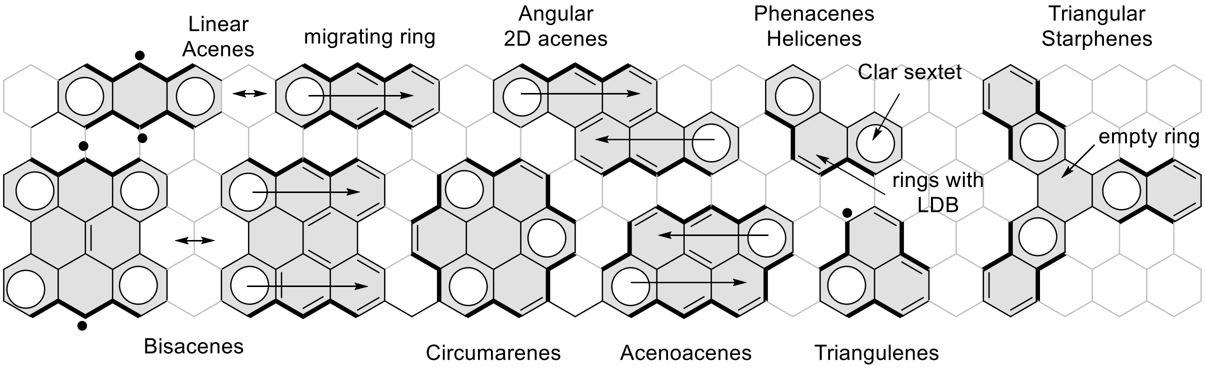
Despite such great interest from material scientists, in contrast to the armchair periphery, zigzag PAHs suffer from significant insufficiency of synthetic methods connected with low stability, rapid oxidation and polymerization [31]. In this work, we aimed to find alternative synthetic approaches to PAHs with zigzag periphery. Methods of synthesis divided by different classes of zigzag PAHs will be introduced in the literature review.

2. Synthesis of PAHs with a zigzag periphery

2.1.Classification of PAHs containing L-region

In contrast to infinite graphene lattice with the zigzag periphery, small PAHs cannot contain only L-regions and include K-, bay- and/or more complex regions additionally. There are in general only two possibilities of condensation of aromatic rings: *cata*, when all carbon atoms belong to one or two benzene rings, and *peri*, when at least one of carbon atom is involved in three benzene rings. Linear *cata*-annelation leads to acenes, whereas angular fusion could result in phenacenes, helicenes or starphenes. *Peri*-annelation of acene motives in a different manner allows for constructing several PAH classes with zigzag edges: 2-D acenes, bisacenes, circumarenes, and acenoacenes (Scheme 2).

It is important to note that all described PAHs contain an even number of L-regions, which allows the forming of Kekule structure (indicating the closed-shell structure). When the number of L-regions in PAH is odd, it is possible to draw only non-Kekule structure (correspond to the open-shell structure). The most notable examples of non-Kekule PAHs are triangulenes (Scheme 2).

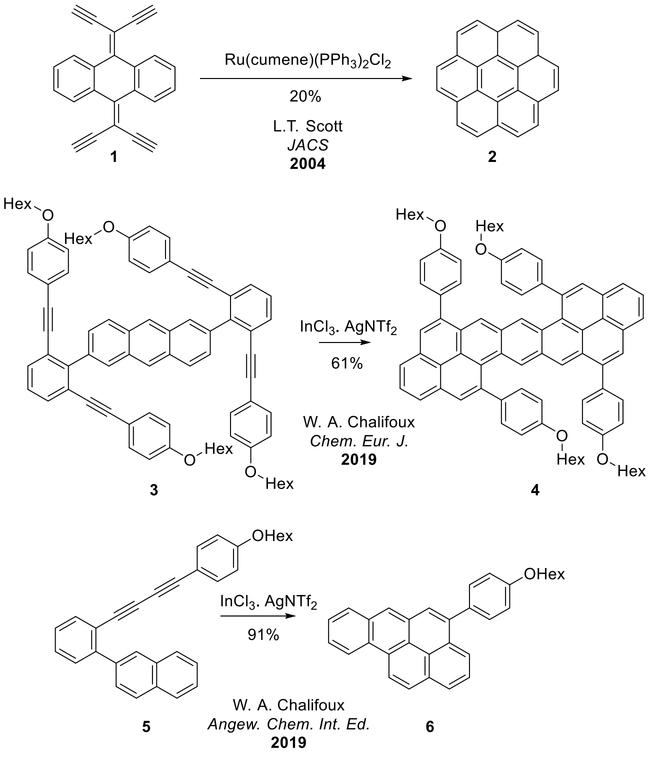


Scheme 2. Classes of PAHs containing zigzag periphery and their Clar sextets.

The Kekule structure alone can not explain drastic differences in the reactivity of PAHs. In 1972 Erich Clar formulated his aromatic π-sextet rule to discuss benzenoid species’ aromatic character qualitatively[32].

According to the Clar’s rule, one can classify the six-membered rings of benzenoid species in four types of rings, namely, aromatic sextets, migrating sextets (typical for acenes), empty rings (typical for triphenylene moiety), and rings with localized double bonds (LDB) (standard for circumarenes arenes and phenacenes). Similarly, three types of benzenoid species can be suggested. First one has only π-sextets and “empty” rings called by Clar “fully benzenoid" (an example is a triphenylene or hexabenzocoronene); the second one has π-sextets and rings with a single, double bond (for instance, phenacenes and coronenes); and the third one that has rings with two or more double bonds and for which one can write more than a single Clar structure (acenes). The last system appears to be the most interesting because the maximum amount of Clar sextets often belongs to the open-shell resonance form. A diradical character (γ) is introduced to characterize this competition quantitatively. The diradical character γ can have a value between 0 and 1. $\gamma = 0$ is referred to a full closed-shell nature, $\gamma=1$ corresponds to 100% contribution of the open-shell resonance structure[33].

As some classes of zigzag PAHs contain *bay* regions or K-regions in their structure (such as phenacenes), their synthesis is not described via the formation of L-regions and frequently starts from small molecules already containing zigzag periphery. For example, the most abundant methods of synthesis of phenacenes are photocyclization [34,35] and alkyne benzannulations[36,37], whereas starphenes are synthesized via aryne trimerization [38]. Also, examples of synthesis of bisacenes by cyclodehydrogenation via Scholl reaction[39–42] and on-surface synthesis are described[43,44].



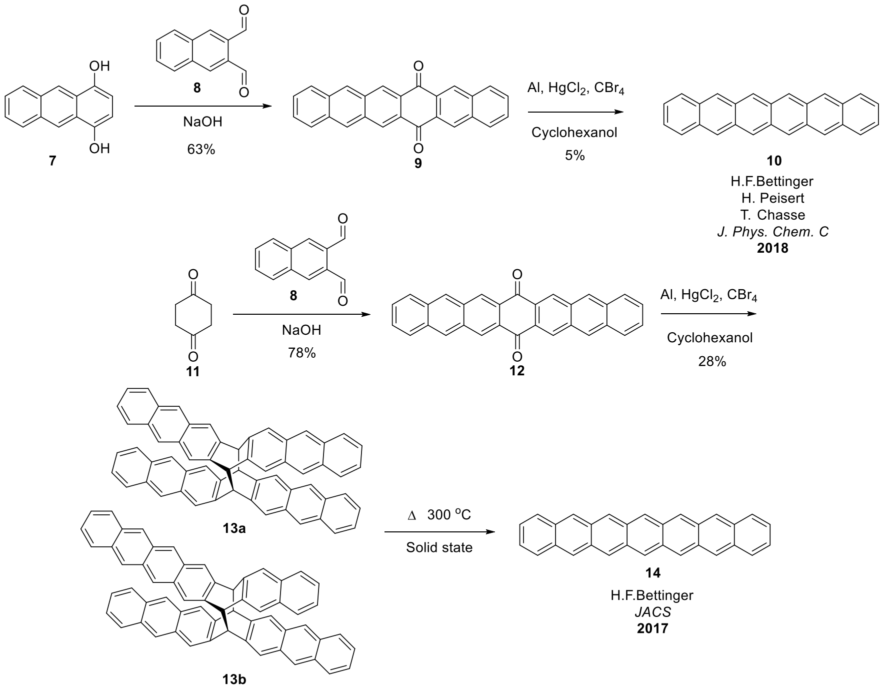
Scheme 3. Synthesis of zigzag periphery via alkyne benzannulations.

Nevertheless, there are exceptions, and several alkyne benzannulations can be considered as an effective methods of the construction of the zigzag periphery. The most notable examples are the synthesis of coronene **2**[45] from 1,1-diaryl-2,2-diethynylethylene **1**, described by Scott et al.; benzodipyrenes **4** via $InCl_3$-$AgNTf_2$ catalyzed four-fold alkyne benzannulation reaction[46] and irregular nanographene **6** via domino benzannulation of buta-1,3- diynes **5** [47] both described in Chalifoux group (Scheme 3).

In the next chapters, the syntheses of zigzag PAHs with more than five condensed benzene rings will be considered in more details.

2.2.Linear pristine acenes

Linear acenes have been investigated thoroughly since the start of the 20th century. The linear annulation leads to the fewest localized Clar resonant sextets per number of aromatic rings. The smallest acenes naphthalene and anthracene are readily available on an industrial-scale because they can be isolated directly from petroleum resources. Tetracene and pentacene, containing four and five condensed rings, are less abundant but still available on a large scale. Their derivatives found a large number of applications[6]. For example, TIPS-pentacene became the benchmark of organic field-effect transistors[48].

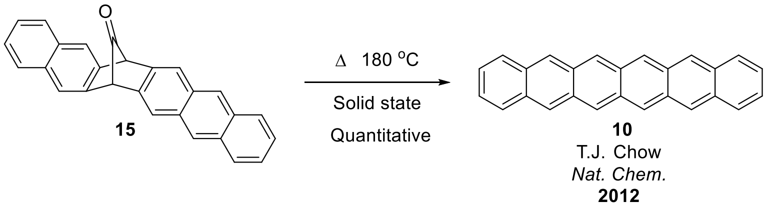


Scheme 4. Synthesis of hexacene and heptacene from corresponding quinones.

The synthesis, characterization, and device applications of pristine acenes larger than pentacene are all hampered by their low solubility and poor stability. Syntheses of hexacene **10** were already reported in the middle of the 20th century[49,50] via the reduction of 6,15-hexacenequinone **9**, which can be synthesized via the dialdol condensation of **7** and **8.** Later investigations indicated a considerable amount of side products in hexacene obtained by this approach. Only in 2018 after modification of the reduction and careful sublimation of the obtained mixture **10** was obtained in pure form with 5% yield (Scheme 4). This allowed the fabrication and investigation of the thin film of **10** on metal surfaces[51].

In 2017, the same group reported the first synthesis of heptacene in the solid state and solution[52]. Heptacene-7,16-quinone **12**, was synthesized via tetra aldol condensation of **8** and two equivalents of **11** and reduced by aluminium amalgam in the presence of CBr_4 yielding the mixture of two dimers of heptacene **13a** and **13b**. Their thermal cycloreversion to heptacene **14** was successfully demonstrated at 300 ºC in the argon stream (Scheme 4). In contrast to **10**, which is stable in the solid state under Ar atmosphere, **14** readily dimerizes at room temperature.

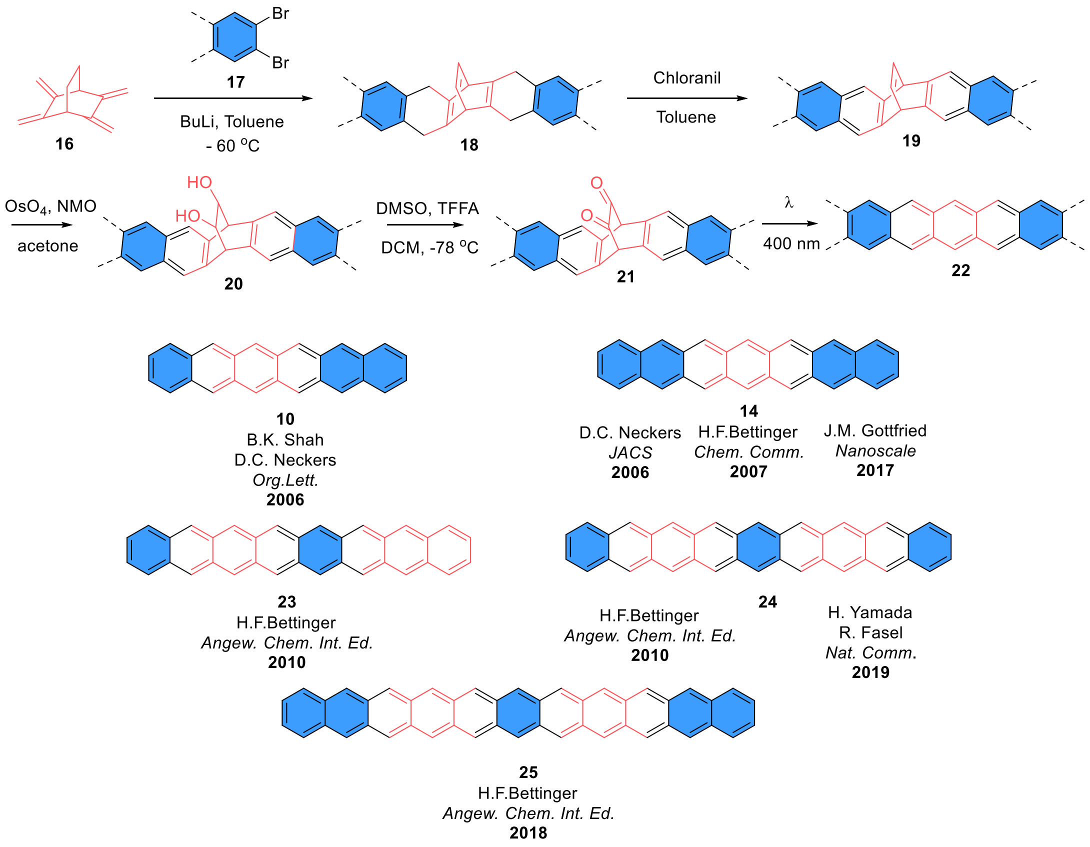
The relative stability of **10** was enough to grow single crystals and perform investigations of semiconducting properties. An improved synthesis of **10** was reported by Chow et al. [53]. It was performed via retro cycloaddition of **15** under heating in the solid state. This approach allows synthesizing **10** in nearly quantitative yield (Scheme 5). Hexacene OFET devices displayed the high hole mobility of 4.28 $cm^2V^{-1}s^{-1}$ and can function in the dark for at least 19 days.



Scheme 5. Synthesis of hexacene in bulk.

Synthesis of octacene and its more extended analogues seems to be even more unrealistic using conventional organic synthesis. Therefore, other alternative methods should be developed for the capture and detection of these elusive compounds. One such approach is based on the Strating –Zwanenburg photobisdecarbonylation[54] of bridged α-diketones **21** in the matrix of inert gas or polymer developed by Neckers et al. (Scheme 6). The required precursors can be synthesized via Diels-Alder reaction of arynes with **16**[55], followed by aromatization, dihydroxylation, and oxidation. Firstly shown on the synthesis of **10**[56] and **11**[57,58], Bettinger at al. extended this method[59] to the synthesis of octacene **23**[60], nonacene **24**[60], and finally undecacene **25**[61]. The effective decarbonylation of the precursor molecule was achieved under irradiation of light with λ>395 nm.

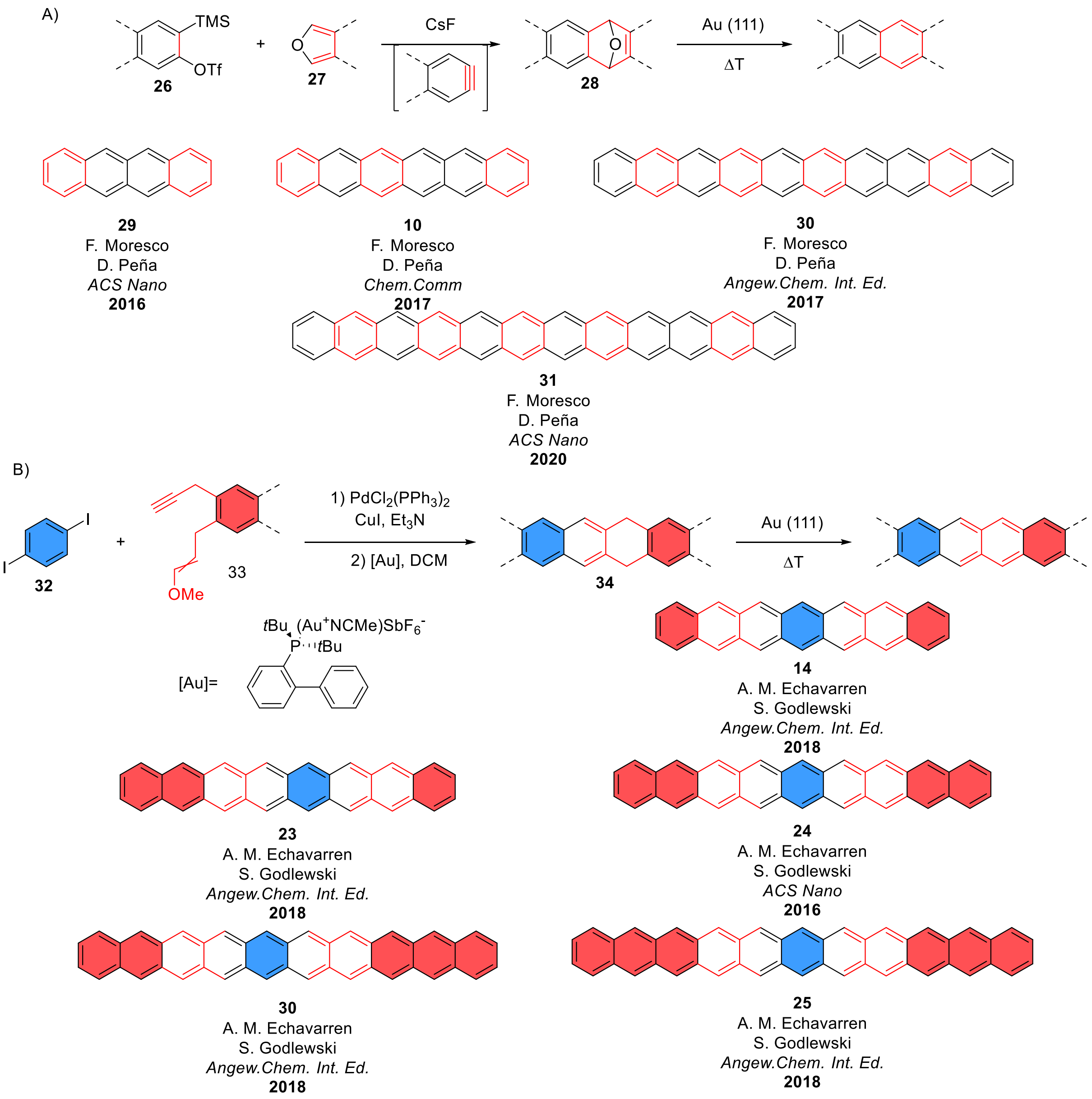
The only possible analysis of synthesized compounds was measuring absorption spectra in UV/Vis and NIR regions. Synthesis in the polymer matrix is less favourable due to acenes' reactions with the matrix and the increased linewidth of the spectra. Nevertheless, only **23** and **24** were synthesized in argon matrix at 4 K. Synthesis of **25** in matrix was not possible, because of the decomposition of the sample during sublimation . Despite these difficulties, all acenes were detected, and their recorded spectroscopical properties were found to agree with DFT/MRCI computations. Also, it was found that the HOMO-LUMO transition energy which is associated with the optical gap follows the linear 1/N relationship, where N is the number of benzene rings in acene.



Scheme 6. Synthesis of acenes in the matrix.

Another opportunity to study highly reactive molecules is provided by scanning tunnelling microscopy (STM), allowing monitoring and probe the electronic properties directly on atomically clean surfaces under ultra-high vacuum conditions. On-surface chemistry's current progress provides a powerful alternative to synthesizing unstable molecules from stable precursors (Scheme 7). Peña et al. demonstrated the efficiency of the on-surface synthesis on the examples of tetracene **29**[62], hexacene **10**[63], decanene **30**[64], and largest known dodecacene **31**[65] utilizing respective stable epoxyacenes. They were obtained via Diels-Alder cycloaddition of furans derivatives **27** with *in situ* generated arynes. Unexpectedly, it was observed that after a progressive closing of the gap and asymptotically converging to the value of about 1.1 eV (acenes **30** and **25)** the energy gap (acene **31)** increases to 1.4 eV. This phenomenon was explained by the destabilization of unoccupied orbitals due to extra-large acenes' possible polyradical nature [66].

Echavarren and Godlewski et al. developed different approach based on atomic manipulation with the tip of a scanning tunnelling and atomic force microscope (STM/AFM) as well as by on-surface annealing of partially hydrogenated acenes. The method's scope was demonstrated on the synthesis of series of acenes from heptacene to undecacene[67,68]. The precursors can be easily synthesized via a two-step procedure, consisting of Sonogashira coupling and gold(I)-catalyzed cyclization of aryl-tethered 1,7-enynes[69].

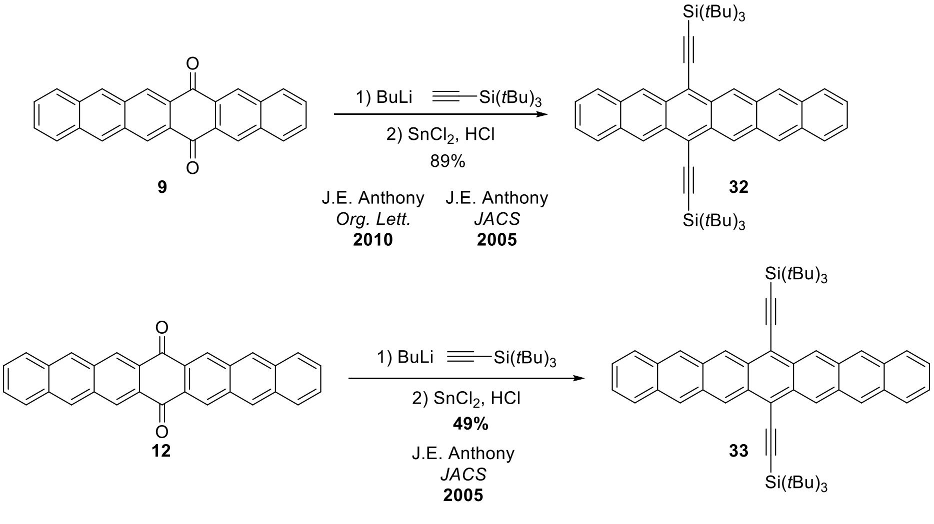


Scheme 7. On-surface synthesis of acenes from epoxyacenes (A) and hydroacenes (B).

Strating–Zwanenburg photobisdecarbonylation can also be used in on-surface chemistry. Heptacene and its organometallic complexes[70–72], nonacene[55] were generated from their corresponding ketone precursors.

2.3.Acenes with bulky substituents.

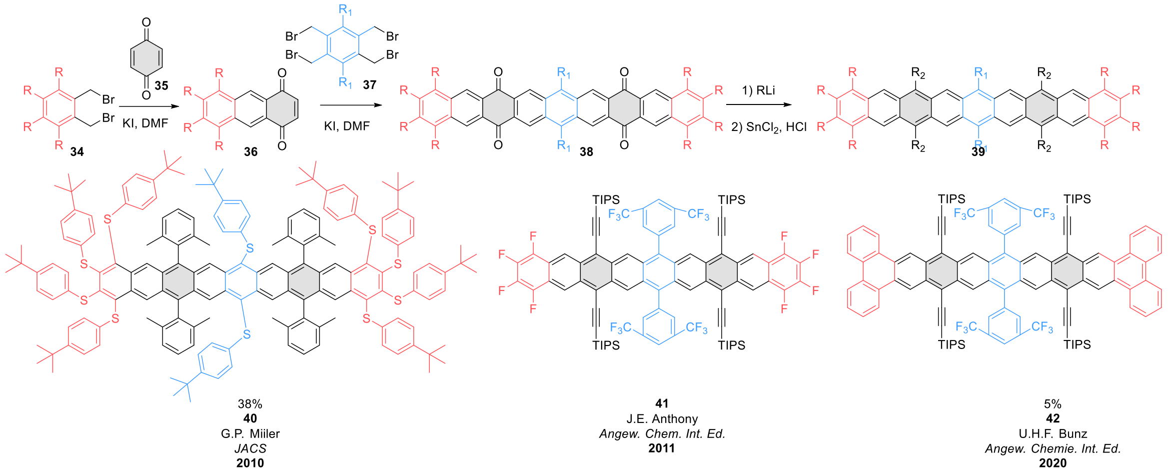
As it was described in chapter 2.2., higher acenes suffer from the low stability and poor solubility. All of these downsides can be overcome by the introduction of bulky substituents[73–75]. Anthony et al. showed that introduction of trialkyl silyl groups in pentacene vastly increases solubility and stability and does not hamper the π-π stacking in the solid state[48]. Using this approach, the same group has synthesized soluble hexacene **32** [76–78] and heptacene **33**[76] derivatives starting from **9** and **12,** respectively, by the two-step procedure (Scheme 8). The first step was the addition of lithium tri-*tert*-butylsilylacetylene to the corresponding quinone resulting in 1,4-diols, which were subjected to the reductive aromatization [79] using $SnCl_2$. Hexacene derivatives were found to be stable in contrast to heptacene derivatives, which degraded completely within a day in solution even under oxygen free conditions. Nevertheless, it was possible to measure NMR spectra of **33**, which showed closed-shell ground state. Compound **32** displays the longest-wavelength absorption λ_{max} at 738 nm, which corresponds to a 100-nm red-shift compared to that of TIPS-pentacene. The UV spectrum of **33** has λ_{max} at 852 nm with a pronounced shoulder at 825 nm, which shows that the fusion of an additional ring leads to a further ∼100 nm red-shift.



Scheme 8. Synthesis of soluble hexacene and heptacene.

The first persistent nonacene **40** derivative was reported by Miller et al.[80]. Arylthio groups[81] were used for stabilization of nonacene core (Scheme 9). Compound **40** was synthesized from

38 by standard two-step procedure: addition of lithium organic compound and subsequent reductive aromatization. The **38** was synthesized via combination of two Diels-Alder reactions of **35** with 1,2 dimethylenebenzene **34** and 1,2,4,5- tetramethylenebenzene **37** precursors. Miller et al. claimed, that nonacene had red fluorescence, which can be used to determine the formation of nonacene core and the molecule has closed-shell character, which allowed to analyze it utilizing NMR.



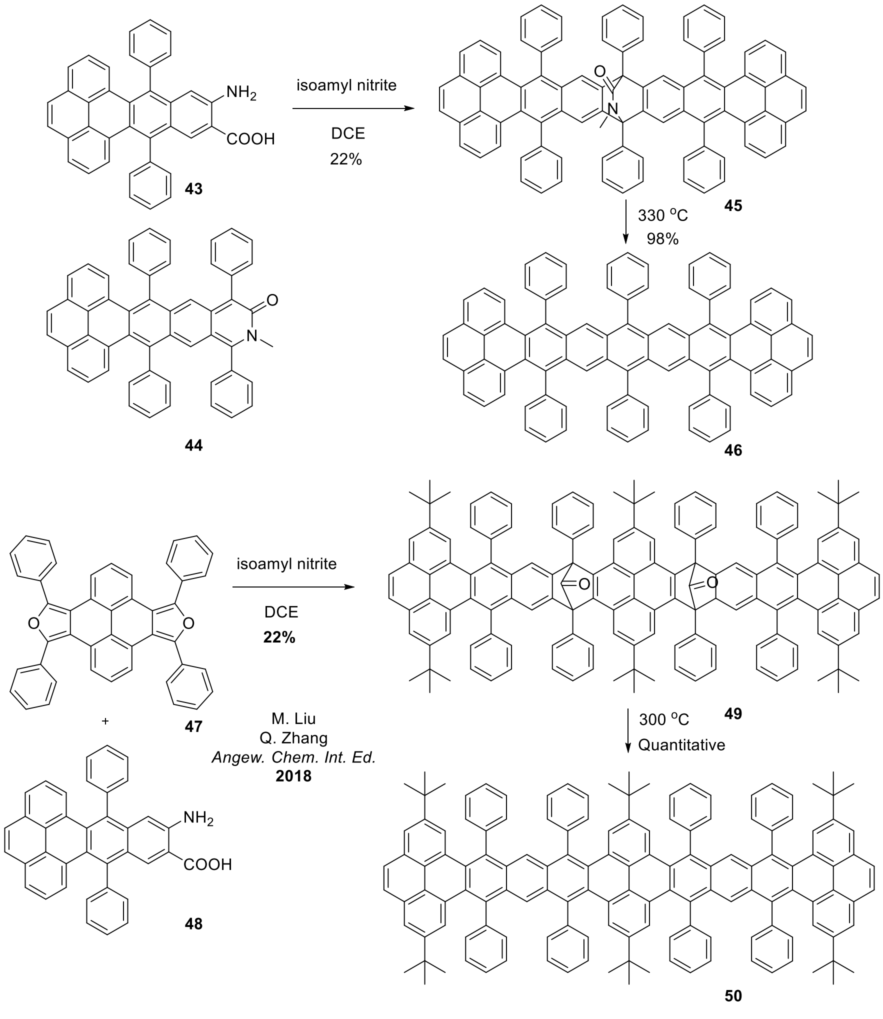
Scheme 9. Synthesis of substituted nonacenes.

Following the same synthetic strategy, Anthony et al. prepared nonacene derivative **41** bearing silylethyne groups [82]. The presence of a significant number of electron-accepting groups remarkably increased the stability of **41**, whereas triisopropylsilylacetylene substituent allowed facile crystallization of **41**. Surprisingly, no red fluorescence or NMR signals were found, indicating the molecule's open-shell character. The authors called into questions the Miller group results and suggested that the product of oxidation is the reason for the red fluorescence and observation of the sharp signals in ^{1}H NMR.

Bunz et al. presented an alternative method of stabilization of higher acenes based on the metamorphosis of the end benzene ring into triphenylene[83,84] ("butterfly wings"). Interestingly, this trick does not significantly change the π system of the acenes, and the UV-Vis spectra look similar to the spectra of molecules without "butterfly wings". Using 9,10-Bis(bromomethyl)phenanthrene as a 1,2 dimetylenebenzene source, they successfully synthesized tetrabenzononacene derivative **42**[85], which was found to be stable in the solid state up to for more than six weeks and has seven hours half-time in solution under nitrogen atmosphere. It was also was found that the NMR spectrum of acene **42** displays sharp signals.

Steric hindrance of substituents can lead to deviation of acene backbone from linear to twist. For example, dodecaphenyltetracene is a molecule with an end-to-end twist angle of 97º. The peripheral phenyl substituents encapsulate the central acene, and as a result, the molecule is relatively unreactive and even displays reversible electrochemical oxidation and reduction[86]. Many examples of twisted acenes are presented in the literature[87–89], whereas the most exciting examples are syntheses of nonatwistacene **46**[90] and dodecatwistacene **50**[91]. The key step in the synthesis of **46** is a retro-Diels–Alder reaction involving the thermal elimination of lactam bridges from soluble acene precursor **45** (Scheme 10). The precursor was synthesized through cycloaddition reaction between **43** and the aryne from **44**. The molecule holds acene type character with longest absorption λ_{max} at 739 nm and has HLG between hexacene and heptacene (1.64 eV). In contrast, **50** loses its acene character and has λ_{max} at 525 nm with a calculated gap around 2.5 eV. The compound was also synthesized by retro retro-Diels–Alder process, but from diketone **49**, which was afforded through cycloaddition of difuran **47** with aryne from **48**.

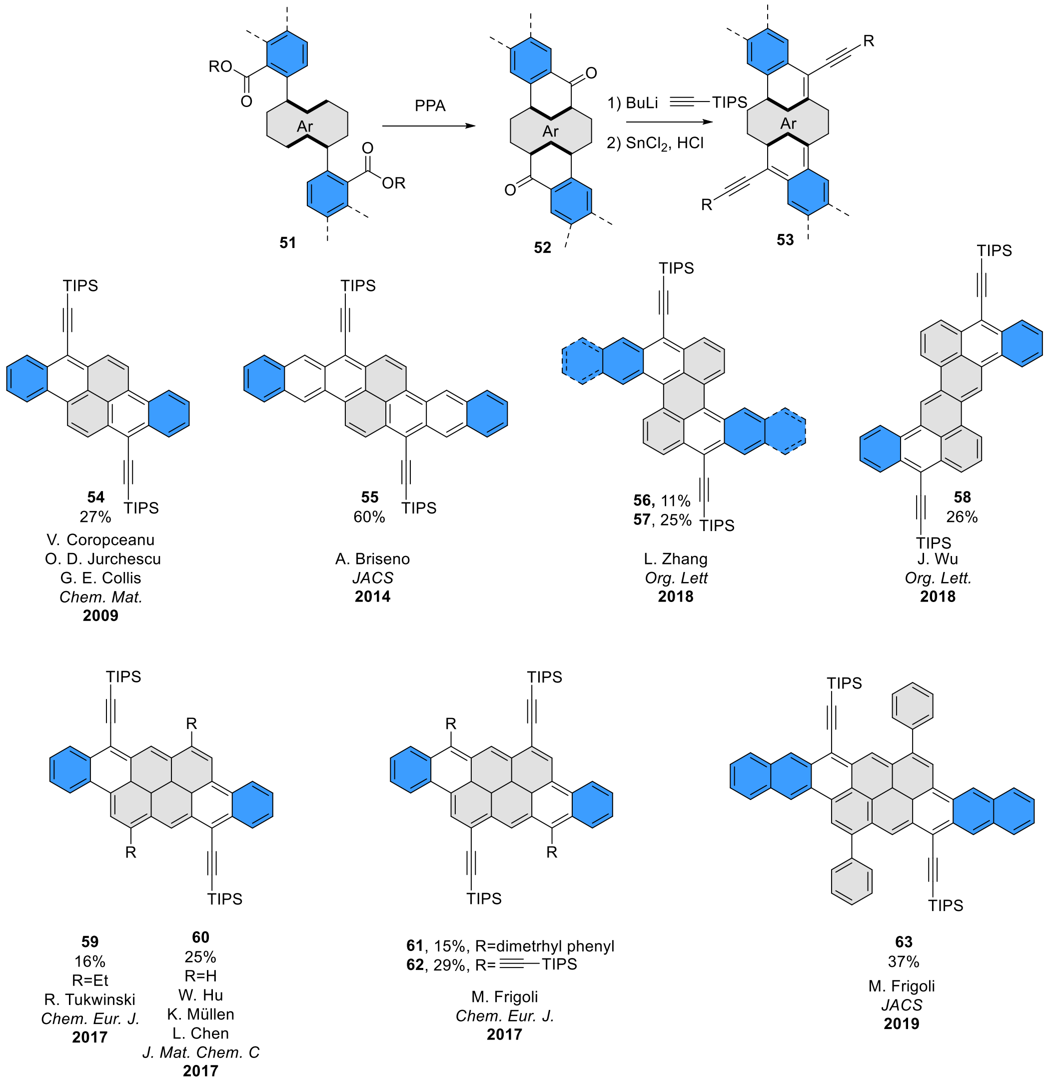
The methods described for these molecules were also used to synthesize their smaller analogues[92–96].



Scheme 10. Synthesis of long twisted acenes.

2.4. 2D acenes.

As discussed in chapter 2.3, even highly substituted higher large acenes have a short lifetime under ambient conditions, so their applications as materials in OFET are minimal. However, for instance, polyacenes' stability can be significantly improved by changing their linear annulation mode to an angular one, which increases the amount of Clar sextets and, therefore, increases the overall aromatic stabilization energy. Nevertheless, the introduction of silylacetylene groups is still required for the convenient processability, solubility and preservation of π-π stacking in the solid state.



Scheme 11. Synthesis of angularly fused 2D acenes from corresponding quinones.

Similarly to the synthesis of substituted linear acenes, the addition of lithium tri-*tert*-butylsilylacetilene to quinones with subsequent reductive aromatization can be used for the synthesis of 2D acenes (Scheme 11). Firstly, this method was applied for commercially available dyes such as dibenzo[*b,def*]- chrysene-7,14-dione (Vat Yellow 4)[97] or pyranthrone (Vat orange 9)[98,99] with high yields. This class of materials efficiently produces low-dimensional charge- transport systems. Transistor based on the single-crystal of compound **54** has shown the mobility up to 0.1 $cm^2V^{-1}s^{-1}$.

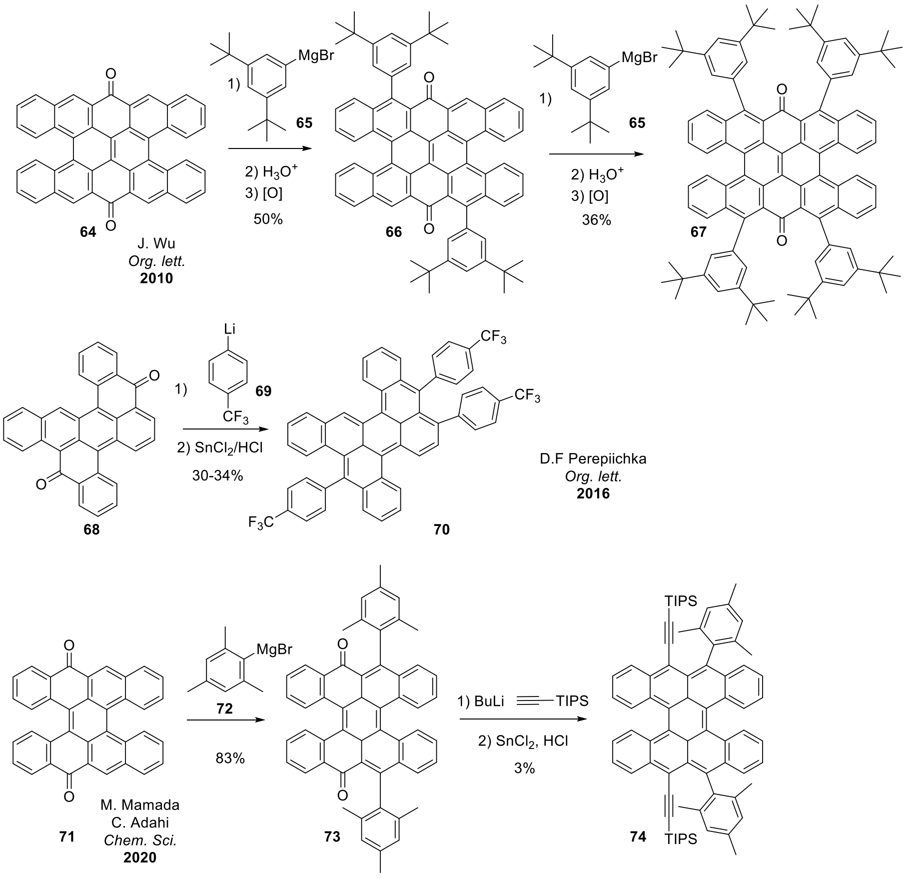
When the starting ketones are not available from commercial structures, they can be obtained from corresponding diacids or diesters using Friedel-Crafts reaction in PPA. Briseno et al. developed new organic semiconductor bistetracene **55** with high mobility (up to 6.1 $cm^2V^{-1}s^{-1}$)' and relatively high stability (200 times more stable than pristine pentacene)[100]. Other groups tested alternative bistetracene (DBATT) derivatives as organic semiconductors[101,102]. Maximum mobility was achieved by Friseno et al. and reached 0.77 $cm^2V^{-1}s^{-1}$.[103] Despite having singlet open-shell structures in its ground state due to high diradical character (γ = 0.64), its bispentacene analogue **63** is stable and shows remarkably high hole mobility of 1.4 $cm^2V^{-1}s^{-1}$[104]. It was shown that hole mobility of soluble twisted diarenoperylenes **56** and **57** could reach 0.74 $cm^2V^{-1}s^{-1}$[105,106].

When chrysene was used as a central aromatic core, kinetically blocked 5,6:12,13-dibenzozethrene **58** was obtained. This compound's notable characteristic is its open-shell ground state with relatively small diradical character (γ = 0.41). More discussion about zethrenes will be presented in chapter 2.4. [107]

However, this approach has two major flaws. The first one is extremely low solubility of the starting quinones, which sometimes prevents them from simple purifying. The second lays in the competition of 1,2- and 1,4 addition of metalorganic compounds to quinones (Scheme 12). The first time it was observed during the addition of 3,5-di-*tert*-butylphenylmagnesium bromide **65** to bispentacenequinone **64**[108]. The addition of an excess of **65** results in exclusively 1,4- addition in trans manner. The intermediate product is unstable and oxidizes in disubstituted fused bispentacenequinone **66**. Interestingly, no derivatives with more than two aryl substituents were detected, which can be explained by Coulombic repulsion in the dianion resulting after the addition. Treatment of **66** with an excess of **65** followed by acidification in the air gave the tetraaryl-substituted fused bispentacenequinone **67** in 36% yield. Similar problems were detected in the synthesis of substituted DBATTs, which led to a significant decrease in yields[101,102]. Other notable examples include perylene-3,9-dione **68**, which undergoes selective triarylation using 4-trifluoromethylphenyl lithium **69**[109] and tetrabenzo[a,f,j,o]perylene-9,20-dione **71**, which can be modified selectively by double

Michael addition on the first step and 1,2- addition/reductive aromatization on the second step[110].

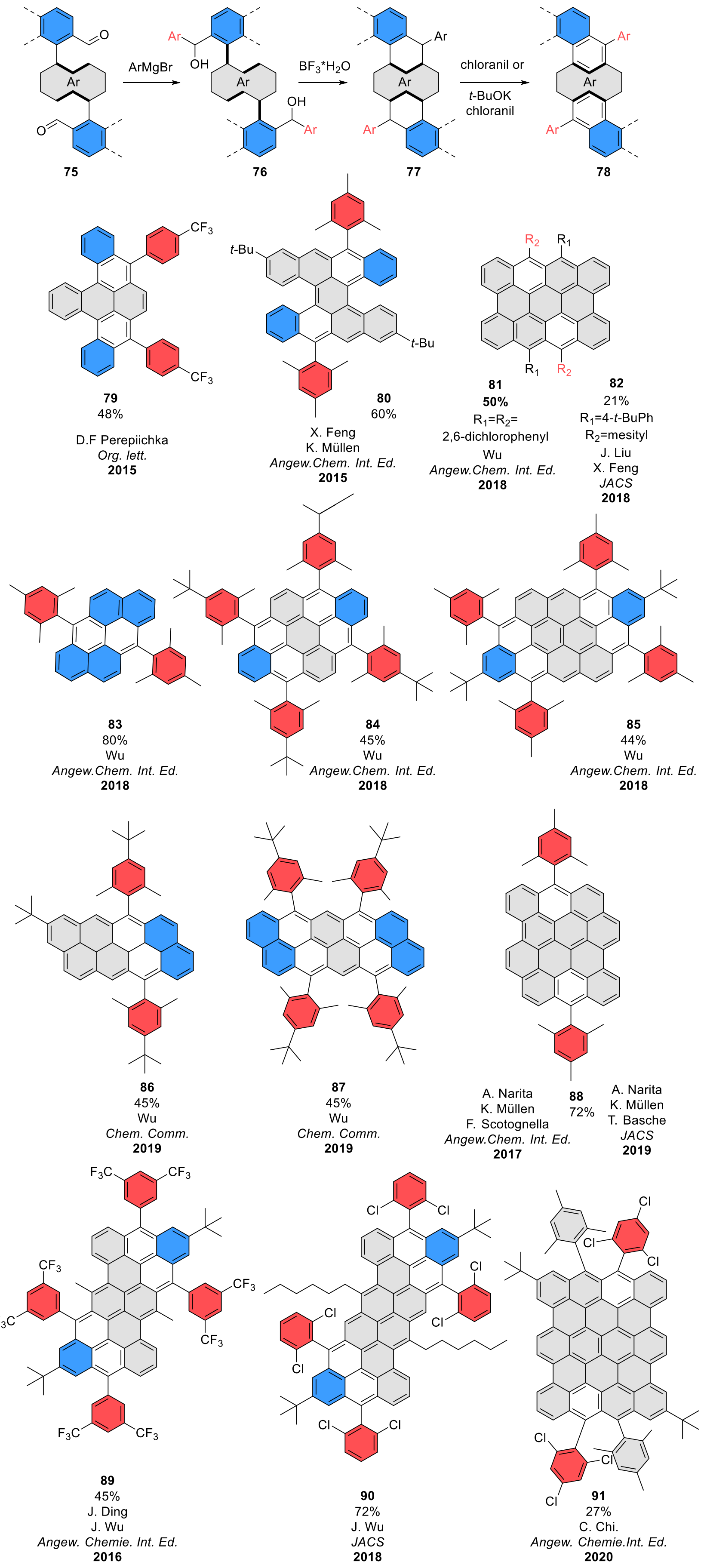
This outcome can be apparently explained by the low reactivity of carbonyl groups due to the extended conjugation[111], which raised questions about the possibility of synthesis of more extended 2D acenes via this approach and, eventually, led to the alternative way of synthesis of zigzag nanographenes.



Scheme 12. 1,2 and 1,4 addition of metalorganic compounds to the quinones.

This approach consists of three-step synthesis, namely, treatment of dialdehyde **75** with aryl magnesium bromide yielding diol **76**, which is subjected to Friedel–Crafts alkylation promoted by BF_3*Et_2O to afford dihydro PAH **77**., As a final step, the oxidation of **77** with *p*-chloranil in the dry solvent under argon results in the target nanographene (Scheme 13).

The application of such approach to 2,2’-(anthracene-9,10-diyl)dibenzaldehyde results in **79**, which in contrast to **70** did not demonstrate semiconducting properties [112]. Another notable example is the synthesis of bistetracene **80** (tetrabenzo[*a*,*f*,*j*,*o*]perylene) " which display open-shell character with diradical character of 0.615[113]. Since the radical centres are not properly blocked kinetically, **80** undergoes fast oxidation under ambient conditions.



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D.F Perepiichka
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K. Müllen
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50%
$R_1=R_2=$
2,6-dichlorophenyl
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21%
R_1=4-*t*-BuPh
R_2=mesityl
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C. Chi.
Angew. Chemie.Int. Ed.
2020

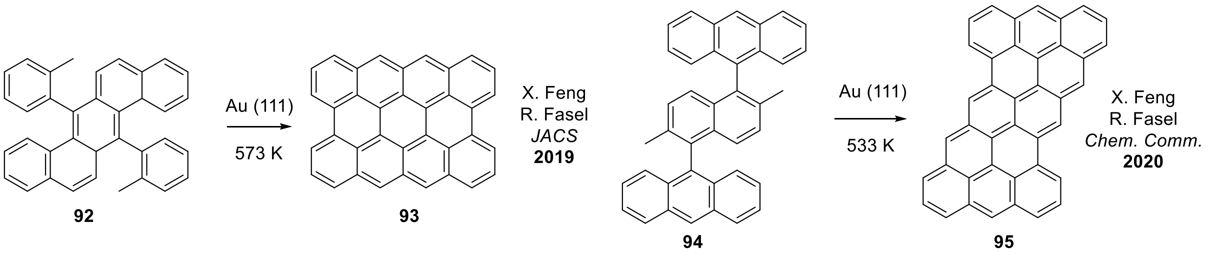
Scheme 13. Synthesis of 2D acenes and superzethrenes from corresponding aldehydes**.**

Wu et al. and Feng et al. almost simultaneously reported the synthesis of substituted *peri*-tetracenes **81** and **82**[114,115]. In contrast to its homologue bisanthrene, this type of acenes exhibits open-shell structure with very small HLG (1.12 eV). It can be stabilized enough for isolation in the solid state only if radical centres are blocked with electron-poor 2,6-dichlorophenyl groups[114].

Wu et al. synthesized series of graphene-like molecules containing four zigzag edges **83-87**[116,117]. In contrast to *peri*-tetracenes, which also contains bay-regions and only two zigzag regions, new molecules have smaller HLG, are closed-shell and are more stable. Another exciting compound is dibenzoovalene **88**, which was synthesized by Mullen et al.[118,119] This compound features a low energy gap and strong red emission with a remarkable quantum yield of 79%, small Stokes shift and high photochemical stability promising for applications in single-molecule spectroscopy.

Molecules with very high diradical character can be afforded through the mentioned procedure. For example, “superheptazethrene” **89** [120], “superoctazethrene” **90** [121] and [4,3]*peri*-acene **91**[122] were successfully synthesized and fully characterized, including single-crystal X-ray analysis. All compounds show very high diradical character (0.71, 0.81 and 0.948 respectively).

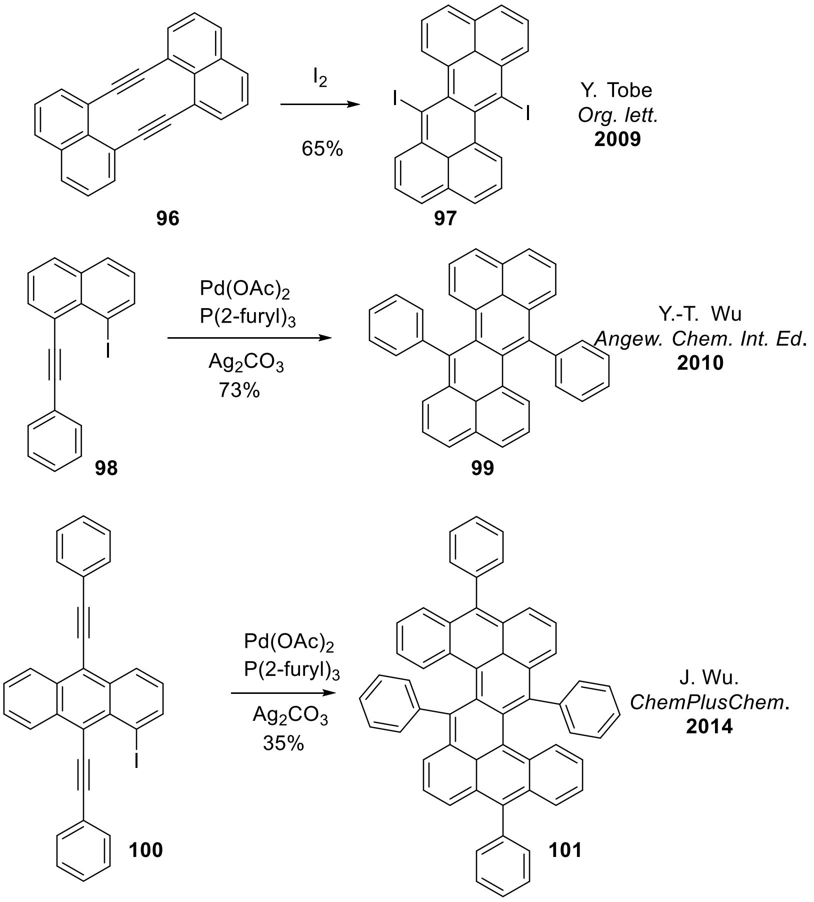
Fasel et al. have developed nanoribbons’ synthesis with zigzag periphery via cyclodehydrogenation and oxidative ring-closure reactions upon annealing of methyl-substituted PAHs on Au(111) surface during the synthesis of graphene nanoribbons.[123] Later this approach was successfully adopted to synthesize pristine 2D acenes with extremely low HLG (Scheme 14). Thus, following this strategy, pristine bistetracene **93** (HLG = 0.35 eV), which has open-shell nature was successfully generated on the Au surface[124] Another interesting example is the synthesis of superheptazethrene **95** [125], which has HLG 0.23 eV but surprisingly display closed-shell nature on Au (111) surface.



Scheme 14. Synthesis of 2D acenes via on-surface cyclodehydrogenation.

2.5. Zethrenes.

As it has been mentioned in chapter 2.4, members of zethrene family exhibit remarkable biradical character. Zethrene is Z-shaped PAH which can also be regarded as a dibenzoacene. From heptazethrene onward, zethrenes contain an embedded quinodimethane unit and tend to recover aromaticity of the quinoidal moiety and become diradical[126], which can have potential applications as NIR dyes and spintronic materials[127,128].

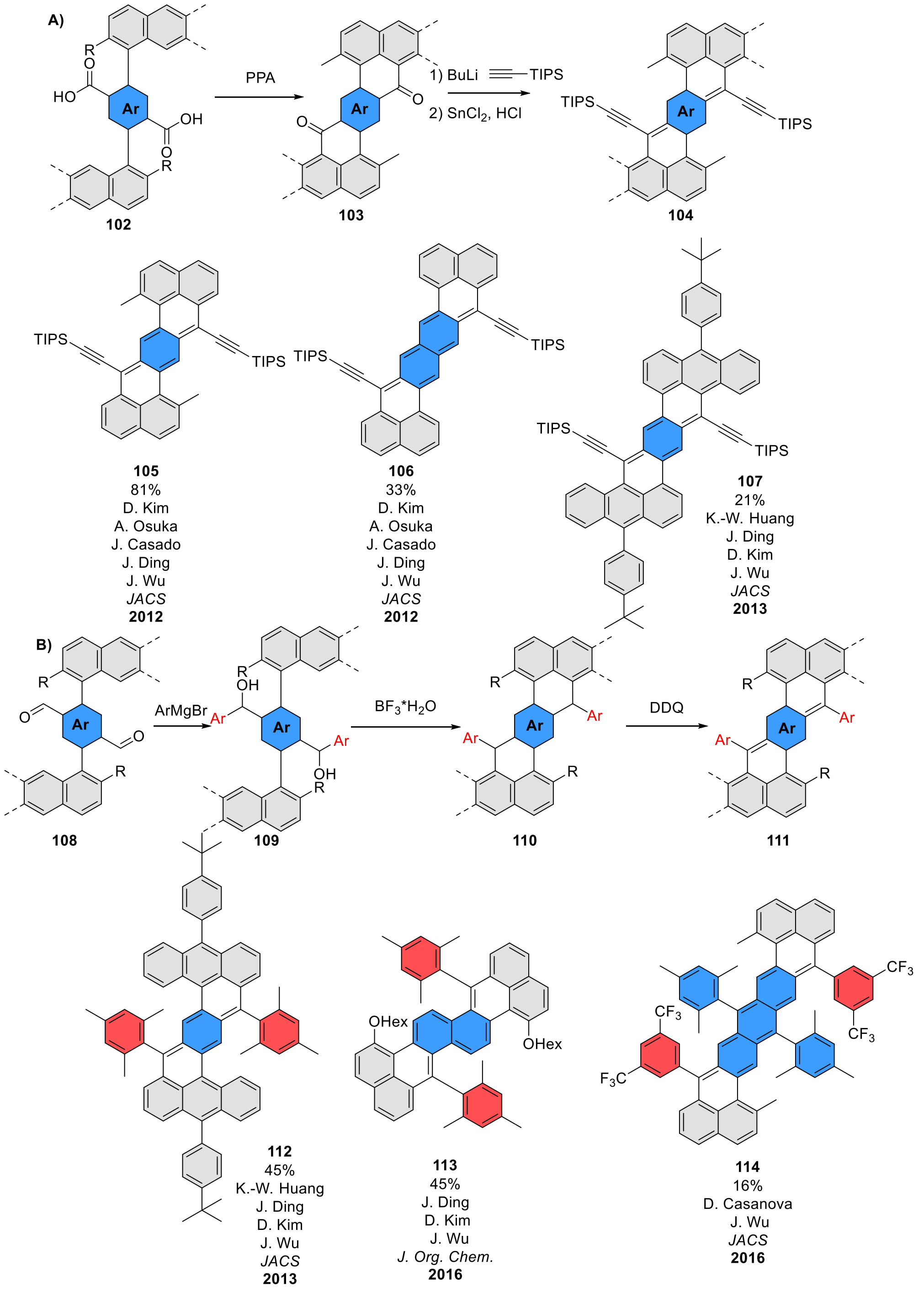


Scheme 15. Synthesis of zethrene and dibenzozethrene.

The first syntheses of zethrenes were reported by Clar in 1960-s[129,130], but all extended analogues of zethrene are highly reactive species, and they tend to polymerize or react with air and acid. As a result of high reactivity, zethrenes have been forgotten by chemists for a long time.

In 2009 the renaissance of zethrene derivatives began (Scheme 15). Tobe et al. reported iodine-triggered transannular cyclization of **96**, which opens the path to 7,14-disubstituted zethrenes **97**[131]. Synthesis of **96** is quite tricky and, therefore, Wu et al. developed more straightforward approach towards substituted zethrenes **97** via cyclodimerizaion of 1-ethynyl-

8-iodonaphthalenes **98**[132], which allowed studying the influence of substituent on biradical character and the nature of the ground state. 1,2:8,9-dibenzozethrene derivatives **101** can be also synthesized through similar cyclization[133]. It was found that phenyl substituents drastically the ground state, which becomes closed-shell in contrast to the pristine zethrene and dibenzozethrene, which exhibit open-shell nature[134].

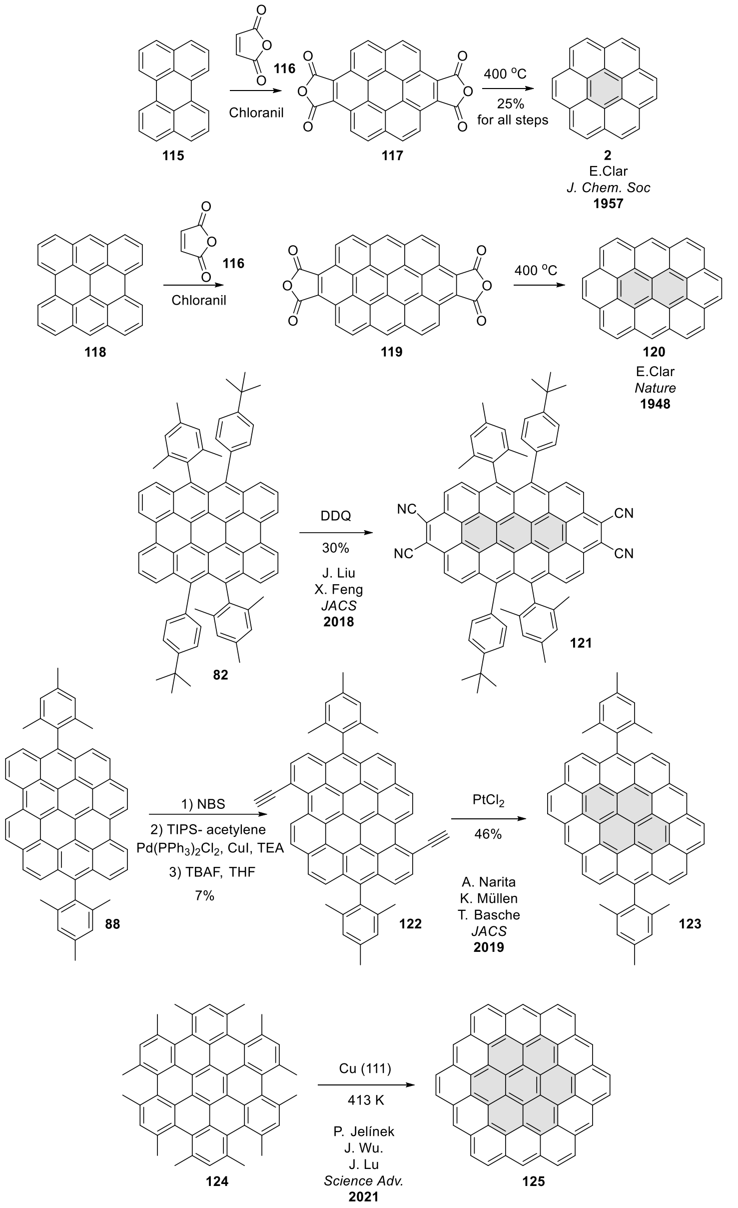


Scheme 16. Synthesis of extended zethrenes. A) Two-step procedure. B) Three-step procedure.

Synthesis of extended zethrenes can be broken down into two types of approaches similar to the synthesis of 2D acenes mentioned in chapter 2.4 (Scheme 16). To take a form of Z letter, naphthalene or anthracene units are used for the Friedel-Crafts reaction as starting blocks. In contrast to the synthesis of acenes, aldehyde/carboxyl moieties, are usually placed in the central building block to simplify the synthesis. Heptazethrene **105**[135], octazethrene **106**[135], as well as one of the dibenzoheptazethrene isomers **107**[136] were synthesized through the first approach (Scheme 15A). Another dibenzoheptazethrene isomer **112** [136] together with isomer of octazethrene **113**[137] and nonazethrene **114**[138] were afforded through second approach (Scheme 15B). It is important to note that isomers **107** and **113** have higher biradical character than their isomer counterparts **112** and **106**. Wu et al. both experimentally and theoretically have shown a faster decrease of the singlet−triplet energy gap and a faster increase of biradical character with the increase of the number of benzenoid rings in the zethrene series in comparison to linear acenes.

2.6. Circumacenes.

Circumarenes are a subclass of nanographenes bearing only zigzag edges and K-regions. They feature a central aromatic core surrounded by one outer layer of annulene. Interesting, despite possessing multiple zigzag edges, these molecules exhibit remarkably high stability under ambient conditions. The smallest representatives coronene **2** (circumbenzene) [139] and ovalene **120** (circumnaphtalene)[140] can be synthesized via pioneer examples of APEX (annulative π-extension)[141]. In this case, the key reaction of π-extension is Diels-Alder cycloaddition of perylene **115** and bisanthrene **118** with **116**, followed by thermal decarboxylation forming pristine circumarenes (Scheme 17). **82** can also be transformed into circumanthracene **121** via Diels-Alder reaction with an excess of DDQ used to synthesize **82**. Selective bromination of **88** [142], followed by Sonogashira reaction with TIPS acetylene, deprotection and finally Pt-catalyzed benzannulation yielded circumpyrene **123**[143]. circumcoronene **125** represents the biggest known circumarene synthesized by on-surface cyclodehydrogenation of hexa-*peri*-hexabenzocoronene carrying twelve methyl groups in *bay*-regions (compound **124)**[144].



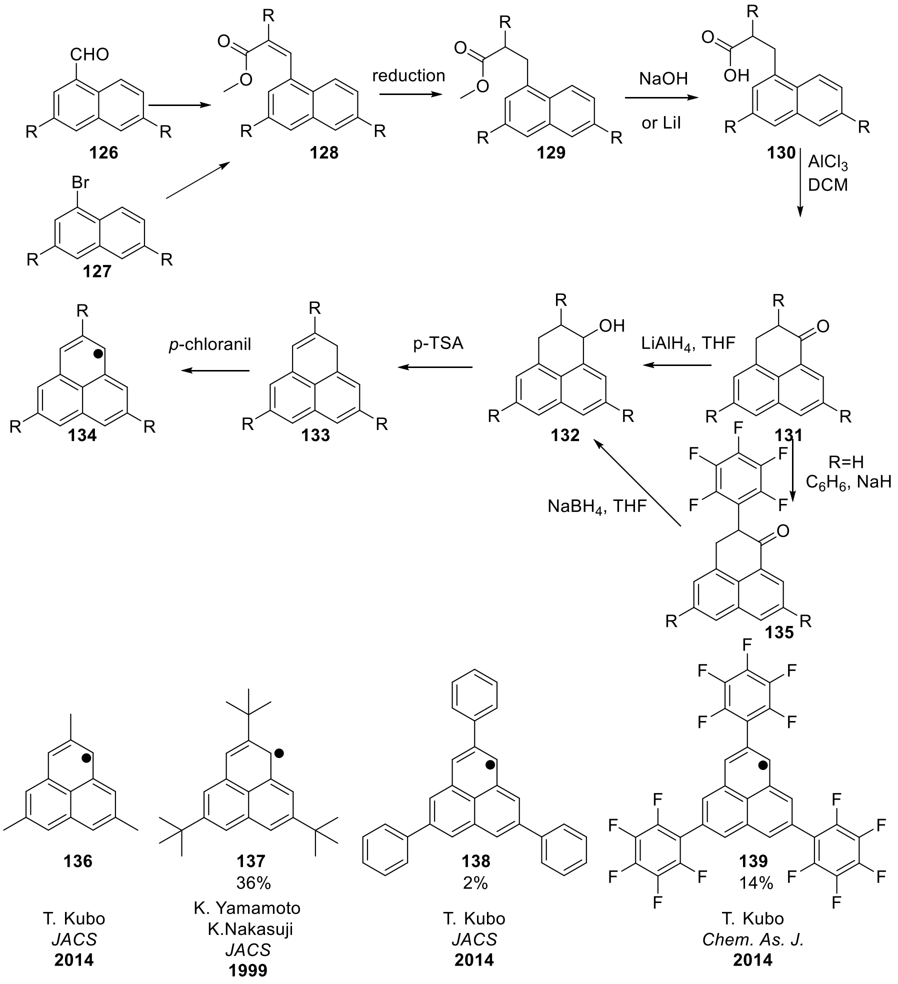
Scheme 17. Synthesis of circumacenes.

2.7. Non-Kekule open-shell PAHs.

The extension of fused benzene rings in a triangular shape leads to a series of non-Kekule open-shell zigzag-edged triangular nanographenes. The most prominent members of this family are the monoradical phenalenyl (n = 2), the diradical [3]triangulene (n = 3), the π-extended triradical [4]triangulene (n = 4), the tetraradical [5]triangulene (n = 5), where n is the number of carbon atoms at each zigzag edge[145].

The formation of the smallest pristine phenalenyl was already observed in 1957[146]. However, the isolation of this elusive compound has not been achieved due to fast dimerization and oxidation. Nevertheless, the substitution of phenalenyle in 2,5 and 8 positions with bulky *tert*-

butyl groups drastically increases the radical's kinetic stability, allowing it separation and characterization [147].

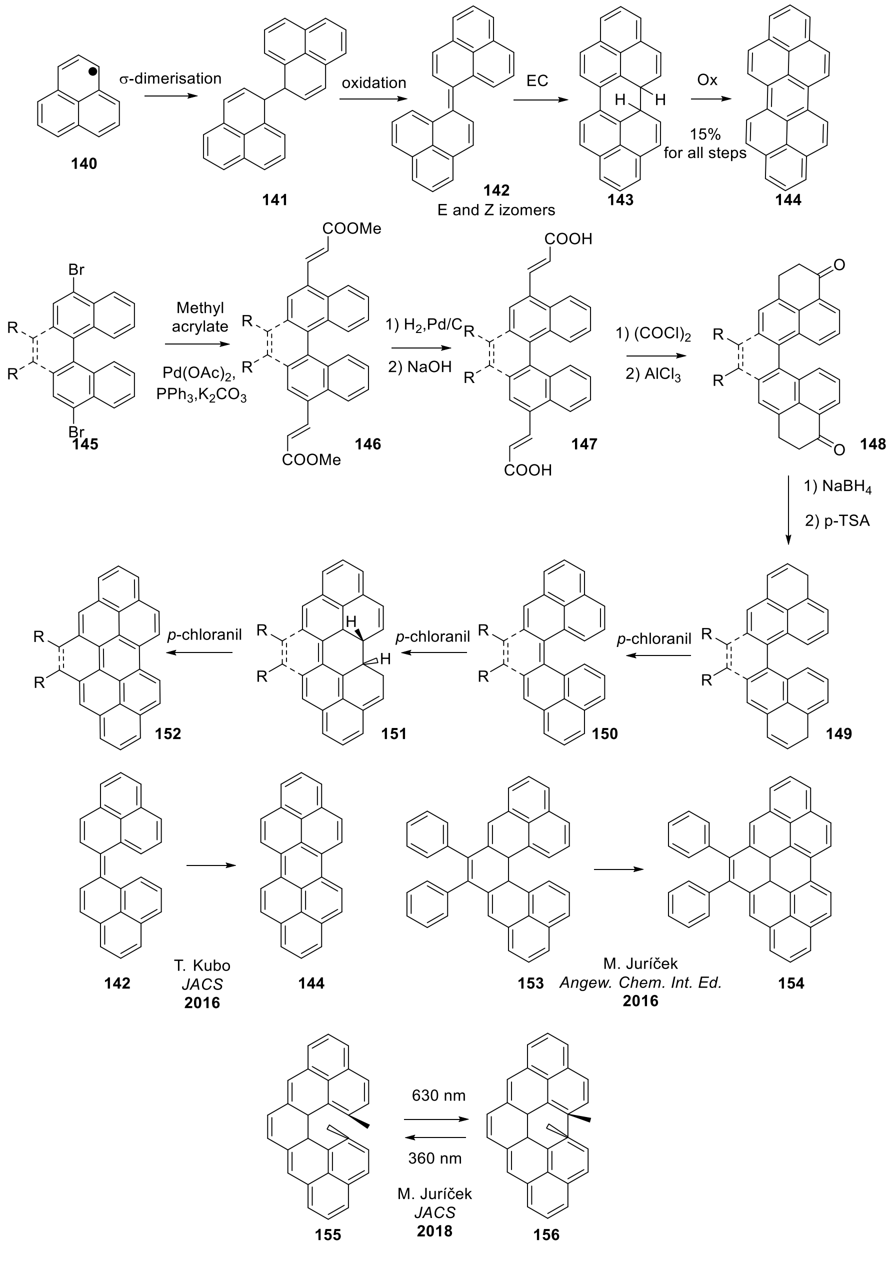


Scheme 18. Synthesis of phenalenyl radicals.

The radical **137** was synthesized from 2,7-di-*tert*-butylnaphthalene by ten steps protocol (Scheme 18). Its bromination was followed by Bouveault aldehyde synthesis. Then, the ester **128** was obtained by the Reformatsky reaction of **126**, was reduced with triethylsilane to afford **129**. Hydrolysis of **129** with LiI gave the acid **130** in high yield. The acid was converted into its chloride and subjected to the Friedel-Crafts cyclization, which gave the phenalanone **131**. The phenalene **133**, was obtained by reduction of **131,** followed by dehydration of **132**. Treatment of **133** with an oxidant such as DDQ or *p*-chloranil in degassed toluene gave a blue neutral radical solution of **137**. Similar treatment in hexane can give the crystalline products as deep blue needles.

The proposed approach was found to be prolific for the synthesis of other substituted phenalenyls [148,149]. However, instead of Bouveault aldehyde synthesis and Reformatsky reaction Heck reaction and Horner–Wadsworth–Emmons reactions were used for introducing propionic acid moiety.

Dimerization of phenalenyl and its derivatives attracted attention due to a unique two-electron, 12-center (2e/12c) π–π stacking bonding interaction between two phenalenyl monomers. This type of π–π stacking bonding has been called pancake bonding[150]. This stabilization is quite robust and can compete energetically with σ-bonding, and they can even flux into each other in solution[151,152] or solid state[148]. Sterically hindered phenalenyls mostly form π-dimers, whereas σ-dimers are preferred for the sterically free radicals.

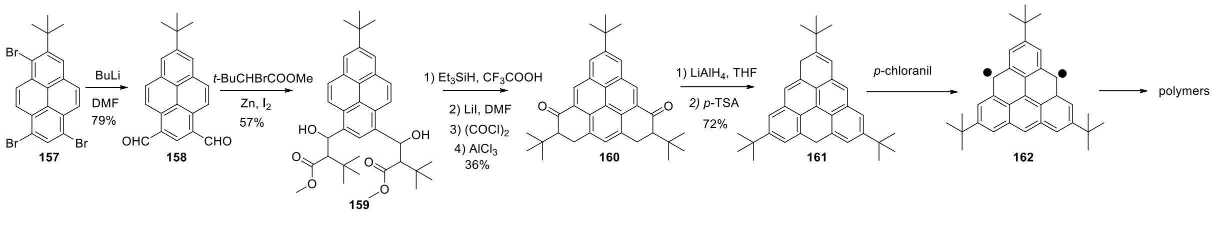


Scheme 19. Study of the decomposition pathway of phenalenyl radical and electrocyclization of diradicaloids.

σ-dimer of pristine phenalenyl **141** can be easily oxidized by oxygen[153], and the final decomposition product was assigned as peroperylene **144**[154,155]. The product analysis suggested that *E*- and *Z*-biphenalenylidene **142** and dihydroperoperylene **143** should be the reactive intermediates on the pathway of phenalenyls[156]. Nevertheless, only in 2016, Kubo et al. finally characterized these reactive intermediates[157]. Oxidation of bisphenalene **150**, which was synthesized similarly to the approach suggested for phenalene, afforded *anti*-**143**, which can be photochemically converted to *E*-**142** (Scheme 19). When the photochemical reaction was carried out at a low temperature in the rigid matrix of solvent, the formation of *Z*-**142** was observed. The most important finding observed was the thermal ring-closure in conrotatory process of **142** into *anti*-**143**, which is forbidden by the Woodward−Hoffmann rules[158]. This unusual reaction was ascribed to the ground states destabilized by its singlet biradical character[159].

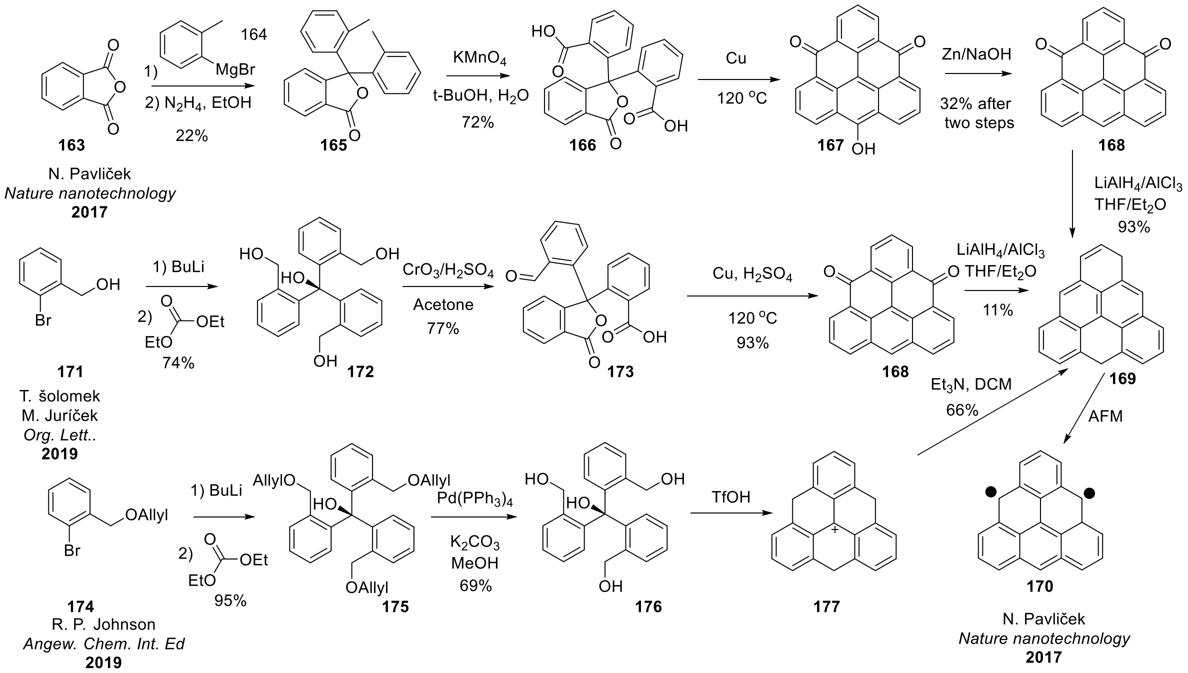
Another example of such an exciting transformation was observed in the case of cethrene **153**, an isomer of heptazethrene, which undergoes a 6π-electrocyclization within several hours at room temperature[160]. When the 6π-electrocyclization can not be followed by subsequent dehydrogenation, i.e. blocked by methyl groups like in dimethylcethrene **155**, the reversibility of this reaction can be used as a switching function[161]. The conrotatory electrocyclization is facilitated by irradiation of light (630 nm) or heat, and the reverse process proceeds exposure to light with λ = 365 nm.

[3]Triangulene is next C_3 symmetric non-Kekule hydrocarbon. Little effort was made to synthesize stable [3]triangulene, and only one molecule with triplet ground-state was synthesized: 2,6,10-tri-*tert*-butyltriangulene **162**.[162] Its synthesis was accomplished through a similar approach to **137,** starting from 2-*tert*butylpyrene. The triple ground state was confirmed by ESR spectroscopy. The compound was found to be rater unstable due to “weak” protection which did not prevent **162** to undergo intermolecular polymerization. Interesting, that tri-*tert*-butylated trioxotriangulene shows closed-shell nature due to conjugation with heteroatoms[163].



Scheme 19. Triangulene synthesis.

Pristine [3]triangulene **170** was generated on the surface of Cu(111) and NaCl(100) via dehydrogenation using the tip of a combined scanning tunnelling and atomic force microscope (STM/AFM) from dihydroprecursor **169**[164]. The respective precursor **169** was obtained by modified previously reported procedure [165,166]. Nevertheless, it involved the oxidation of methyl groups, which sometimes can lead to an explosion. Later the facile synthesis of **168** was suggested by Juríček et al., which involved the reaction of dilithium salt of **171** with diethyl carbonate, Jones oxidation of **172** and subsequent Friedel−Crafts acylation of **173**, employing concentrated sulfuric acid as the solvent and copper as a reducing agent. The overall yield in this gram-scale synthesis was 53%, the best known up to date. They also modified the procedure of reduction of 168 to afford highly pure **169**[167].

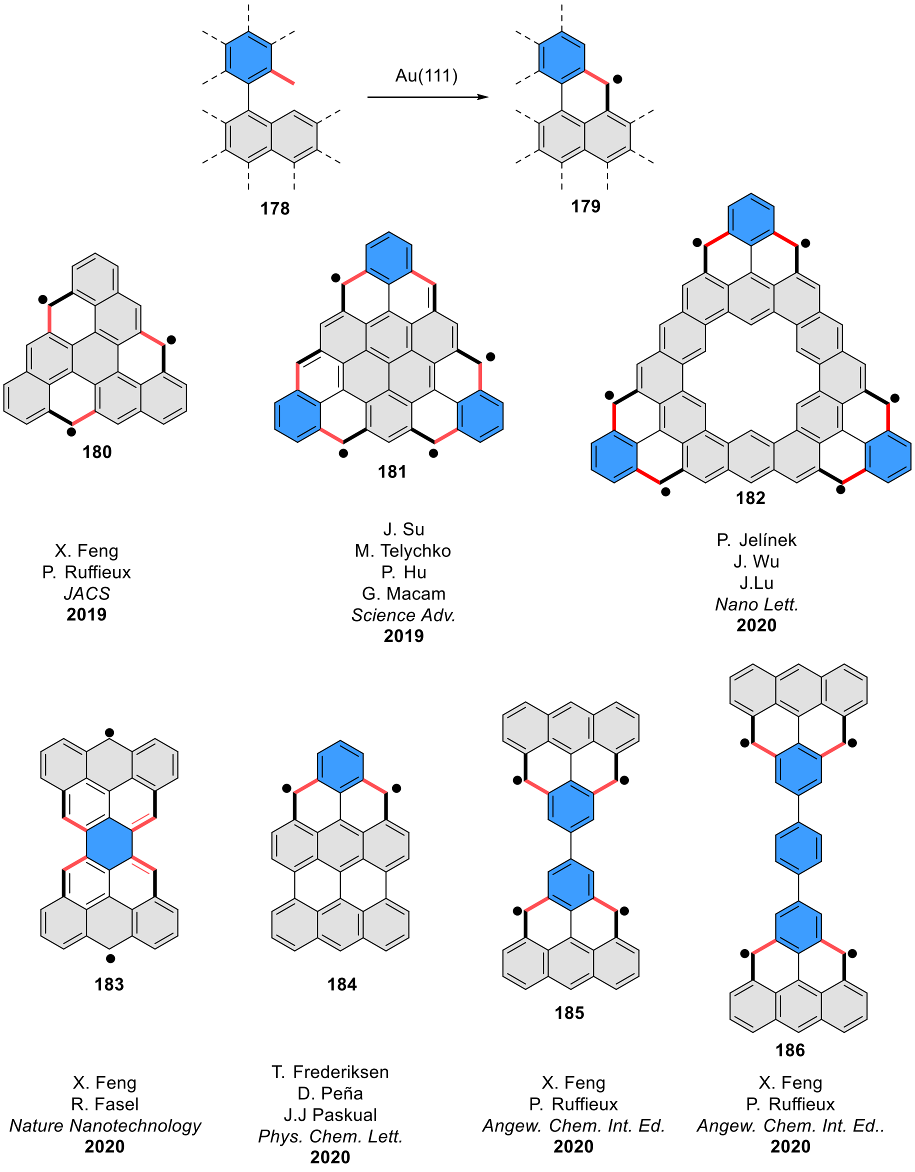


Scheme 20. Synthesis of [3]triangulene.

Johnson et al. described the three-step synthesis of the 4,8,12-trihydro[3]triangulenium cation **177** by cascade cyclization of **176** in triflic acid solution. Quenching the cation by hydride transfer from triethylsilane provides access to stable **169** in 66% yield.

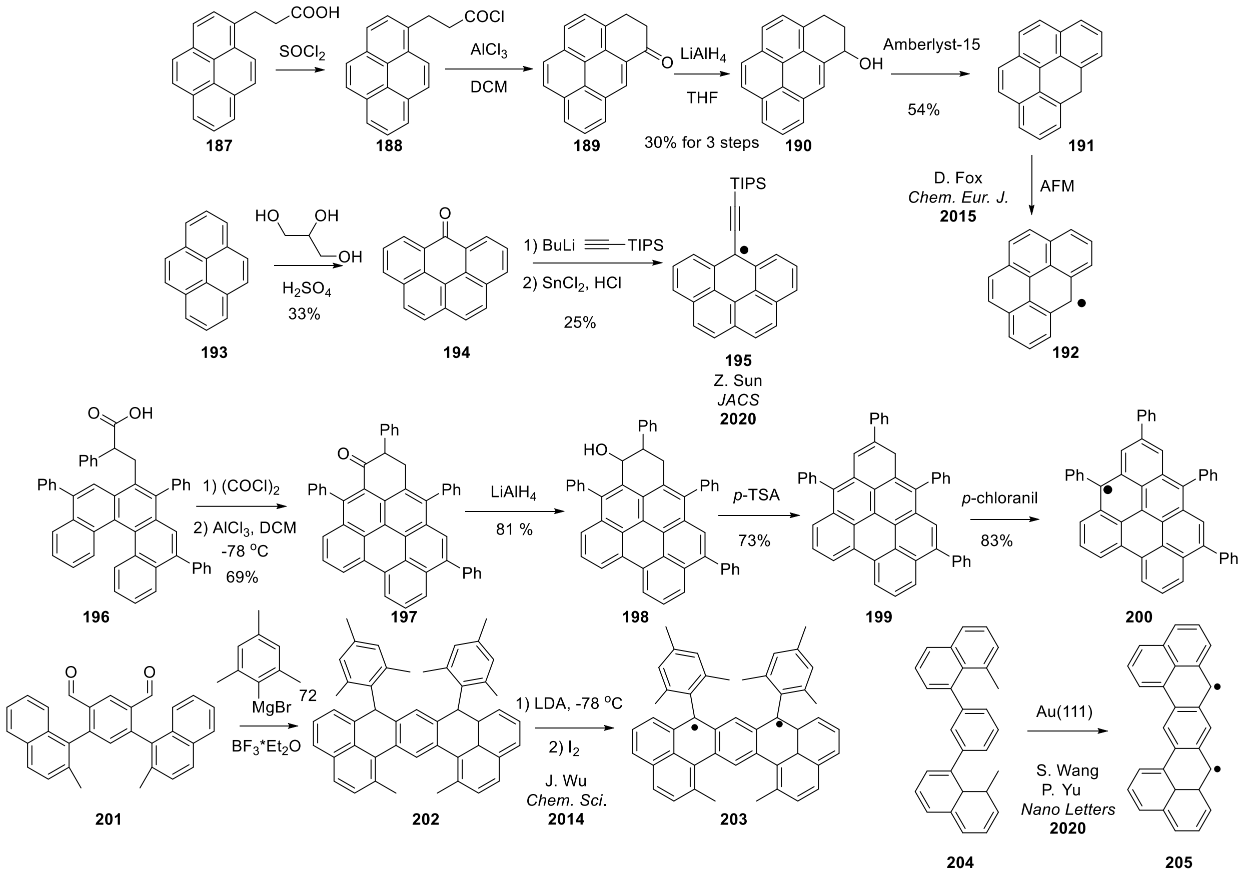
As briefly mentioned in chapter 2.4, oxidative cyclodehydrogenation of the methyl group in the formal cove region is the only reported method for synthesizing the zigzag periphery on the surface of metals. This approach (Scheme 21) was used for the generation of [4]triangulene **180**[168] and [5]triangulene **181**[169]. Wu et al. suggested that it is not essential to have all carbons in triangulene lattice and synthesized [7]triangulene quantum ring **182** on Au (111) surface, which resembles septuple ground-state identical to [7]triangulene[170].

Antiferromagnetic Clar's goblet **183** [171,172] and ferromagnetic graphene flakes 184[173] were also generated by this approach. Feng and Ruffieux et al. showed that [3]triangulene dimers **185** and **186** retain their high-spin magnetic ground states, and can efficiently couple to give rise to collective magnetism[174].



Scheme 21. On-surface synthesis of non-Kekule structures.

Other non-Kekule aromatic hydrocarbons have received much less attention (Scheme 22). Olympicene **192** is one of such examples which was generated for the first time from 6H-benzo[*cd*]pyrene **191** via single-atom molecular manipulation using non-contact atomic force microscopy (NC-AFM)[175]. Synthesis of the precursor **191** was accomplished by standard four steps protocol (formation of acyl chloride, Friedel-crafts acylation, reduction and dehydration) starting from 3-(pyren-1-yl)propanoic acid **187**. Substituted analogue of **195** was synthesized from 6H-benzo[*cd*]pyren-6-one **194** (which can be synthesized by the reaction of pyrene **193** with glycerin in sulfuric acid[176]) via standard two-step procedure: addition of lithium organic compound and subsequent reductive aromatization [177]. The monomeric radical species were found to exist in equilibrium with the π-dimer in the solution similar to dimers observed in the case of phenalenyl radicals.



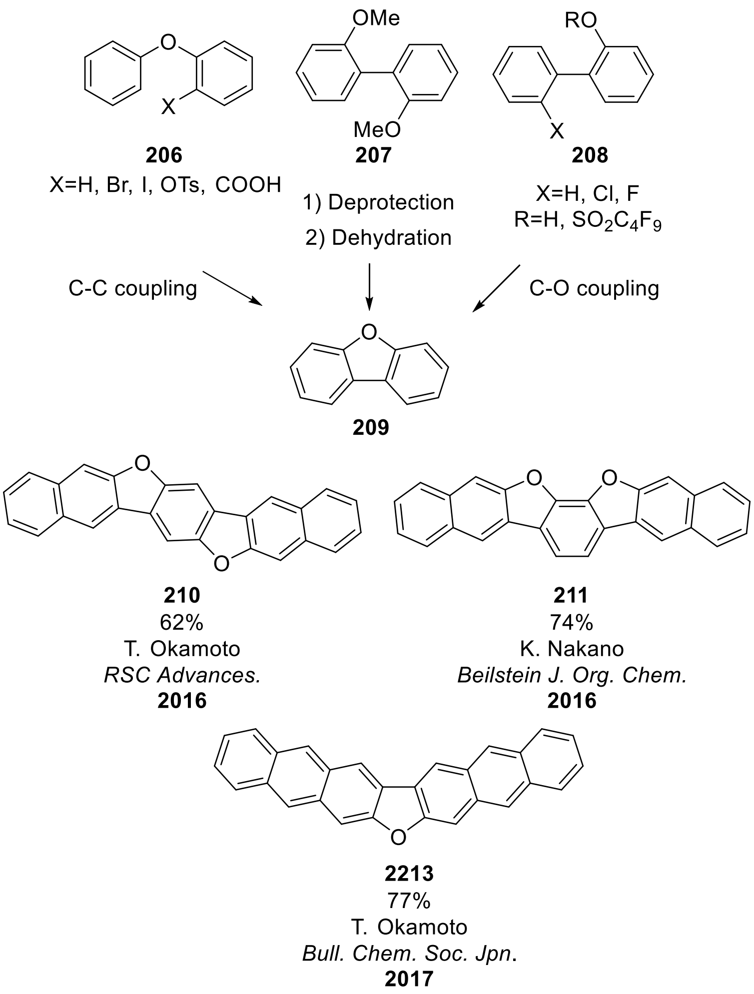
Scheme 22. Synthesis of non-Kekule PAHs.

Juríček et al. reported the synthesis of the homologue of triangulene **200** and showed how spin distribution could be controlled by the edge topology. Compound **200** was synthesized via *peri*-annulation of 5-helicene similar to the synthesizes of **138**[178].

Another interesting family of non-Kekule PAH are uthrenes. Heptrauthrene **205** is a structural isomer of heptazethrene and belong to the non-Kekule polycyclic benzenoid hydrocarbon. Worth mentioning heptrauthrene has triplet ground state in contrast to heptazethrene, which has a singlet biradical ground state. Wu et al. reported the synthesis of substituted derivative **203**, where bulky mesityl groups were introduced to block the most reactive 5,7-positions. Nevertheless, this compound was persistent in solution only below -78 °C under inert atmosphere[179]. The synthesis of **205** was performed on Au (111) surface via cyclodehydrogenation of 1,3-bis(8-methylnaphthalen-1-yl)benzene **204**, and the underscreened Kondo resonance unambiguously confirmed its triplet ground state.[179]

2.8. O-heteroacenes.

First reports of the application of heterocyclic compounds in material science appeared in 1980-s when poly(thiophene)s were used as semiconducting compounds[180]. Further development of fabrication techniques has shown superior device performance of poly(thiophene)s based devices. As mentioned in chapter 2.2, acenes are also eventually become the models for organic semiconductors. Thus it appears to be a natural consequence of combining the thiophene rings with the acene structures. The respective ladder-type sulfur-containing π -conjugated molecules take advantages from both classes displaying remarkable stability and effective π- π stacking in the solid state.

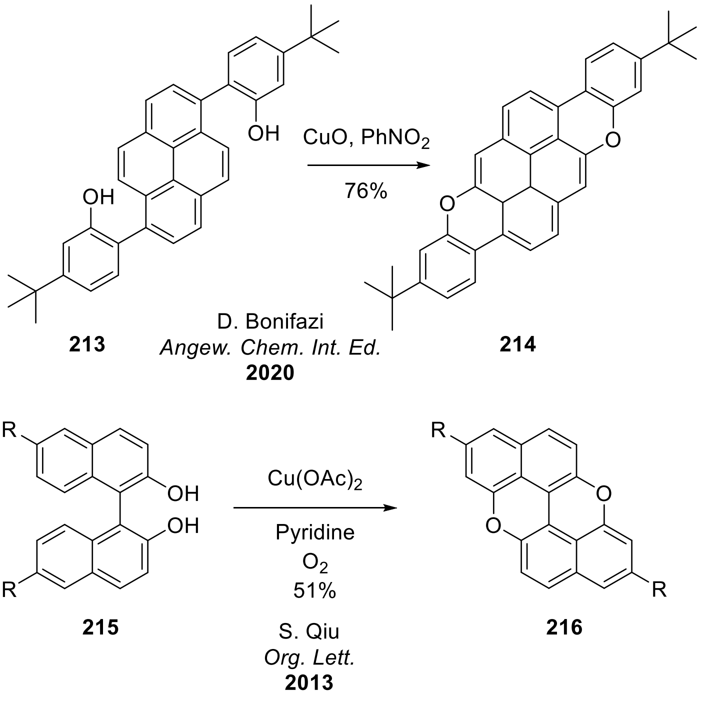


Scheme 23. Synthesis of O-heteroacenes with furan rings.

This idea led to the splash of the implementation of different sulfur-containing compounds[9,10,181,182]. Interesting, their oxygen counterparts have drawn much less attention and became an object of interest only recently partly due to the lability of most simple oxygen derivatives, especially furans[183].

Dibenzo[*b,d*]furan **209** is the simplest stable model of O-heteroacenes, which frequently is utilized as a standard model compound for introducing synthetic approaches towards O-heteroacenes. Despite many works aimed to develop facile incorporation of the furan ring, the principal synthetic strategies are not so numerous and break down into few categories (Scheme 23). The final step includes either transition metal-catalyzed C-C coupling from substituted diphenyl ethers **206**[184–188] or C-O bond creation from 2,2-disubstituted biphenyls **207-208**, [189–198] which is usually implemented via a two-step deprotection/dehydration procedure. [199–204]. The most notable examples of furan-containing O-heteroacenes are dinaphtho[2,3-d:2',3'- d']benzo[1,2-b:4,5-b']difuran **218**, dinaphtho[2,3-d:2',3'- d']benzo[2,1-b:3,4-b']difuran **211**, dianthra[2,3-b:2',3'-d]furan **212** with mobility up to 1.8, 0.1, and 1.2 cm^{2}V^{-1}s$^-$ respectively.

Interesting that most synthetic approaches to dibenzofuran core require an oxygen atom in the precursor's structure and only recently the method with an external oxygen source was described by Akhmetov et al. utilizing alumina-promoted oxodefluorination[205].



D. Bonifazi
Angew. Chem. Int. Ed.
2020

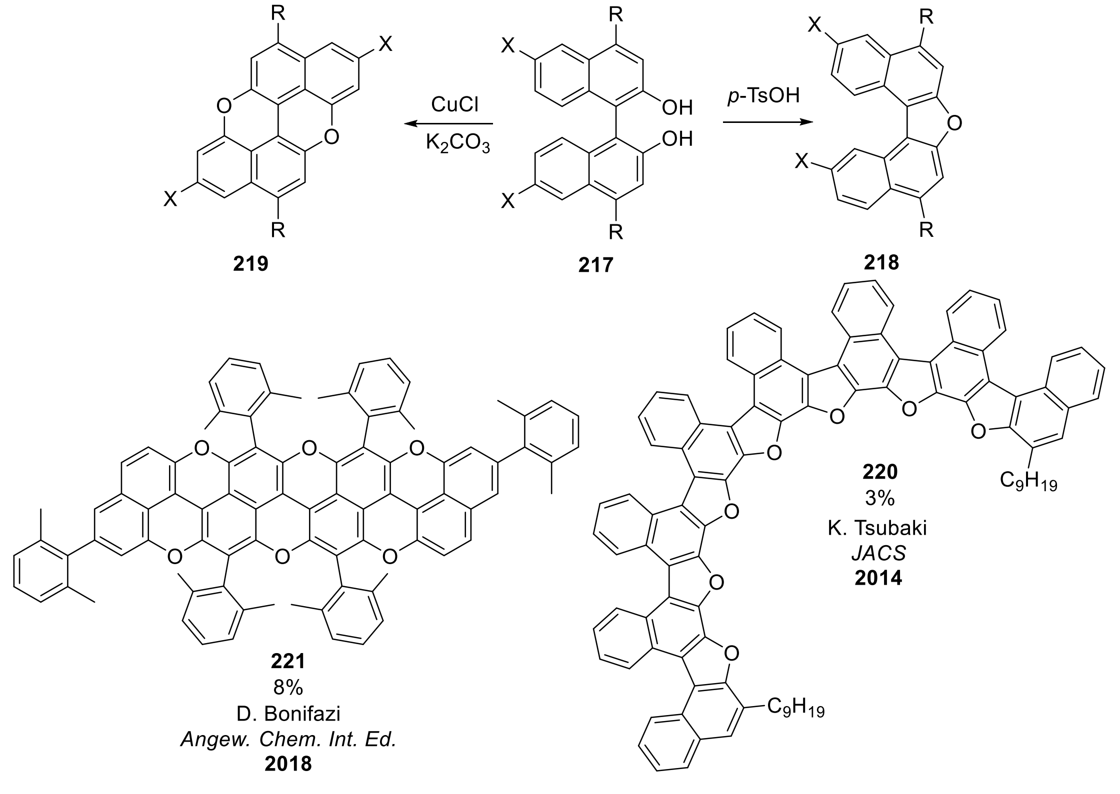
S. Qiu
Org. Lett.
2013

Scheme 24. Synthesis pyranyl O-heteroacenes via Pummerer reaction.

Syntheses of conjugated 6-member rings are even scarcer (Scheme 24). The most convenient method for introducing pyrane ring into the acene moiety is Pummerer reaction[206]. Bonifazi et al. eventually developed methods of syntheses of O-doped nanographenes[207,208] derived from the π-extension of pyrene (for example, oxygen analogue of DBATT **214**). These molecules have low oxidation potential, allowing growing crystals of cationic mixed-valence complexes with remarkably high conductivity at room temperature.

Another example of a privileged O-heteroacene is *peri*-xanthenoxanthene **216**, which derivatives have an immense amount of applications[209–213]. Such advances became possible due to the pretty easy synthesis of 216 from 6,6’ disubstituted 1,1′-bi-2-naphthol **215** using copper salts as oxidants[214,215].

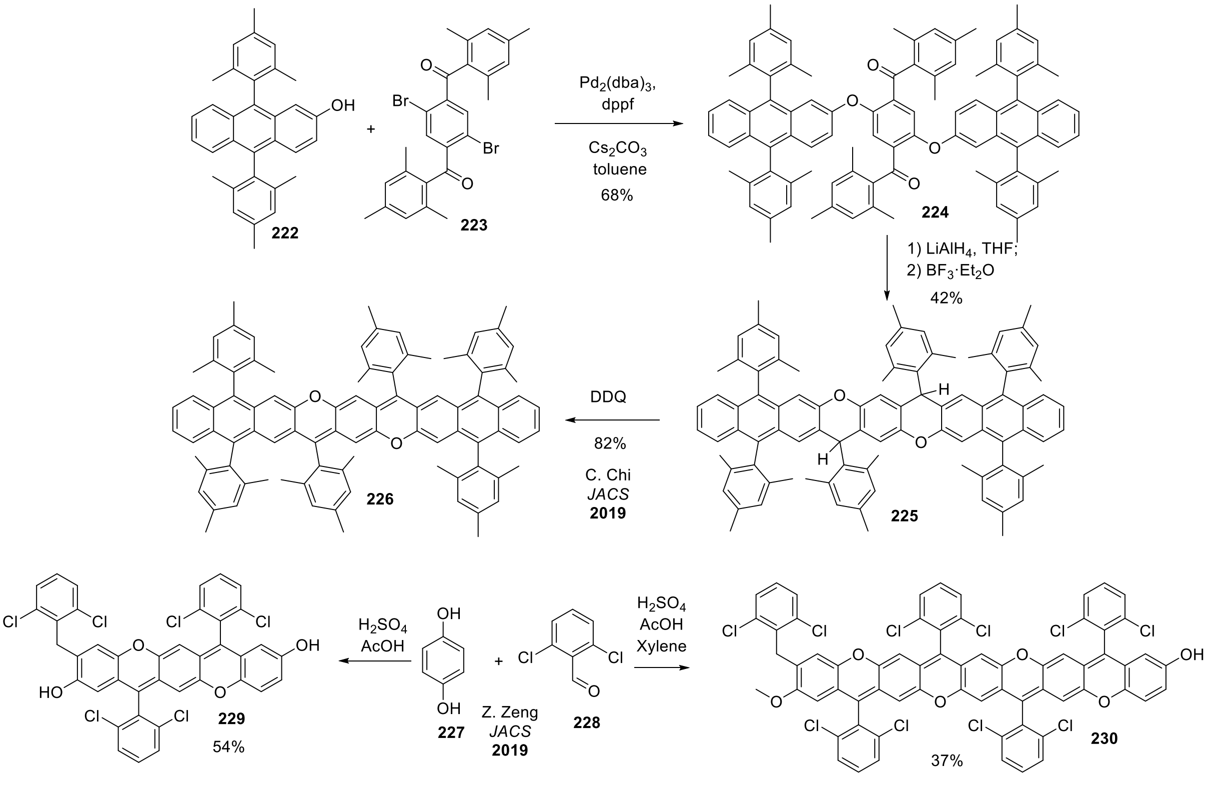
Interestingly, starting from the substituted 1,1′-bi-2-naphthols **217,** both dinaphtylfurans **218** and *peri*-xanthenoxanthenes **219** can be synthesized (Scheme 25)[190]. Step-by-step growth of small blocks (via oxidative coupling of arenols) allows synthesizing fan-shaped oligonaphthofurans **220** [195] oxygen-doped zigzag molecular ribbons **221** [216,217]



Scheme 25. The fusion of PAHs through furanyl (left) and pyranopyranyl (right) cyclization strategies.

All mentioned efforts have been intensively exerted toward the PAHs, in which oxygen atoms usually strengthen their electron-donor character and display short-absorption wavelengths. In the contrast, O-annulated quinoidal structures **226**, **229** and **230**[218,219] exhibit highly red-shifted absorptions (up to ∼699 nm) and narrowed energy gaps (down to ∼1.5 eV) (Scheme

26). **226** was synthesized in the three-step procedure, whereas oxygen was incorporated through palladium-catalyzed C-O coupling between **222** and **223**, and quinoidal stricture was constructed similar to the syntheses of 2D acenes. **229** and **230**, in contrast, were prepared in one-pot condensation of hydroquinone **227** and 2,6-dichlorobenzaldehyde **228**. In **227**, the α-positions are nucleophilic and subjected to electrophilic attack. In strongly acidic conditions, protonation of the carbonyl carbon at **228** or intermediate of diphenylmethanol derivatives generates highly electrophilic hydroxymethylium, which successively reacts with **227** through a Friedel−Crafts-type reaction. The ring closure step is furthermore promoted with acid catalysis. The phenolic molecule with an enlarged size actively participates in stabilizing the generated charge and attacks in the α-position to form an extended structure, which subsequently converts into quinoidal pentacene with increased conjugation. In order to afford **230** xylene was used as a high boiling point solvent order to increase the temperature of the reaction and promote further condensation.



Scheme 26. Synthesis of O-annulated quinoidal structures

■

3. Proposal

This work is oriented on the development of the synthesis of pristine 2D acenes with zigzag edges. Until recently, these compounds were investigated only in the form of their substituted derivatives, which from one side, increases solubility and processability, but on the other hand, lead to the significant downgrade in performance in such areas as single-molecule spectroscopy. The synthesis of pristine 2D acenes was mainly founded and investigated by E. Clar in the middle of the 20th century, whereas the when the lack and low sensitivity of analytical techniques did not show the reasonable amount of impurities. Until recently, organic synthesis of pristine 2-D acenes could barely meet the characteristics dictated by physical experiments, such as purity, scale, and simplicity of the procedure.

It is also essential to have a similar approach towards the wide range of different 2-D acenes because it can simplify the understanding of the subsequent structure–property relationships. It is also crucial to investigate the synthesized compounds from the theoretical perspective to find correlations between calculations and experiment and build some predictive theories (Publications 1 and 2).

The developed method allowed the synthesis of molecules with high diradical character. These molecules tend to undergo uncontrollable oligomerization in solution. This reaction was always considered as a parasitic process and did not convert in something useful. However, if the radicals are localized in the “right” places, this tendency can be used to promote intramolecular processes in a domino manner. Using Clar model, we aimed to design the precursor and predict the outcome of this cascade reaction. (Publication 3).

Incorporation of oxygen into the zigzag periphery is the least developed area of heterocycle synthesis. Also, no reliable outer oxygen source was known for the formation of oxygen periphery. We endeavour to find this kind of source and use it for the multiply annulation of different size of oxygen cycles on the last step of the synthesis, which can be used to synthesize big carbon nanostructures. (Publication 4).

4. Index of publications.

Publication 1.

Dehydrative π-extension to nanographenes with zigzag edges.

Dominik Lungerich, Olena Papaianina, **Mikhail Feofanov**, Jia Liu, Mirunalini Devarajulu, Sergey I. Troyanov, Sabine Maier & Konstantin Amsharov*, Nat. Commun., **2018**, 9**,** 4756.

Konstantin Amsharov and Dominik Lungerich conceived the concept of the project. Dominik Lungerich, **Mikhail Feofanov**, and Olena Papaianina carried out the experiments and prepared supporting information. Sergey Troyanov performed X-ray crystal structure analysis. Jia Liu, Mirunalini Devarajulu, and Sabine Maier conducted the structure determination by low-temperature STM. Dominik Lungerich conducted the computations. Dominik Lungerich and Konstantin Amsharov prepared the manuscript with feedback from others.

Publication 2.

Modular Approach to the Synthesis of Two-Dimensional Angular Fused Acenes.

Mikhail Feofanov,* Vladimir Akhmetov, Dmitry I. Sharapa, and Konstantin Amsharov*, Org. Lett., **2020**, 22, 1698−1702.

Mikhail Feofanov and Konstantin Amsharov conceived the concept of the project. **Mikhail Feofanov** and Vladimir Akhmetov carried out the experiments. **Mikhail Feofanov** prepared the supporting information. Dmitry I. Sharapa conducted the computations. All authors contributed to the preparation of the manuscript.

Publication 3.

Oxidative Electrocyclization of Diradicaloids: C−C Bonds for Free or How to Use Biradical Character for π-Extension.

Mikhail Feofanov,* Vladimir Akhmetov, Dmitry I. Sharapa, and Konstantin Amsharov*, Org. Lett., **2020**, 22, 5741−5745.

Mikhail Feofanov and Konstantin Amsharov conceived the concept of the project. **Mikhail Feofanov** and Vladimir Akhmetov carried out the experiments. **Mikhail Feofanov** prepared the supporting information. Dmitry I. Sharapa conducted the computations. All authors contributed to the preparation of the manuscript.

Publication 4.

Catalyst-Free Synthesis of O-Heteroacenes via Ladderization of Fluorinated Oligophenylenes.

Mikhail Feofanov,* Vladimir Akhmetov, Ryo Takayama, and Konstantin Amsharov*, Angew. Chem. Int. Ed., **2020**, accepted. Doi: 10.1002/anie.202007427. First published online on 13th of September, 2020.

Konstantin Amsharov conceived this work. **Mikhail Feofanov**, Vladimir Akhmetov and Ryo Takayama performed the experiments. **Mikhail Feofanov** analyzed the data and prepared supporting information. **Mikhail Feofanov** and Konstantin Amsharov wrote the manuscript with input from Vladimir Akhmetov and Ryo Takayama.

5. Results and discussions.

This chapter will cover our successful modular approach to obtain pristine 2D angular fused acenes. It will also be shown how the generation of structures with high diradical character can be used for the subsequent in situ π-extension. Moreover, the new method of synthesizing O-heteroacenes from fluorinated oligopheylenes using external oxygen source will be described.

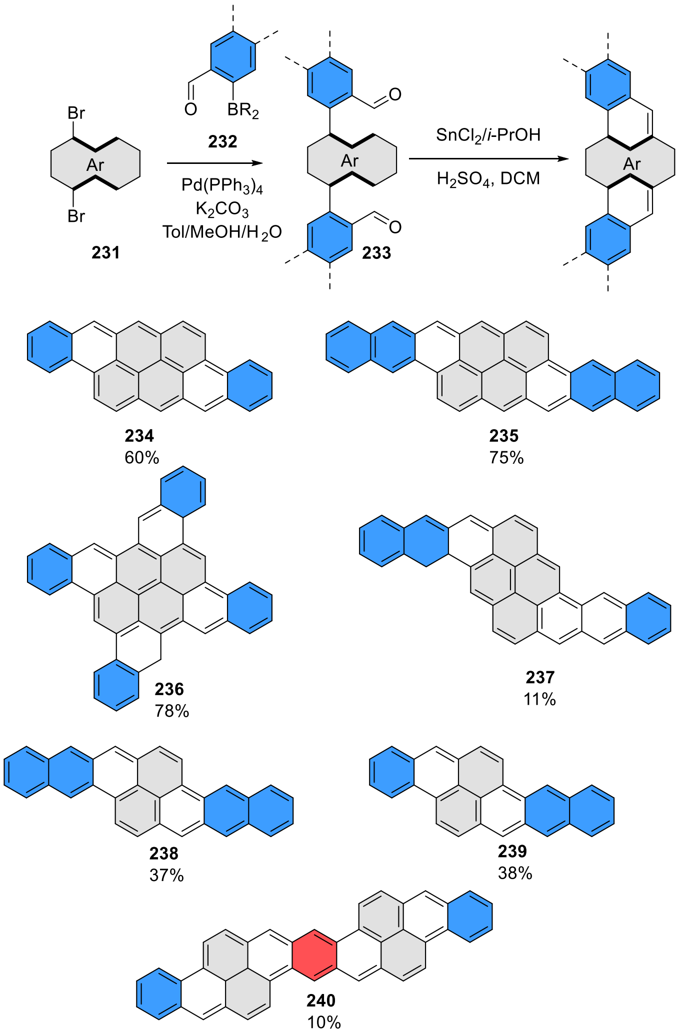
5.1. Modular approach in the synthesis of pristine 2D angular fused acenes.

As discussed in the introduction, only a few syntheses of PAHs with zigzag edges are described in the literature. The overwhelming majority of the zigzag periphery formation methods are based on the Friedel-Crafts reaction and Diels-Alder addition. Synthesis of acenes by the reduction of ketones afforded after Friedel-Crafts reaction was essentially founded and investigated by E. Clar in the middle of the 20th century[220]. Nevertheless, development of analytical techniques has shown that his methods are not suitable for synthesizing a substantial share of PAHs, especially 2D acenes, as they contain considerable amounts of contaminants. Repetition of Clar's route of synthesis of DBATT **234** [221,222] yielded it only in trace amounts of pure product, which required intensive purification procedures. To our knowledge, before this work, organic synthesis of pristine 2-D acenes could barely meet the characteristics dictated by physical experiments, such as purity, scale, and simplicity of the procedure.

In Publications 1 and Publication 2, we report a very successful two-step modular approach to synthesizing two-dimensional acenes. The approach consists of Suzuki coupling of building blocks (dihalogenarenes and formylareneboronic acids) and a new attractive technique, called DPEX (a dehydrative π-extension). This reaction is acid promoted reductive intramolecular cyclization of the aromatic aldehydes, which yields directly in the pristine zigzag periphery. The critical success of DPEX reaction is that low solubility of acenes benefitted to the isolation of pure samples of compounds since only soluble by-products form during the reaction.

On the scheme, we show the modular approach with the most notable synthesized PAHs. The technique allows synthesizing not only known compounds such as **234** in gram scale but also previously unknown nanographenes bearing zigzag edges (for example, **235**-**237**). Also, this method allows to synthesize asymmetrical molecules such as **239** and, in such a manner, remarkably extends the number of possible structures. Utilizing of so-called “block splitter”, 1,4-dibromoterephtaldehyde between the moieties allows a simple prolongation of the acene-like structures, avoiding virtually any foreseeable end. Therefore, we demonstrated 4-fold cyclization yielding the longest known pristine fused acene dianthra[2,1,9-jkl:2′,1′,9′-uva]pentacene **240**, which was found to be surprisingly stable in solution.

Comparison of DFT calculated of HOMO− LUMO levels with experimentally obtained data shows good compatibility. Also, surprisingly, the UV-Vis spectrum can instantly give the idea of the degree of diradical character.



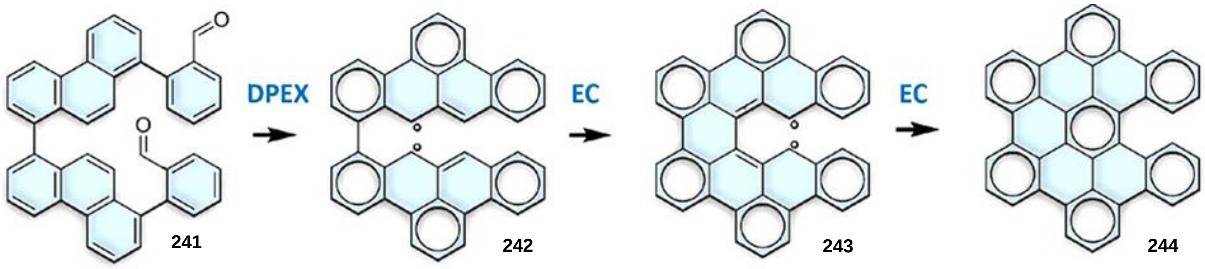
Scheme 27. The modular approach to pristine 2D angular fused acenes.

5.2.Oxidative electrocyclization of diradicaloids.

The developed DPEX reaction allowed us to synthesize PAHs with high diradical character (for example, **235**), which tend to undergo oligomerization in the solution if the radical centres are not blocked with bulky substituents. Since typical publications with such molecules often focus on the physical properties of them, no one considers taking control under this reactivity and using it for the π-extension.

In publication 3, it is shown that if the radicals are localized in the “right” places, they can undergo thermal 6π-electrocyclization at room temperature. In the case of unactivated hexatrienes extremely high temperatures or photochemical activation are required for successful transformation. However, low HOMO−LUMO gaps of open-shell molecules result in the partial occupation of HOMO and LUMO in the ground state and allow the electrocyclization to proceed by photochemical pathway but without the presence of light.

Domino reaction of DPEX and oxidative electrocyclization opens a path to violanthrenes and π-extended 5-helicenes unavailable via alternative methods. The favoured placement of radicals crucial for successful EC can be evaluated by using the Clar model, which can also explain the reaction’s outcome.



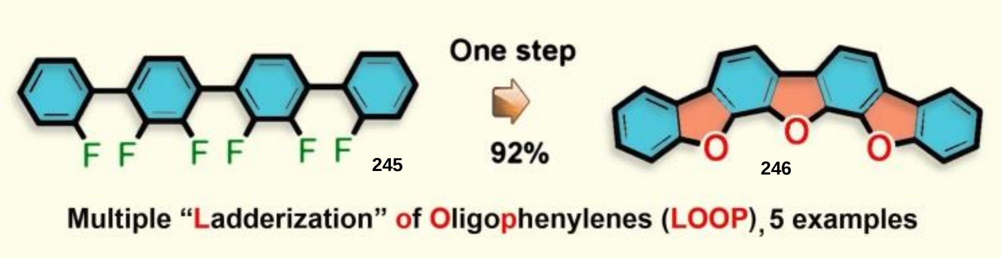
Scheme 26. Synthesis of tetrabenzobisanthrene (TBBA) via domino reaction consisting of DPEX and two oxidative electrocyclizations.

5.3. Synthesis of O-Heteroacenes.

The incorporation of heteroatoms into the carbon skeleton is an excellent tool to adjust and improve the compounds’ electronic properties. In contrast to other PAHs containing abundant heteroatoms (nitrogen and sulfur), oxygen heteroacenes got the least attention in recent years. This is mostly connected to difficult synthetic approaches. To our surprise, almost all existing synthetic approaches to the O-heteroacenes require an oxygen atom in the precursor’s structure.

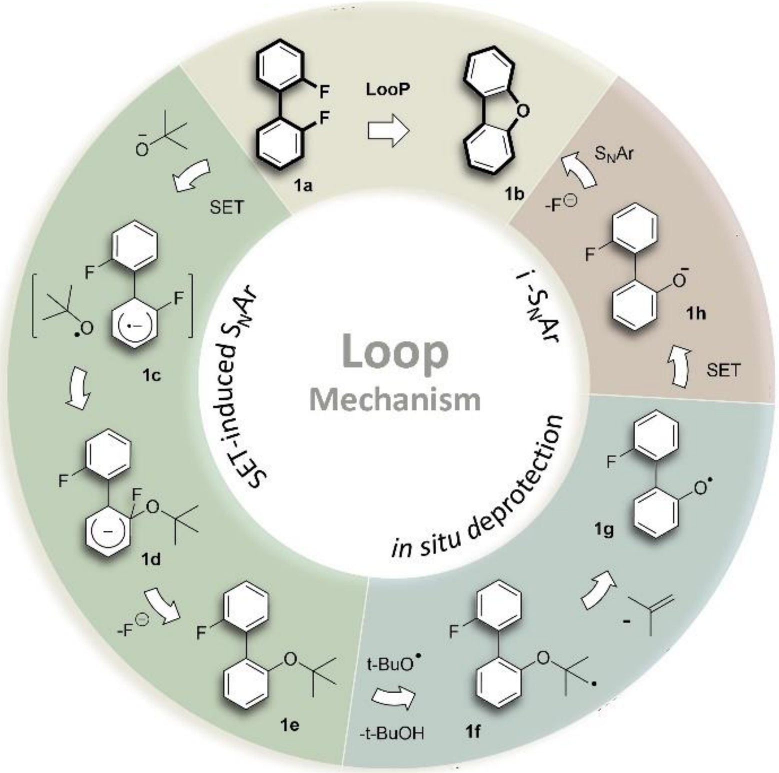
In publication 4 we report a new catalyst-free approach to a wide range of O-heteroacenes via “ladderization” of fluorinated oligophenylenes (**LooP**).

According to our screenings of the transformation of 2,2'-difluoro-1,1'-biphenyl with different oxygen sources, *t*-BuOK was chosen as an optimal one. It can convert two fluorines into oxygen and form five-, six- and even 7-member rings in high yields. Also, the most critical aspect of this transformation is the possibility to perform multiply annulations in one step. We show it on five examples, and in the synthesis of heteroacene **246**, six bonds were formed eventually. Also, fluorinated *meta*-oligophenylenes transform into dibenzofuran oligomers instead of a mixture of products.



Scheme 27. Synthesis of oxygen heteroacenes in from oligophenylenes.

From the mechanistic perspective, the reaction can be formally broken down into three steps: substitution, deprotection, and second substitution. After thorough literature research and experimental mechanistic investigations, we concluded that the mechanism of the first step at least partially involves SET-induced aromatic nucleophilic substitution and the deprotection proceeds via the radical pathway. All these unique steps were able to proceed thanks to the key feature of *t*-BuOK: ability to induce SET in such solvents as HMPA.



Scheme 28. The suggested mechanism of LooP.

6. Publications

Publication 1.

Dehydrative π-extension to nanographenes with zigzag edges.

Dominik Lungerich, Olena Papaianina, **Mikhail Feofanov**, Jia Liu, Mirunalini Devarajulu, Sergey I. Troyanov, Sabine Maier & Konstantin Amsharov*, Nat. Commun., **2018**, 9**,** 4756.

Abstract:

Zig-zag nanographenes are promising candidates for the applications in organic electronics due to the electronic properties induced by their periphery. However, the synthetic access to these compounds remains virtually unexplored. There is a lack in efficient and mild strategies origins in the reduced stability, increased reactivity, and low solubility of these compounds. Herein we report a facile access to pristine zigzag nanographenes, utilizing an acid-promoted intramolecular reductive cyclization of arylaldehydes, and demonstrate a three-step route to nanographenes constituted of angularly fused tetracenes or pentacenes. The mild conditions are scalable to gram quantities and give insoluble nanostructures in close to quantitative yields. The strategy allows the synthesis of elusive low bandgap nanographenes, with values as low as 1.62 eV. Compared to their linear homologues, the structures have an increased stability in the solid-state, even though computational analyses show distinct diradical character. The structures were confirmed by X–ray diffraction or scanning tunneling microscopy.

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Dehydrative π-extension to nanographenes with zig-zag edges

Dominik Lungerich[1,2], Olena Papaianina[1], Mikhail Feofanov[1], Jia Liu[3], Mirunalini Devarajulu[3], Sergey I. Troyanov[4], Sabine Maier[3] & Konstantin Amsharov[1]

Zig-zag nanographenes are promising candidates for the applications in organic electronics due to the electronic properties induced by their periphery. However, the synthetic access to these compounds remains virtually unexplored. There is a lack in efficient and mild strategies origins in the reduced stability, increased reactivity, and low solubility of these compounds. Herein we report a facile access to pristine zig-zag nanographenes, utilizing an acid-promoted intramolecular reductive cyclization of arylaldehydes, and demonstrate a three-step route to nanographenes constituted of angularly fused tetracenes or pentacenes. The mild conditions are scalable to gram quantities and give insoluble nanostructures in close to quantitative yields. The strategy allows the synthesis of elusive low bandgap nanographenes, with values as low as 1.62 eV. Compared to their linear homologues, the structures have an increased stability in the solid-state, even though computational analyses show distinct diradical character. The structures were confirmed by X-ray diffraction or scanning tunneling microscopy.

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he chemistry of polycyclic aromatic hydrocarbons (PAHs), essentially founded by E. Clar in the middle of the 20th century[1], is nowadays flourishing more than ever in form of structurally precise carbon nanostructures[2,3]. Driven by the vast potential in next generation technologies[4–6], and accelerated by the continuous development of synthetic methodologies[7–12], the field of PAHs and nanographenes (NGs) remains intensively studied by researchers from the physical sciences. The high interest origins in the fact that the physical and chemical properties of the hydrocarbons are directly related to their size, shape, and especially edge topology (Fig. 1a)[13]. In that respect, PAHs with zig-zag periphery are especially interesting, because they show typically higher charge carrier mobilities than compounds with an armchair periphery. Further, they exhibit strong absorptions in the visible region as a result of a decreased highest occupied molecular orbital–lowest unoccupied molecular orbital gap (HOMO-LUMO gap; HLG)[14,15]. As a consequence, significant contributions from open-shell resonances in the ground state are frequently observed[16]. Keywords that highlight acene-type PAHs with zig-zag periphery range from singlet fission[17–21], auspicious charge carrier mobilities[22,23], to amplified spontaneous emission[24], and enlarge the interest in PAHs by the fields of spintronics and molecular magnetism[25-27]. Recently, various research groups reported on substituted angularly fused-tetracenes[28–32], which overcome the low stability of linear acenes, by increasing the intrinsic number of Clar's-sextets[33]. These fused structures showed excellent performances in field-effect transistors[28,29,31,32]. Among these slipped bis-tetracenes, a significant focus was set on derivatives of the 2.3,8.9-dibenzanthanthrene (**DBATT**) aromatic carbon skeleton. Earlier, **DBATT** was already revealed as a probe for the Shpol'skii effect[34–36], it was used as single molecule optical transistor[37], or as solid-state single-quantum emitter[38]. Interestingly, even though this molecule was known since the early explorations of E. Clar in the 1940s, to date its structure has been assigned only by chemical rational and UV/Vis spectroscopy[39,40]. However, repetition of Clar's route in our own laboratories yielded **DBATT** only in trace amounts and required intensive purification procedures.

Herein, we report on the preparation and investigation of π-extended molecules based on the **DBATT** carbon skeleton. We developed a facile three-step synthesis, which utilizes an acid-promoted reductive intramolecular cyclization of aromatic aldehydes – a dehydrative π-extension (DPEX) reaction – as key transformation. Our DPEX protocol allows the synthesis of **DBATT** in highly pure form in close to quantitative yield. Importantly, DPEX is suitable for the preparation of pristine zig-zag edges, without the need of bulky or electronically stabilizing substituents, which preserves and allows to study the true nature of the zig-zag nanographenes (zzNGs). Finally, the power of DPEX is demonstrated by the preparation of the π-extended and unprecedented homologues, fused tetrakis-tetracene (**TTc**), slipped bis-pentacene (**BPc**), and fused tetrakis-pentacene (**TPc**); pushing the boundaries of the bottom-up preparation of zzNGs (Fig. 1b).

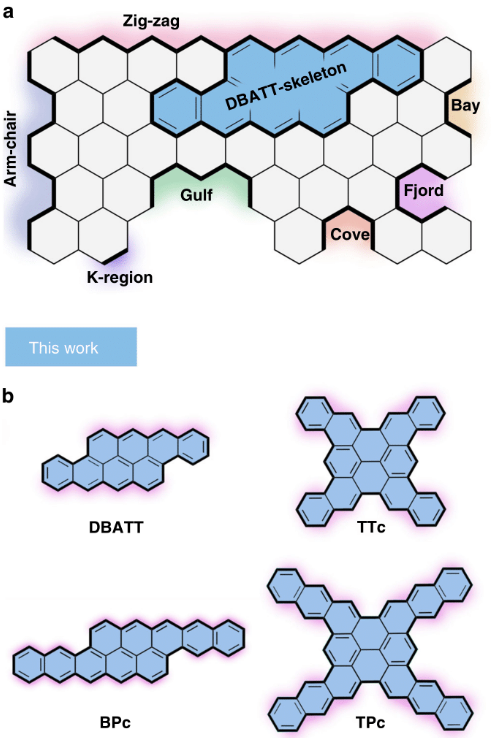

Fig. 1 Relevant terminologies and overview of this work. **a** Nomenclature and schematic depiction of relevant edge structures; **b** Herein enabled zig-zag NGs by the DPEX reaction

Results

Synthesis of nanographenes by DPEX. In the case of **DBATT** and its derivatives, pyrene was brominated with bromine in chloroform, yielding 1,6-dibromopyrene **1** on a decagram scale, which was purified by a single recrystallization step from xylenes (see Supplementary Methods)[41,42]. Two-fold Suzuki-Miyaura coupling of **1** with 2-formylphenylboronic acid **2** gave the diarylated pyrene precursors, 1,6-bis(2-formylphenyl)pyrene **3**, which was obtained in pure form and good yields after silica gel plug filtration and precipitation with hexanes from dichloromethane. The preparation of **BPc**-precursor **4**, was achieved analogously by the coupling with 3-formylnaphthalene-2-boronic acid pinacol ester **5**, which was obtained in three steps from 1,2,4,5-tetrabromobenzene (see Supplementary Methods). As proof of principle, regioselective 3,8-functionalization of **3** could be easily achieved by bromination to **6** which can be either directly condensed to dibromo DBATT (**bBr-DBATT**) via DPEX (see Supplementary Methods) or converted to the respective aryl derivative by Suzuki-Miyaura coupling with e.g., phenylboronic acid to **3a**, yielding respective diaryl **DBATT**s (see also compound **16** and pyridinyl substituted compound **S5**). This route avoids the earlier reported formation of non-selective 1,2 and 1,4-Michael addition products[30,43]. For small scale brominations, the 1:2 hexamethylentetramine-bromine complex (HMTAB) was found to be particularly useful, however not mandatory for the selective bromination[44]. Starting from 1,3,6,8-tetrabromopyrene **7**, four-fold-substituted pyrenes **8** and **9** were obtained in equal manner. An overview on the synthetic scheme is shown in Fig. 2. Precursors **3**, **3a**, **4**, **8**, and **9** were subjected to the elaborated DPEX conditions (vide infra, see also Supplementary Table 1), giving the target NGs in close to quantitative yield, without any sign of side-product formation, as determined by HPLC and MS. Supplementary Table 2 shows all synthesized precursors and Supplementary Table 3 shows all nanographenes accessed by

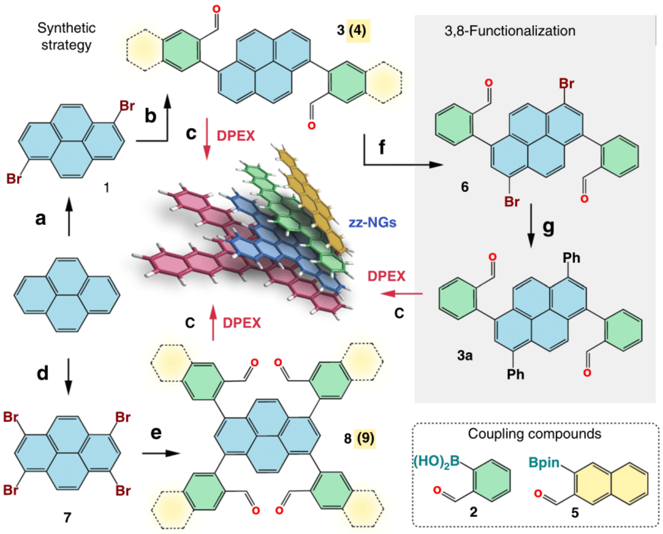

Fig. 2 Synthesis of zig-zag NGs. **a** $CHCl_3$, Br_2; **b** 2:1 toluene/MeOH, 2.5% $Pd(PPh_3)_4$, K_2CO_3, 80 °C, N_2 (3: 61%, 4: 65%); **c** DPEX: CH_2Cl_2, 2 vol% sat. $SnCl_2$•$2H_2O$/*i*-PrOH, 1 vol% conc. H_2SO_4, rt, (quant.); **d** nitrobenzene, Br_2; **e** 2:1 toluene/MeOH, 4% $Pd(PPh_3)_4$, K_2CO_3, 80 °C, N_2 (8: 81 %, 9: 91 %); **f** CH_2Cl_2, 1.6 equiv. HMTAB, rt (quant.); **g** 2:1 toluene/MeOH, 2.5 % $Pd(PPh_3)_4$, K_2CO_3, 80 °C, N_2 (**3a**: 66 % with phenylboronic acid); HMTAB: 1:2 hexamethylentetramine-bromine complex

DPEX (**DBATT**, **bPh-DBATT**, **bBr-DBATT**, **TTc**, **BPc**, **TPc**, **11**, **13**, **17**, and **S7**). Even though DPEX takes place already in neat H_2SO_4 in moderate yields (see Supplementary Table 1), the best possible conditions were first refined by the conversion of **3** to **DBATT** on an analytical scale. The reaction outcome was followed by quantitative HPLC analysis.

3 and the other nanographene precursors show relatively good solubility in CH_2Cl_2 and THF compared to other tested solvents like e.g., hexanes, toluene, and ethyl acetate, which subsequently determined the tested reaction media for the DPEX reaction. However, only CH_2Cl_2 as solvent provides the best reaction outcome. As reducing agent, we focused on common $SnCl_2$•$2H_2O$. The addition of 2 vol% of a saturated solution of $SnCl_2$•$2H_2O$, dissolved in iso-propanol is superior over all other investigated reduction systems. Interestingly, using methanol instead, which dissolves $SnCl_2$•$2H_2O$ by far better than iso-propanol, the conversion appears to be faster, however the reaction is accompanied by the formation of unidentified side products. Although the side products are formed in trace amounts, as indicated by HPLC analysis, further post synthetic purification appears to be difficult due to the low solubility. On the other hand, the addition of iso-propanol significantly slows down the conversion but remarkably improves the selectivity and the reaction outcome; used as mere solvent however, the reaction is inhibited completely. The addition of 1 vol% conc. H_2SO_4 initiates the reaction, which is indicated (in case of **3** and **3a**) by a rapid purple coloration of the mixture, accompanied by the formation of a white precipitate. Supplementary Fig. 1 shows a pictured illustration of the single reaction steps. Hereby, the empiric ratio of 2:1 of the $SnCl_2$/*i*-PrOH–solution and the H_2SO_4 plays a crucial role for a successful outcome. After work-up with aqueous hydrochloric acid and extraction, the product is precipitated with MeOH, which gives pure **DBATT** in close to quantitative yields. The usage of stronger acids like e.g., trifluoromethanesulfonic acid (TfOH), or 34% oleum shows good performances, however significantly worse than conc. H_2SO_4. On the other hand, weaker acids like e.g., trifluoroacetic acid (HTFA) and acetic acid, show no conversion at all. As mentioned above, reactions carried out in neat H_2SO_4 and thus lacking a reducing agent were found to give **DBATT** in moderate yields. Since the required two-electron reduction process cannot stem from H_2SO_4, we surmise a disproportionation reaction between two intermediate molecules, leading to **DBATT** and oxidized derivatives. This assumption is further supported by the fact that the yields of **DBATT** decreased upon lowering the concentration of **3** and never exceeded yields of 50%. Further details can be extracted from Supplementary Table 1.

With respect to the scope of the DPEX protocol, the reactivity is demonstrated using the less reactive naphthalene core as the central aromatic unit. The respective precursor molecules **10** and **12** are obtained from 1,4-dibromonaphthalene and 1,5-diiodonaphthalene by standard two-fold Suzuki-Miyaura coupling reactions (see Supplementary Methods). Despite the lower activity of the naphthalene core, the DPEX cyclization results the desired benzo[*rst*]pentaphene **11** and dibenzo[*b,def*]chrysene **13** in moderate yields (Fig. 3a). Interestingly, in both cases the cyclisation is only successful in the presence of $SnCl_2$, indicating that $SnCl_2$ plays a crucial role in the DPEX process and participates already in the first reaction step. Thus, the mechanism of DPEX appears to be more complex than the intuitively assumed two-step domino reaction. This is also supported by the lack in formation of undesired pentagons under DPEX conditions, which otherwise would be expected for protonated forms of aldehydes. This transformation however, is completely suppressed as demonstrated by the attempt to synthesize indeno[1,2-*b*]fluorene **15** from *p*-terphenyl dicarbaldehyde **14** (Fig. 3b). Surprisingly, compound **14** remains completely intact under DPEX condition, pointing out that the

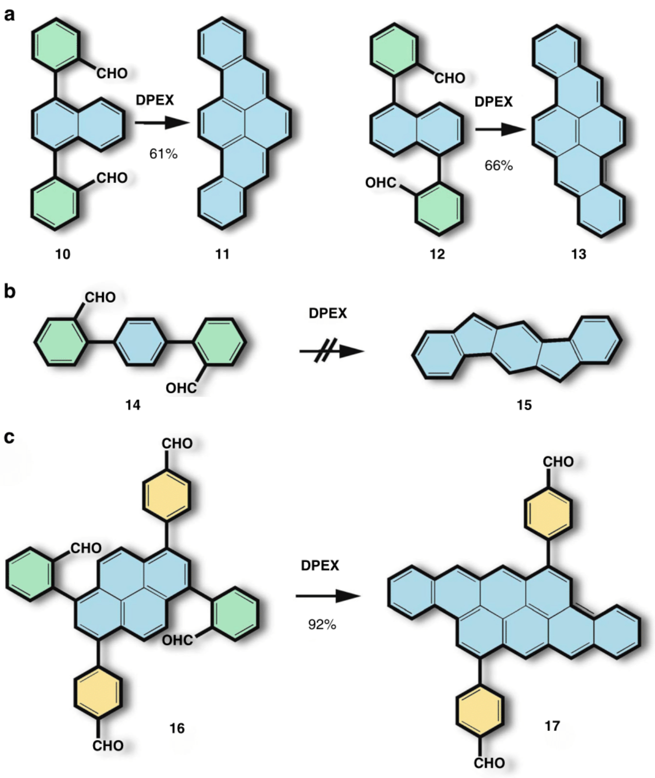

Fig. 3 The scope of the DPEX protocol. **a** Reaction with less reactive naphthalene core units; **b** No formation of five-membered rings; **c** Tolerance towards misplaced formyl groups

aldehyde functionality tolerates the reaction conditions if being misplaced. In other words, the aldehyde group shows activity only if it is placed in the formal cove region of the PAH. In order to support further this claim, the para-formylphenyl DBATT precursor **16**, bearing two aldehyde groups in active, and two in inactive positions was prepared, starting from dibromo precursor **6**. As shown in Fig. 3c, **16** reacts under typical DPEX conditions selectively, yielding the desired **DBATT** derivative **17** in 92% isolated yield. This unprecedentedly high regioselectivity of DPEX provides essential flexibility in design and facile access to complex functional PAHs. Regarding other functionalities, DPEX shows to be tolerant towards keto-groups, which undergo no transformation (compare compound **S6** in the Supplementary Methods); heterocycles like pyridine substituted precursors do not affect the outcome of DPEX and nearly quantitative conversions are obtained (see compound **S7** in the Supplementary Methods).

Noteworthy, the solvents were neither degassed, pre-distilled or purified, and used as obtained from the suppliers, which underpins the applicability of this protocol. Moreover, the reactions were performed under ambient atmosphere at room temperature. The only pre-caution taken was the avoidance of direct light irradiation, since **DBATT** is known to undergo light-induced oxidative decomposition[39]. In order to proof that this reductive-condensation protocol is suitable for the preparative–scale production, we carried out the reaction on a 0.50 g scale of **3**, which allowed us to isolate **DBATT** in 0.44 g as pure dark blue solid (isolated yield 96%). Supplementary Fig. 1 shows a detailed and pictured illustration of the single reaction steps. Accordingly, **TTc** was prepared on a 100 mg scale and **BPc** and **TPc** on a 20 mg scale.

Structure elucidation. Structure analysis of highly insoluble pristine NGs is evolving as major problem in modern nanographene sciences. Therefore, solubilizing groups are typically attached to the PAH's skeleton, leading inevitably to an alteration of its original characteristics[28–30,32]. Spectroscopically at the border of solubility for NMR analysis, we elucidated the ^{1}H NMR spectrum of **DBATT**, obtained at 100 °C in *o*-DCB (Fig. 4a). The peaks were assigned by the correlation with its computed NMR spectrum (RB3LYP 6–311 + G(d,p) GIAO). The absorption and emission spectra of **DBATT** are shown in Fig. 4b. The lowest energy absorption maximum is found at $\lambda_{max} = 586$ nm; it is absorption onset of $\lambda_{onset} = 600$ nm corresponds to the HOMO–LUMO transition of 2.07 eV and compares well to its computed HLG (vide infra). The small Stoke's shift of 4 nm gives an emission maximum at 600 nm and is characteristic for the rigid carbon skeleton. For the irrefutable structure determination, we took advantage of the stability of our zzNGs towards thermal

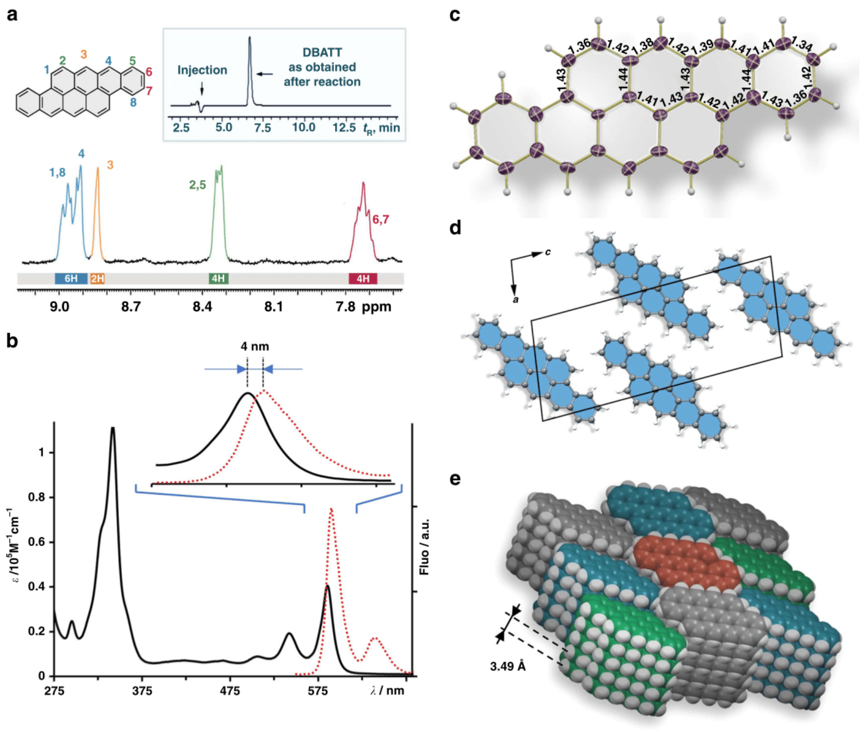

Fig. 4 Spectroscopic analysis and structure elucidation of **DBATT**. **a** ^{1}H NMR (o-DCB-D$_4$, 100 °C, 400 MHz); proton assignments were correlated with computed NMR spectra at the DFT RB3LYP 6–311 + G(d, p) GIAO level of theory; inset shows HPLC chromatogram after reaction work-up; **b** absorption (black) and emission (red) in THF at rt; **c** single crystal X-ray structure depicted as ORTEP model with 50% thermal ellipsoids, independent C–C bond lengths are indicated; **d** View onto the (101) face of the crystal (lattice) structure; depicted as balls and sticks model; **e** columnar crystal packing motif of **DBATT** with an interlayer distance of 3.49 Å; depicted as space filling model

sublimation. In case of **DBATT**, we were able to grow crystals in shape of dark blue needles (see Supplementary Fig. 2) by sublimation at 310 °C at 10^{-5} mbar, suitable for single crystal X-ray diffraction (see Fig. 4c). Unlike the examples from substituted **DBATT** structures[28–30,32], the aromatic skeleton of pristine **DBATT** remains flat. However, the lack of substituents becomes most apparent in view of the crystal packing. While e.g., threefold substituted triisopropylsilylethynyl-**DBATT**[30], packs in a pseudo-sandwich herringbone motif with a π–π distance of 3.61 Å, pristine **DBATT** assembles in slipped co-facially aligned columnar stacks with an interlayer distance of 3.49 Å (Fig. 4d, e). This particular arrangement is especially favorable for energy efficient exciton splitting processes, known as singlet fission, as the eclipsed conformation maximizes the frontier molecular orbital overlap of the HOMO and the LUMO[45,46].

With 10, 12, and 16 annulated benzene rings respectively, the actual highlight-NGs – **TTc, BPc** and **TPc** – could not be brought into solution without decomposition (boiling 1,2,4-trichlorobenzene). In that respect, laser desorption ionization mass spectrometry, as shown in Fig. 5a–c, indicate the high selectivity and full completeness of the DPEX process. No starting material, intermediates and other side products can be detected by LDI-MS which gave the first evidence for the constitutional integrity of the NGs. In the case of **BPc** a small intensity signal corresponding to the oxygen adduct can be detected, indicating slow oxidation of the compound under ambient conditions (no special precautions were taken during the MS preparation and analysis).

The structural proof was unambiguously obtained by low-temperature scanning tunneling microscopy (STM). The NGs were sublimed in ultra-high vacuum between 300 and 395 °C onto a Au(111) or Ag(111) surface, which was kept at room temperature. The STM results shown in Fig. 5d–f reveal that the size and shape of the NGs fit perfectly to the superimposed structural models, which were obtained by DFT. **BPc** and **TPc** adsorb as single molecules on Au(111) and Ag(111) respectively, while **TTc** forms a self-assembly on Au(111) (detailed analysis of the self-assembly is discussed in the Supplementary Discussion and depicted in Supplementary Fig. 14). This is the first report on the successful preparation and characterization of such extended zig-zag nanographenes.

Computations. In order to shed light into the electronic properties of the NGs, we carried out DFT calculations. We determined the HOMO–LUMO levels at the B3LYP-6–311 + G(d,p) level of theory; the theoretical diradical character y ($y = 0$ pure closed-shell; $y = 1$ pure open-shell) was determined according to

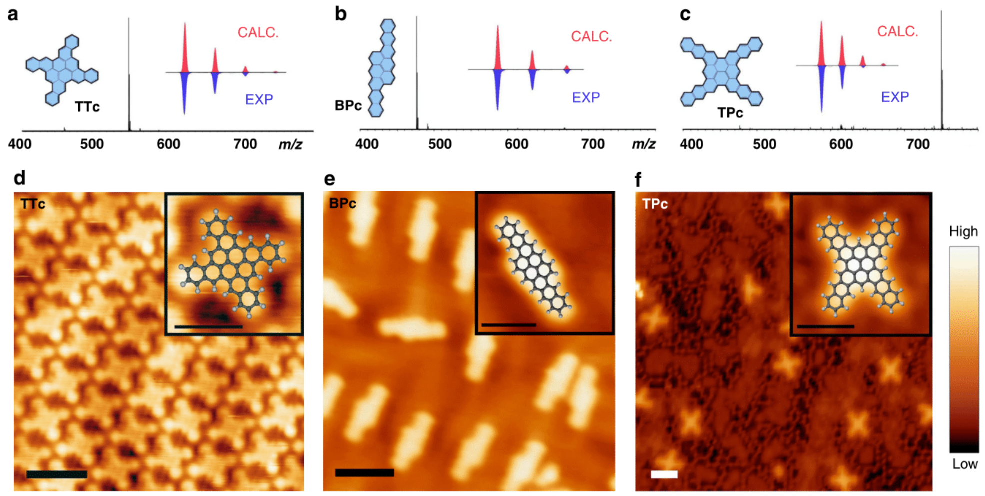

Fig. 5 Structure elucidation of larger NGs – **TTc**, **BPc** and **TPc**. **a**–**c** LDI-MS, insets show the calculated and measured isotope pattern, respectively; **d**–**f** STM images of **TTc** on Au(111) at 77 K, **BPc** on Au(111) at 4.7 K and **TPc** on Ag(111) at 4.7 K. The perfect fit of the superimposed DFT models corroborates the unambiguous identification of the NGs. The **TPc**'s are surrounded by bright protrusions that are assigned to halogens, which are residues from the synthesis (see SI). Scale bars: 2 nm and 1 nm for the insets with the DFT model overlaid images, respectively. Tunneling conditions: 100 pA/1 V, 50 pA/-500 mV, and 100 pA/-500 mV

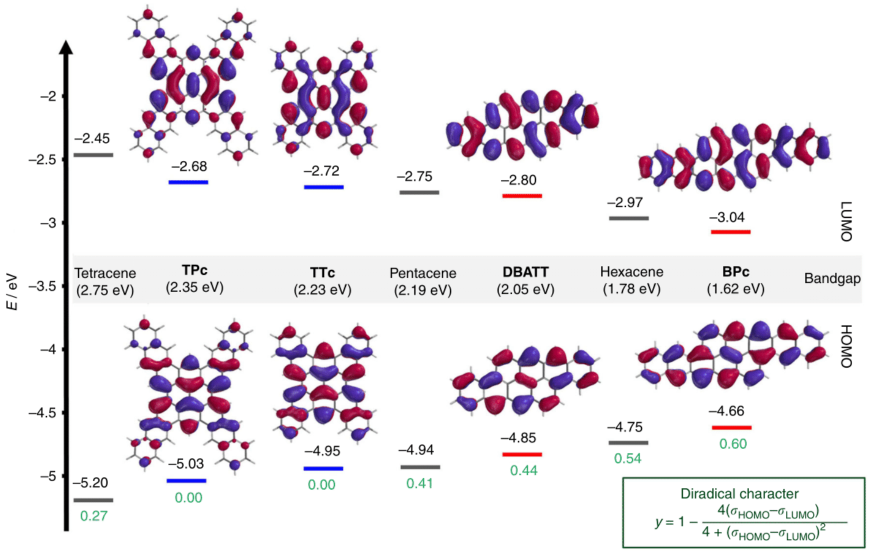

Fig. 6 Computational analysis of the zzNGs. Calculated HOMO-LUMO energies and frontier orbitals (isoval: 0.02 a.u.) at the DFT B3LYP 6–311 G + (d,p) level of theory; Theoretical diradical character *y* (green digits) was obtained from the broken symmetry calculation at the UHF 6–31 + G(d,p) level of theory

the equation in the inset in Fig. 6[47], from the occupation number of the frontier molecular orbitals (σ_{HOMO}, σ_{LUMO}), at the UHF 6–31 + G(d,p) level of theory[48,49]. The values were compared to the parent linear acenes (tetracene, pentacene, and hexacene) and are depicted in Fig. 6. With respect to the HOMO–LUMO gap the cross-shaped NGs **TTc** and **TPc** allocate values of 2.23 eV and 2.35 eV between tetracene and pentacene, respectively. At the first glance counterintuitive, **TPc** reveals a larger gap than **TTc**. However, this can be attributed to the stabilizing effect of Clar's sextets in the outer benzene rings, which are more dominant in

TPc and thus lower the HOMO level due to an increased aromatic stabilization energy. Interestingly, from broken symmetry calculations, no mixing of the highest occupied natural orbital (HONO) and lowest unoccupied natural orbital (LUNO), and therefore no diradical character ($y = 0$) for **TTc** and **TPc** can be observed. Even though the bandgap of tetracene is bigger than of the respective fourfold fused NGs, it shows already a diradical character of $y = 0.27$. Unlike the cross-shaped NGs, the bis-fused compounds **DBATT** and **BPc** show, with an increasing number of annulated benzene rings, a decreasing HOMO–LUMO gap (HLG). With a computed gap of 2.05 eV, which is in good agreement with its absorption spectrum, **DBATT** can be located between pentacene and hexacene; with $y = 0.44$ it shows a slightly higher diradical character than pentacene. However, in the solid-state **DBATT** shows to be kinetically much more stable than pentacene, which tends to undergo [2 + 2] cycloaddition reactions rapidly and requires typically stabilizing groups like e.g., triisopropylsilylacetylene. With a gap of only 1.62 eV, which corresponds to a theoretical transition at 765 nm, **BPc** shows the smallest HLG of the herein discussed NGs and compares well to notoriously unstable heptacene[50]. Even though a significant diradical character of $y = 0.60$ is computed for **BPc**, its persistence during the synthesis, thermal sublimation conditions, and storage in the solid state is remarkable.

Discussion

The recent progress in nanographene chemistry benefitted to a large extend from synthetic methodologies that allow the design of carbon nanostructures, such as nanographenes (NGs) and graphene nanoribbons, in high structural precision. While the edge-topology displays a strong lever in order to tune the electronic properties of NGs, major achievements towards zzNGs have been achieved only by on-surface synthesis under UHV conditions[14], or utilizing solubilizing and protective side groups[51,52]. Wet chemically, little synthetic efforts have been made to synthesize pristine zig-zag peripheries. As demonstrated in this study, we developed a facile reaction protocol that allows for the introduction of peripheral zig-zag-methine units into nanographene molecules. The key-step – the dehydrative π-extension (DPEX) – shows to be, due to its mild conditions, highly efficient in the preparation of nanographenes with small HOMO–LUMO gaps and significant diradical character. Furthermore, we show that the dehydrative cycloaromatization of aldehydes can be realized very effectively; utilizing readily available chemicals, we circumvent the usage of precious transition metals, or otherwise uncommon reagents in the final stage of the synthesis. DPEX showed to be expandable in any direction – larger acenes with low bandgaps, and multiple C=C bond formations in one molecule, yielding NGs with up to sixteen annulated benzene rings in close to quantitative yield. Its selectivity towards misplaced aldehydes, or ketones, its toleration of halogens, as well as heterocycles like pyridine, allows for a sophisticated compound design. The tolerance of the reaction towards moisture and air, the scalability to gram-quantities, and the extraordinary performance towards the preparation of highly insoluble NGs, makes this methodology a powerful and versatile instrument in the chemists' synthetic toolbox. Thus, we truly believe that alongside the recent synthetic development of synthetic methodologies towards NGs[7–12], DPEX will substantially contribute to the blooming field of carbon-based nano-architectures in physical sciences.

Methods

Synthesis of 2,3,8,9-dibenzanthanthrene DBATT (typical DPEX procedure). A 250 mL round bottom flask equipped with a magnetic stir bar was charged under ambient atmosphere with precursor **3** (20.0 mg, 48.7 μmol) and dissolved in CH_2Cl_2 (100 mL). While stirring, a solution of $SnCl_2 \bullet 2H_2O$ (500 mg, 2.22 mmol) in *i*-PrOH (2.0 mL) was added, followed by the addition of conc. H_2SO_4 (1.0 mL). The mixture was stirred at rt with protection from daylight for 18 h. The dark purple mixture was quenched by vigorous shaking with 1 *M* HCl (2.0 mL). The mixture was diluted with CH_2Cl_2 (20 mL) and washed with H_2O (1 × 50 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL) including the dark insoluble solids (product). The combined organics were diluted with MeOH (100 mL) and the CH_2Cl_2 was removed on the rotary evaporator at atmospheric pressure at 50 °C. The formed precipitate in the MeOH layer was centrifuged, the MeOH layer was decanted and the solid was washed with MeOH. The product was dried in vacuo and obtained in 98% yield (18.0 mg, 47.8 μmol) as dark blue solid. ^1H NMR (400 MHz, *o*-DCB-D_4, 373 K): δ (ppm) = 9.02–8.88 (6 H, m), 8.84 (2 H, m), 8.38–8.29 (4 H, m), 7.79–7.67 (4 H, m); HRMS (MALDI; DCTB matrix) (*m/z*) calculated for $C_{30}H_{16}$ (M^+) 376.1247, found 376.1764; EA calculated: C 95.72, H 4.28, found: C 94.88, H 4.54; further details are given in the Supplementary Discussion and Methods.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request. CCDC 1835109 (**DBATT**) contains the Supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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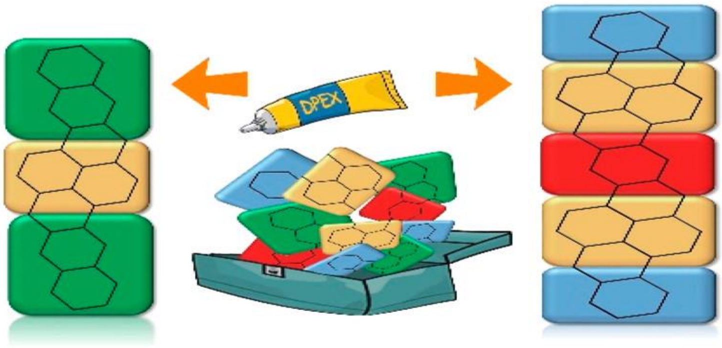
Publication 2.

Modular Approach to the Synthesis of Two-Dimensional Angular Fused Acenes.

Mikhail Feofanov,* Vladimir Akhmetov, Dmitry I. Sharapa, and Konstantin Amsharov*, Org. Lett., **2020**, 22, 1698−1702.



Abstract:

Herein, we present a modular approach to pristine angularly fused planar acenes. The approach includes the Pd-catalyzed fusion of several building blocks and implements a dehydrative π-extension (DPEX) reaction as a key step enabling facile access to diverse two-dimensional acenes. The scope was demonstrated on nine examples with up to quantitative yield.

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Modular Approach to the Synthesis of Two-Dimensional Angular Fused Acenes

Mikhail Feofanov,* Vladimir Akhmetov, Dmitry I. Sharapa, and Konstantin Amsharov*

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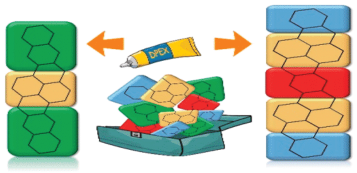

Despite its venerable age, the chemistry of polycyclic aromatic hydrocarbons (PAHs) fueled by vast potential in next-generation technologies holds a leading position in the modern materials science.[1−3] Renewed interest has been stimulated by recent advances in the atomically controlled synthesis of various carbon-based nanostructures.[4−7,7−11] The fact that the physical properties are directly related to the size, shape, and edge topology provides an opportunity to design a material with extraordinary properties in a conscious manner.[12] Edge topology plays a particularly crucial role, strongly influencing the electronic and optical properties of the compound. From this perspective, PAHs bearing zigzag edges (sometimes referred to as zigzag nanographenes or zzNGs)[13] appear to have an impressive scope of potential fields of studies and applications. For instance, PAHs containing zigzag edges exhibit strong absorption in the visible region, because of the decreased HOMO−LUMO gap (where HOMO represents highest occupied molecular orbital and LUMO represents lowest unoccupied molecular orbital), which results in a high diradical character and a sufficient contribution of open-shell resonance structure.[12,14] This type of molecule is regularly mentioned in the exploration of singlet fission,[15−17] semiconductors with high carrier mobilities,[10,18,19] and spintronics and molecular magnetism.[20−22]

However, these properties come at a price. Linear fused acenes with more than five rings immediately dimerize, even in highly diluted solutions.[23] Meanwhile, the stability of polyacenes can be greatly improved by changing their linear annulation mode to an angular one. This concept has been recently established and investigated in different groups.[24−29] Until now, angular fused acenes have been mainly studied in forms of their derivatives bearing bulky substituents, the introduction of which often leads to drastic changes in properties such as packing, π-interactions, and optical features.[27,30] As for pristine molecules, DBATT (2.3,8.9-dibenzanthanthrene) has very promising applications in single-molecule physics,[31−33] where bulky substituents lead to a significant downgrade in performance. Meanwhile, full-scale studies of structure−property relationships in this area are severely limited, because of a lack of simple and clean synthesis of pristine acenes connected to their low solubility.

The synthesis of nonsubstituted PAHs was essentially founded and investigated by E. Clar in the middle of the 20th century,[34] whereas the developed analytical techniques have pulled up the requirements to the purity of the compounds and therefore made Clar's approach inadequate since a substantial share of the obtained PAHs turned out to contain considerable amounts of contaminants. Until recently, organic synthesis of pristine 2-D acenes could barely meet the characteristics dictated by physical experiments, such as purity, scale, and simplicity of the procedure.

Previously, we have reported a very successful approach to synthesis of DBATT and its homologues. A new attractive technique, called DPEX (a dehydrative π-extension) acid-promoted reductive intramolecular cyclization of the corresponding aromatic aldehydes served as a key step in this approach.[30] The technique exploits unusually mild conditions, together with available reactants, and allows gram-scale synthesis of DBATT in almost-quantitative yield.

Herein, we report a versatile modular approach exploiting facile conventional synthetic methods (i.e., combination of Suzuki coupling and DPEX reaction) enabling a variety of zzNGs. We show the synthesis of eight zzNGs in yields of 43%−98%. The obtained products have high purities, which were confirmed, along with the structures by means of high-

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performance liquid chromatography (HPLC), high-resolution mass spectroscopy (HRMS), ^{1}H and ^{13}C nuclear magnetic resonance (NMR) analysis techniques. Moreover, we demonstrate a 4-fold cyclization yielding the longest known pristine fused acene dianthra[2,1,9-*jkl*:2′,1′,9′-*uva*]pentacene, which was obtained in bulk and was found to be surprisingly stable in solution. DFT-calculated biradical character and HOMO−LUMO bandgaps were obtained, whereas the latter were also compared to electrochemical and optical values.

The major advantage of our modular approach is based on the simplicity and availability of the building blocks (Figure 1).

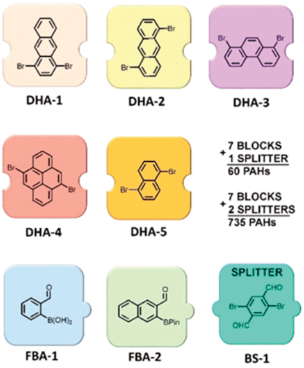

Figure 1. Selected building blocks used in this study. To illustrate the potential scope of our approach, we provide the information given in Tables S1 and S2 in the Supporting Information (SI).

We allocate dihalogenarenes (DHA) and formylareneboronic acids (FBA) as two principle types of building blocks, which can be easily interfused via Suzuki coupling. In this work, we have selected the most representative cases, picking five DHA with two FBA blocks enabling eight nanographenes (NGs).

The required precursors were obtained by the combination of the chosen building blocks exploiting standard Suzuki coupling (Figure 2), followed by DPEX reaction directly yielding target NGs in a highly pure form. As a matter of fact, the obtained UV−vis spectra of NG1, NG3, and NG7, as described only by Clar,[34] were not consistent with previously published information, apparently because of impurities in the samples described earlier. While the low solubility of NGs makes the Suzuki-DPEX procedure extremely straightforward, it also entails significant difficulties in the analysis and characterization. Nevertheless, the NMR measurements and HPLC analysis at elevated temperatures commonly overcome the issue and allow sufficient confirmation of both the structure and purity of the isolated compounds. In the extreme case, such as NG9, which possesses low solubility insufficient for NMR measurements, even in *ortho*-dichlorobenzene at 120 °C, we rely on the combination of high-temperature HPLC and LDI-HRMS analyses.

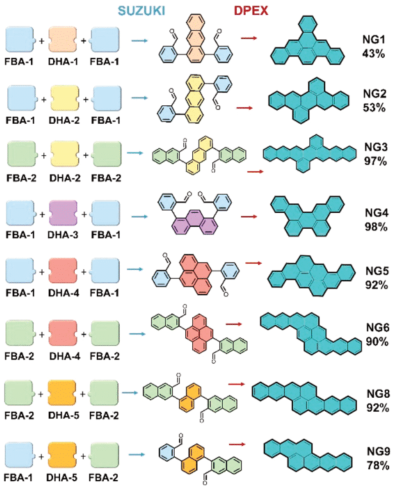

Figure 2. Synthesis of NG1−NG8 via Suzuki/DPEX molecular assembly strategy. Suzuki coupling: Pd(PPh$_3$)$_4$, K$_2$CO$_3$, toluene/methanol/H$_2$O. DPEX: SnCl$_2$/*i*-PrOH, H$_2$SO$_4$, DCM.

Thus, we have isolated NG1 and NG2 in rather moderate quantities, in comparison to the rest of the molecules (43% and 53% yields, respectively). This fact is associated with a lower degree of precipitation; nevertheless, such an outcome still deserves to be counted as decent, given the purity of compounds determined by means of ^{1}H and ^{13}C NMR. In accordance with our data, decreased solubility is generally accompanied by improved efficiency of the DPEX reaction. Thus, NG3 was obtained in quantitative yield (isolated yield of 97%), whereas the purity was demonstrated exploiting ^{1}H NMR and HPLC. We have also obtained NG4, NG5, NG6, and NG7 in yields of 98%, 92%, 90%, and 92%, respectively. We provide ^{1}H NMR spectra of NG5 and NG7, which were previously assigned only by means of UV−vis spectra. Meanwhile, NG6 is a previously unknown molecule; its ^{1}H NMR spectrum was registered at 120 °C in *o*-dichlorobenzene-d_4. Besides symmetrical NG1−NG7, DPEX also allows the synthesis of asymmetrical molecules and, in such a manner, remarkably extends the number of possible structures. This possibility to construct asymmetrical NGs has been demonstrated on the example of NG8, which was obtained via a step-by-step fusion of three blocks (see Figure 2).

Even using the arsenal of our modular approach providing both symmetrical and asymmetrical NGs, the scope of the reachable structures is quickly exhausted as the variety of available middle blocks (DHA) come to an end. On the other hand, the introduction of the bridge, or so-called “block splitter”, between the moieties allows rather simple prolongation of the acene-like structures, avoiding virtually any foreseeable end (see Table S2 in the Supporting Information). In order to demonstrate the concept, we have fused **DHA-5**, **FBA-2**, and **BS-1** stepwise and performed 4-fold cyclization, yielding unprecedentedly long acene NG9 in 79% (see Figure 3).

To investigate electronic properties of the obtained zigzag NGs, we have performed DFT calculations of HOMO−LUMO levels and compared the results with experimentally obtained data. We have also determined the diradical character *y*, and performed FOD analysis (fractional occupation number weighted electron density). The predicted values were compared to the parent linear tetracene and pentacene (Figure

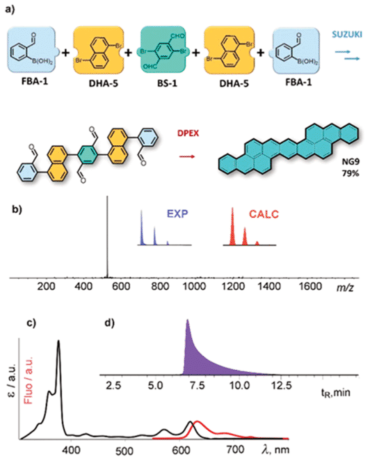

Figure 3. Synthesis and spectroscopic analysis of NG9: (a) synthetic route; (b) LDI-MS analysis (positive mode) (experimental and theoretically predicted isotopic distribution patterns are shown in the inset; and (d) HPLC profile of NG9 with pronounced tailing, indicating strong aggregation in the solution (80 °C, *o*-DCB as an eluent, Cosmosil PBr column). Panel (c) shows plots of absorption (black) and emission (red) in *o*-DCB at room temperature (rt).

4). “Minding the gaps”,[35] we have compared time-dependent density functional theory (TD-DFT) gaps with the respective experimental optical gaps and available electrochemical measurements. Linear correlation was observed in both cases. TD-PBE0 and TD-B3LYP show excellent agreement with the measured optical gaps, in contrast to TD-PBE, which consistently underestimates the value. (see the SI). Fundamental gap, calculated through the ionization potential and electron affinity, generally appears to be significantly larger than measured electrochemical gap. This difference is believed to be based on the systematic errors of the exploited functionals.[36−38] As a measure of diradical character, we calculated parameter *y*, which was in good correlation with the N_FOD value. In accordance with theoretical notions, the optical band, which was retrieved from the observed UV−vis spectrum, should correlate with the diradical character value in a manner that, if the band is lower, then the diradical character is higher and vice versa.[39] Thus, if this correlation occurs, the UV/vis spectrum can instantly give the idea of the degree of diradical character. Rather interestingly, the obtained pristine acenes and their both measured and calculated parameters indeed reveal this dependence, demonstrating strong linear correlation. The considered molecules are also interesting from the fundamental viewpoint of unpaired electron density distribution. Our calculations show that three methodologically different techniques are in excellent agreement: OED, FOD, and the most straightforward, although the most arguable, approximation of singlet diradical as a triplet. All three methods provide virtually the same localization.

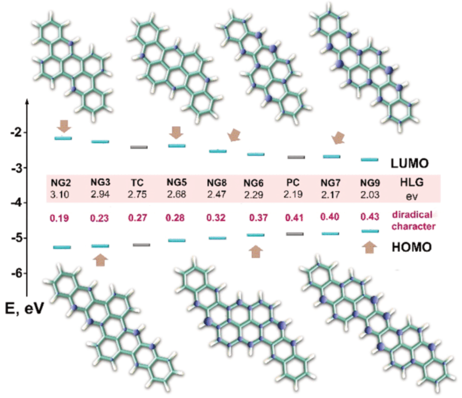

Figure 4. Computational analysis of the zzNGs. Calculated HOMO−LUMO energies and frontier orbitals (isoval: 0.02 a.u.) at the DFT B3LYP/6-311+G(d,p) level of theory. The theoretical diradical character *y* (green digits) was obtained from the broken symmetry calculation at the UHF/6-31+G(d,p) level of theory.

HONO and LUNO (highest occupied natural orbital, lowest unoccupied natural orbital) occupations, biradical character *y*, N_FOD, and measured optical and electrochemical gaps, as well as the results of TD-DFT calculations and HOMO−LUMO gaps, can be found in the SI.

In summary, we report a simple, yet fruitful, modular approach to pristine angularly fused planar acenes. The approach includes two steps: fusion of building blocks via Suzuki coupling and consequent DPEX reaction enabling the desired acenes in exceptionally high yields and purity. Despite its simplicity, it gives rapid access to a wide variety of 2-D acenes, while the introduction of the “block-splitter” extends the scope of accessible structures to virtually inexhaustible.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.9b04382.

Details of the synthetic procedures, DFT calculations, copies of NMR, mass, UV−vis, fluorescence spectra, CV, HPLC chromatograms (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

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Publication 3.

Oxidative Electrocyclization of Diradicaloids: C−C Bonds for Free or How to Use Biradical Character for π-Extension.

Mikhail Feofanov,* Vladimir Akhmetov, Dmitry I. Sharapa, and Konstantin Amsharov*, Org. Lett., **2020**, 22, 5741−5745.

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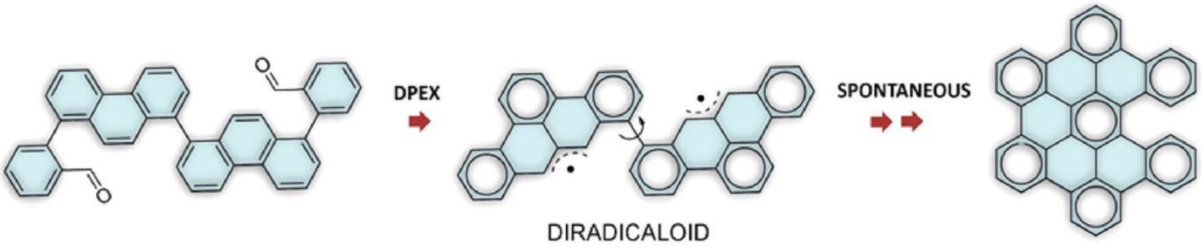

Abstract:

Herein, we show that biradical character and appropriate distribution of spin density can be used for synthetic purposes. We demonstrate the rational domino annulation that includes dehydrative π-extension (DPEX) as the initiation step and subsequent oxidative electrocyclizations (EC) promoted by favorable localization of the unpaired electrons enabling up to four C−C bonds formed during the reaction. Contradicting to the Woodward−Hoffmann rules, the reaction proceeds at room temperature, whereas termination occurs when biradical character vanishes.


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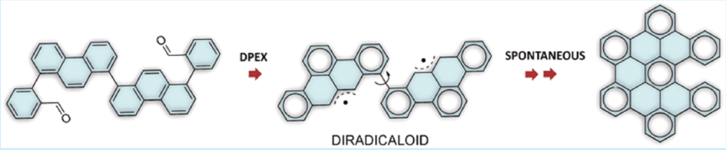

ABSTRACT: Herein, we show that biradical character and appropriate distribution of spin density can be used for synthetic purposes. We demonstrate the rational domino annulation that includes dehydrative π-extension (DPEX) as the initiation step and subsequent oxidative electrocyclizations (EC) promoted by favorable localization of the unpaired electrons enabling up to four C−C bonds formed during the reaction. Contradicting to the Woodward−Hoffmann rules, the reaction proceeds at room temperature, whereas termination occurs when biradical character vanishes.

Synthesis of polycyclic aromatic compounds has become one of the most relevant branches in modern materials science.[1,2] The possibility to manage the physical properties through the size, shape, and edge topology[3] allows the design of materials for a wide variety of optoelectronic applications.[4−11] C−C bond formation techniques serve as the main tools in the bottom-up construction of the desired materials with atomical precision. It is, therefore, crucial to develop new synthetic tools and to broaden the scope of the existing methods such as annulative π-extension (APEX),[12,13] Scholl reaction, alkyne annulation,[14,15] aryne trimerizations,[16] palladium-catalyzed reactions,[17,18] etc. To achieve this goal, it is vital to understand how different substrates behave upon exposure to different reaction conditions. However, it can be not as trivial as it seems. Among vivid examples demonstrating this fact is the Scholl reaction, which has been known for over 100 years, and despite comprehensive studies by Müllen et al.[19] this transformation continues to reveal new examples of intricate transformations.[20−22]

Recently, we have contributed to the field by developing the dehydrative π-extension (DPEX) reaction.[6,23] Ambient conditions and the simplicity of the protocol provide rapid access toward polycyclic aromatic hydrocarbons (PAHs) and nanographenes with zigzag edges and high biradical character. The latter leads to low chemical stability, as open-shell systems tend to undergo uncontrollable oligomerization in solution.[24,25] It is, indeed, a complicated task to gain control over the reactivity of such species.[26,27]

However, as we envision, if the radicals are localized in the "right" places, this tendency can be used to promote intramolecular processes. Among them is 6π-electrocyclization, a subclass of pericyclic reactions that play an important role in both synthetic and theoretical chemistry.[28−30] According to Woodward−Hoffmann rules, this reaction can proceed through photochemical or thermal activation.[31] The second often requires extremely high temperatures, particularly in the case of unactivated hexatrienes.[32] Unlike them, open-shell structures play by different rules. They undergo thermal electrocyclization at ambient temperatures. This is connected with low HOMO−LUMO gaps resulting in the partial occupation of HOMO and LUMO in the ground state.

This transformation represents a challenge for chemists due to the overall complexity of pristine biradicals' synthesis and poor control over degradation pathways that unstable diradicaloids undergo. Several recent reports have studied the mechanistic aspects of 6π-electrocyclization of phenalenyl-based diradicaloids.[33−37] Despite valuable insights, the mechanism of the reaction remains not fully understood.[38] While these works have been foreshadowing new synthetic methods to be developed, to the best of our knowledge there are no direct synthetic applications that emerged from the area.

Herein, we demonstrate such a synthetic application exploiting DPEX and the Clar model for effective cascade reactions. Thus, the DPEX reaction can generate biradical moieties suitable for the "forbidden" 6π-electrocyclization.

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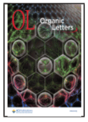

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Meanwhile, the precursor design can be rationalized by using the Clar model, which can predict the favored position of the radicals and explain the outcome of the reaction. This reasoning is also supported by the fractional occupation number weighted electron density (FOD) analysis and DFT-calculated energy barriers. From a synthetic standpoint, this domino reaction gives rapid access to violanthrenes and π-extended 5-helicenes unavailable via alternative methods.

The concept of the domino annulation is shown in Figure 1. The intermediate obtained after DPEX can be represented via three isomeric structures (**1**-*trans*, D1, and **1**-*cis*). D1 has several resonance forms, the most stable of which are depicted in Figure 1. As it will be shown later, the efficiency of intramolecular electrocyclization at room temperature correlates with the stability of the resonance form having radical centers localized on carbon atoms directly participating in the new bond formation. The respective resonance forms are indicated as the Most Contributing Resonance Structure (MCRS).

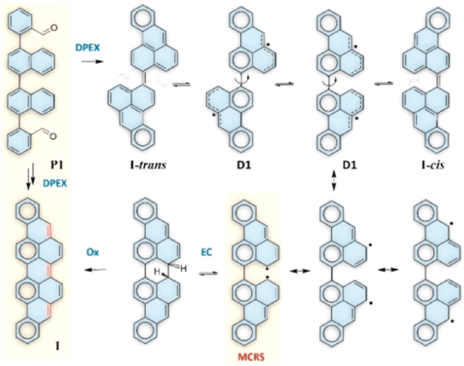


Figure 1. Concept of the report illustrated by the example of violanthrene (**1**) synthesis.

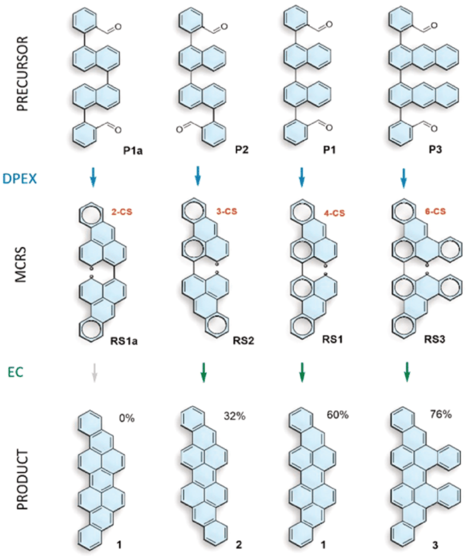


Figure 2. Domino reaction including DPEX as the initiation step and subsequent oxidative electrocyclization of diradicaloids. Reaction conditions: $SnCl_2$/*i*-PrOH, H_2SO_4, DCM, room temperature, overnight.

We have initiated our studies with three simplest model intermediates (obtained from P1, P1a, and P2) containing two interconnected benzophenalenyls, i.e., the smallest fragments which can be constructed via the DPEX reaction. This choice is also justified by similarities to the previously studied phenalenyl fragments.[34,35]

The syntheses of the symmetric precursors P1 and P1a were performed in two steps including mono-Suzuki reaction and subsequent dimerization via Miyaura conditions in the presence of strong base.[39] The asymmetric P2 was obtained via a three-step procedure (see the Supporting Information (SI)). The diradicaloids were generated under conditions of DPEX reaction. For simplicity, only MCRSs of the respective diradicaloids (RS1, RS1a, and RS2) are shown in Figure 2. In the case of P1 and P2, the initiation step was followed by in situ electrocyclization and oxidation yielding violanthrene (**1**) and isoviolanthrene (**2**) as main products, respectively. Noteworthy, no traces of **1** were found in the case of P1a (inseparable mixture of different products was formed).

This outcome can be explained via simple qualitative reasoning.[40] To achieve higher efficiency, it is desirable to have unpaired electrons localized on the corresponding carbon atoms (Figure 2).

Despite several possible resonance forms, it is the form containing the biggest number of Clar's sextets (CS) that mainly contributes to the preferred positions of radicals. Thus, it can be seen from Figure 2 that the more sextets that are involved in the MCRS, the better the yields that are achieved. Therefore, P2 represents the best precursor in this series as it has four sextets in the MCRS. However, even in this case, the unpaired electrons are significantly delocalized (Figure 1). To address the issue, we have designed the precursor P3 that gives diradicaloid RS3 in which spin density is concentrated on the "correct" carbon atoms. Therefore, the yield of the domino reaction increases to 76%. An intriguing aspect of this transformation is that it terminates at the π-extended 5-helicene **3** due to the formation of the closed-shell system.

To investigate whether the approach can be extrapolated to induce longer domino reactions we have prepared precursor P4 which gives diradicaloid **4a** (Figure 3). Oxidative electrocyclization of **4a** leads to diradicaloid **4b**, which finally transforms into tetrabenzobisanthrene (TBBA, **4**). Thus, this cascade enables the transformation of the linear oligophenylene **P4** into π-extended helicene **TBBA** in 60% yield, which corresponds to 88% per C−C bond.

Although it has been recently shown that bulky substituents can prevent TBBA from the cyclization under Scholl conditions,[41] pristine molecules bearing a *fjord*-region cannot be obtained via this reaction. Contrary to hexabenzocoronene,[42] the distortion in **4** caused by the helical moiety enhances solubility and allows not only measurement of the

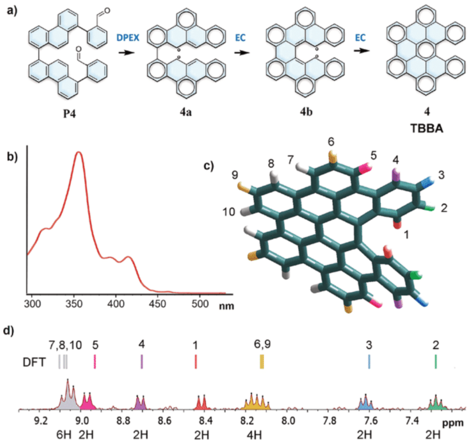


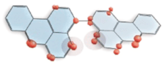
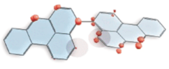
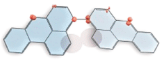
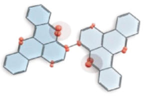
Figure 3. Synthesis and characterization of **TBBA**: (a) Domino reaction including DPEX and two subsequent oxidative electrocyclizations. (b) UV−vis spectrum of **TBBA** in toluene. (c) DFT-calculated structure of **TBBA**. (d) Comparison of DFT-calculated and recorded (300 MHz, $C_2D_2Cl_4$) ^{1}H NMR spectrum of **TBBA**. The calculated spectrum was scaled by a factor of 0.88. The assignment of signals is based on DFT.

UV−vis spectrum but also recording of the ^{1}H NMR spectrum (Figure 3).

To support our qualitative model, we have performed DFT calculations investigating the electronic structures and the transformations of the diradicaloids RS1a, RS1, RS2, and RS3 (computation details can be found in the SI). The distributions of the biradical density obtained from the FOD analysis (Table 1) are in perfect agreement with the prediction based on the Clar model (Figure 2). The applicability of the FOD analysis and its comparison with other alternative methods have been discussed previously.[23,43] Based on the data for RS1, RS1a, and RS2, a strong correlation between N_FOD, biradical character y,[44] the reaction barrier, and the length of the forming C−C bond in transition states can be noticed. This observation can be interpreted as follows: a higher biradical character (measured as y or N_FOD) induces an earlier TS and therefore a lower barrier. Although this trend fits for RS1, RS1a, and RS2, the larger systems (RS3, **4a**, **4b**) are significantly more complex, e.g., chemically irrelevant lengths of the C−C contacts in the corresponding TSs were found. Recent work of Juríček et al.[36] demonstrates that even CASSCF treatment of such diradicaloid reactions does not provide barriers quantitatively comparable with the experimental results. Thus, despite all the efforts applied to the investigation of the electronic structures and qualitative agreement with the experimentally obtained yields, the presented results should be taken as a semiquantitative evaluation.

In summary, we present how DPEX together with a simple empirical model provides rapid access to intricate PAHs. While DPEX enables the effective generation of diradicaloid intermediates, the Clar model allows the rational design of the domino reaction enabling up to four C−C bonds formed in one step.

Table 1. Plots of the FOD Density (σ = 0.01 e/bohr^3) of Diradicaloids, Their Biradical Characters, Barriers of Electrocyclization, and Length of C−C Bonds in Transition States

FOD isosurfaces of diradicaloids and N_FOD value	y	Barrier (kcal/mol)	C-C in TS (A)
 **RS1a**, 1.69	0.79	8.5	2.46
 **RS2**, 1.41.	0.67	20.2	2.34
 **RS1**, 1.12	0.54	33.5	2.26
 **RS3**, 1.49.	0.67	9.7	2.89

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01717.

Details of the synthetic procedures, DFT calculations, copies of NMR, mass, UV−vis, and HPLC chromatograms (PDF)

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Notes

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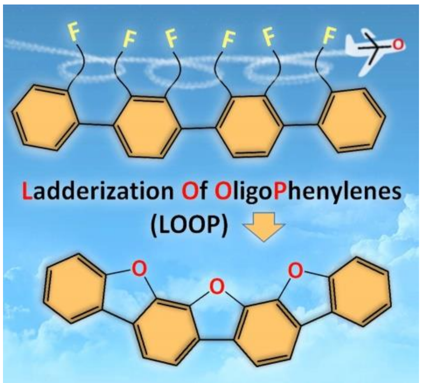
Publication 4.

Catalyst-Free Synthesis of O-Heteroacenes via Ladderization of Fluorinated Oligophenylenes.

Mikhail Feofanov,* Vladimir Akhmetov, Ryo Takayama, and Konstantin Amsharov*, Angew. Chem. Int. Ed., **2020**, accepted. Doi: 10.1002/anie.202007427. First published online on 13th of September, 2020.



Abstract:

We report a novel catalyst-free approach to benzoannulated oxygen-containing heterocycles from fluorinated oligophenylenes. Unlike other existing methods, the presented reaction does not require oxygen-containing precursor and relies on outer oxygen source i.e. potassium *tert* -butoxide, which serves as an O^{2-} synthon. The radical nature of the reaction facilitates nucleophilic substitution even in the presence of strong electron-donating groups and enables de- *tert* -butylation required for the complete annulation. We demonstrate the applicability of the method to introduce five-, six- and seven-membered rings containing oxygen, whereas multiple annulations also open up a short synthetic path to ladder-type O-heteroacenes and oligodibenzofurans.

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Catalyst-Free Synthesis of O-Heteroacenes via Ladderization of Fluorinated Oligophenylenes

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Supporting information for this article is given via a link at the end of the document.

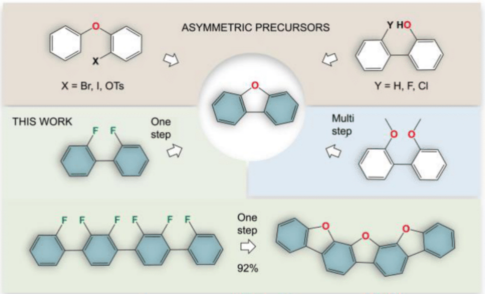
Abstract: We report a novel catalyst-free approach to benzoannulated oxygen-containing heterocycles from fluorinated oligophenylenes. Unlike other existing methods, the presented reaction does not require oxygen-containing precursor and relies on outer oxygen source i.e. potassium *tert*-butoxide, which serves as an O^{2-} synthon. The radical nature of the reaction facilitates nucleophilic substitution even in the presence of strong electron-donating groups and enables de-*tert*-butylation required for the complete annulation. We demonstrate the applicability of the method to introduce five-, six- and seven-membered rings containing oxygen, whereas multiple annulations also open up a short synthetic path to ladder-type O-heteroacenes and oligodibenzofurans.

Organic π-conjugated materials have been under constant focus in academia and industry during recent years. Due to their outstanding optical and charge properties, they play a key role in the development of organic light-emitting diodes (OLEDs)[1], organic field-effect transistors (OFETs)[2,3] and organic photovoltaics (OPVs).[4]

The incorporation of heteroatoms into the carbon skeleton is an excellent tool to adjust and improve the electronic properties of the compounds. [5,6] In contrast to nitrogen- and sulphur-analogs,[7–9]oxygen heterocycles, e.g. containing furan's moiety, have drawn much less attention and became an object of interest only recently. [10–19]

Among the main reasons for such a late splash of interest are synthetic difficulties connected to lability issues of furans. Meanwhile, a fusion of furan ring(s) to an all-carbon aromatic system appears to be a viable strategy for obtaining stable furan derivatives (also called ladder-type O-bridged heteroacenes[20]).[21] Dibenzo[*b,d*]furan (**1**) serves as a model target compound for the development of new synthetic approaches. Despite a large number of works aimed to develop facile incorporation of the furan ring, the principal synthetic strategies are not so numerous and break down into few categories depicted in Figure 1. The final step includes either transition metal-catalyzed C-C coupling[22–26] or C-O bond creation, [27–36] which is usually implemented via a two-step deprotection/dehydration procedure. [10,14,37–40]

With rare exceptions[41], the existing synthetic approaches to the dibenzofuran core require an oxygen atom in the precursor's structure. Meanwhile, a technique enabling the incorporation of oxygen and simultaneous formation of a heterocycle could simplify overall synthesis. In the ideal case, the technique should exploit a functionality that stays unreactive otherwise. In this context, C(aryl)-F bond appears to be a potential functionality as it, in contrast to other C-Hal bonds, remains intact during conventional Pd-catalyzed C(aryl)-C(aryl) couplings. Therefore the direct transformation of C-F bond into C-O functionality appears to be a highly attractive approach to O-heteroacenes.



Multiple Ladderization of oligo-Phenylenes (LooP)

Figure 1. Synthetic approaches to dibenzofuran and scope of this work.

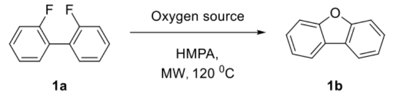
Herein, we report a new catalyst-free approach to a wide range of O-heteroacenes via "ladderization" of fluorinated oligophenylenes (**LooP**).

Activated, i.e. containing strong electron-withdrawing groups, fluorobenzene derivatives are known to undergo substitution with O-nucleophiles[42–48], whereas such intermolecular substitution of fluorine in unactivated aromatics is less common[49].

We started our investigations with the reactions of 2,2'-difluoro-1,1'-biphenyl **1a** with potassium hydroxide. We have carried the reaction out in HMPA (hexamethylphosphoramide)[50,51] and under microwave irradiation, which greatly accelerates S_NAr reactions [52,53]. Although the reaction does not proceed in the presence of KOH, the substitution of the latter with *t*-BuOK enables the formation of **1b** in 10% yield (table 1, entry 2). Increasing the amount of *t*-BuOK up to 6 equiv., we have achieved an excellent (93%) yield of **1b** (table 1, entry 6).

Despite the anticipated stability of *tert*-butyl ether under basic conditions[61], intermediates containing *tert*-butoxy substituents were not found in the mixture. The reaction also proceeds in other aprotic solvents such as DMA and DMSO, although in slightly lower yields (table 1, entry 7-8). Interestingly, **1b** was not detected in the experiment with MeOK **(**table 1, entry 9). In the case of EtOK the yields do not exceed 20 % **(**table 1, entry 10; more detailed information is in SI).

Table 1. Reaction of 2,2'-difluoro-1,1'-biphenyl with different oxygen sourses.

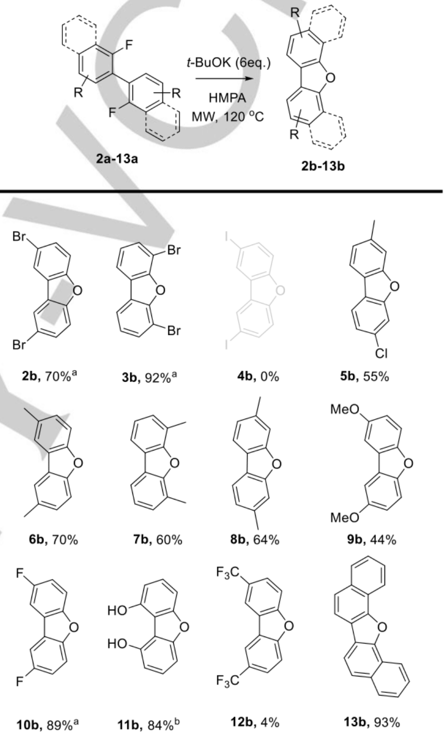


Entry	Oxygen Source	Solvent	Yield of **1b**
1	KOH (2 equiv.)	HMPA	0
2	t-BuOK (2 equiv.)	HMPA	10
3	t-BuOK (3 equiv.)	HMPA	25
4	t-BuOK (4 equiv.)	HMPA	41
5	t-BuOK (5 equiv.)	HMPA	82
6	**t-BuOK (6 equiv.)**	**HMPA**	**93**
7	t-BuOK (6 equiv.)	DMSO	78
8	t-BuOK (6 equiv.)	DMA	72
9	MeOK (6 equiv.)	HMPA	0
10	EtOK (6 equiv.)	HMPA	20
11	KOH (6 equiv.)	HMPA	0

Based on the screening, *t*-BuOK can be considered as an optimal oxygen source and the O^{2-} synthon, which enables one-pot substitution of two fluorines yielding benzoannulated furan derivatives. To test the viability of this claim and to investigate the scope and limitation of this reaction, we have studied other fluorinated precursors **2a**-**11a** bearing halogen-, methyl-, and methoxy- substituents (Table 2).

Dibromodibenzofurans **2b** and **3b** were synthesized in 70% and 92% yields, respectively. Although the method seems to be not compatible with C-I, the tolerance towards C-Br functionality can be achieved by decreasing the reaction temperature to 80 ºC. As of methylated representatives **6b**-**8b**, the yields vary from 60 to 70%, The yields are slightly decreased due to partial demethylation, the mechanism of which will be discussed later. Notably, the reaction conditions are suitable even for the synthesis of dibenzofurans with strong donor substituents such as OMe group. Thus, **9b** bearing methoxy groups in 4- and 8-positions was isolated in 44% yield. It is also interesting, that the reaction reveals a pronounced regioselectivity to fluorine substituents. We have found that the nucleophilic substitution process favors fluorine atoms in 2,2'- positions since 4,8-difluorodibenzofuran (**10b**) was isolated in 89% yield. However, if biphenyl bears fluorine atoms at 2,2',6,6'- positions, it is not possible to stop the reaction at the formation of 1,9-difluorodibenzofuran, whereas a complex mixture of different oxygen-containing compounds is observed. Meanwhile, the addition of 12 equiv. of potassium *tert*-butoxide allows oxodefluorination and full hydrolysis of the two remaining C-F bonds yielding **11b** in 84% yield. We assume that the observed phenomena are connected to mutual activation of C-F functionalities in close proximity, while the second annulation in the case of **11a** does not occur due to strain energies needed to be overcome [54]. Surprisingly, we did not observe and isolate any reasonable products in the case of 2,2',4,4'-tetrafluoro-1,1'-biphenyl. We assume that increased acidity of the hydrogen between fluorines facilitate the formation of aryne, which leads to the formation of inseparable mixture of compounds. The reaction poorly tolerates CF_3 groups. The furan **12b** was isolated only in 4% yield. Moreover, the conditions are also suitable for the synthesis of π-extended homologs of dibenzofuran. Thus, dinaphtofuran **13b** was isolated in excellent 93% yield.

Table 2. Synthesis of substituted dibenzofurans from 2,2'-difluoro-1,1'-biphenyls.



a) 80 °C. b) 12 eq. of *t*-BuOK from 2, 2', 6, 6'-tetrafluorobiphenyl.

Another aspect that we find extremely, if not the most, important is the possibility to implement multiple annulations in one step (Figure 2). Having the established synthetic protocol, we have turned our attention to benzobisbenzofurans **14b**-**16b** containing two oxygen atoms. To our pleasure, excellent efficiency of the double-annulation enables target benzobisbenzofurans in high (up to 91%) yields. Furthermore, the consequential formation of six C-O bonds enables a triple annulation of **17a** in 92% yield making the new ladder-type heteroacene **17b** readily available through a three-step procedure. Rather unexpectedly, fluorinated *meta*-oligophenylene **18a** transforms solely into trisdibenzofuran **18b** instead of a complicated mixture. Surprisingly high 90% yield indicates that the process has certain preferences over C-F bond substitutions' sequence and, presumably, is not connected with self-correction (see SI)[55].

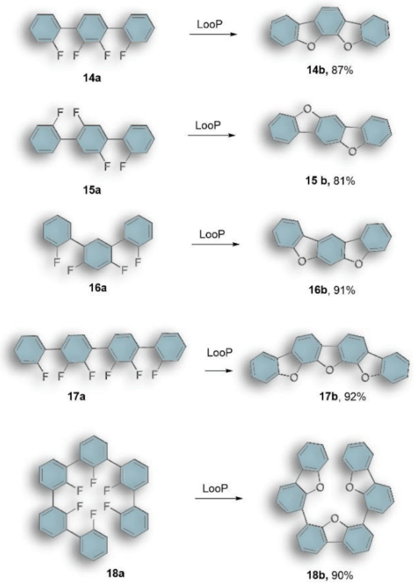


Figure 2. a) Multiple ladderization of fluorooligophenylenes.

The incorporation of benzoannulated oxygen-containing heterocycles other than five-membered is less-known transformations [56–61]. However, the compounds containing six- and seven-membered rings have some promising applications as OLED materials[62,63]. To test whether our method is capable of tackling such synthesis, we have obtained fluorinated precursors **19a** and **20a**, which under reactionary conditions transformed into **19b** containing pyrane ring and **20b** containing oxepine ring. Extrapolation of the approach to other oxepines has been proved successful as **21b** and **22b** were obtained in excellent 90% and 85% yields.

From the mechanistic perspective, the reaction can be formally broken down into three steps: substitution, deprotection, and second substitution (Figure 4). While the last step represents a well-established S_NAr process exploited for the synthesis of dibenzofurans[30], the rest of the mechanistic route is less trivial and requires thorough consideration.

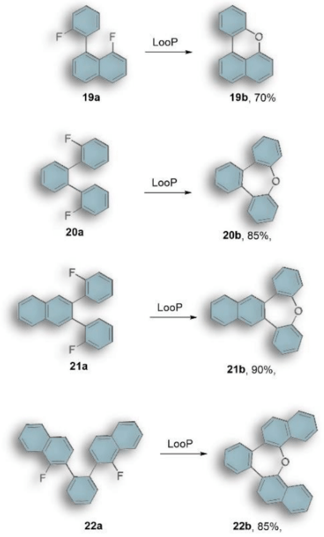


Figure 3. Synthesis of benzoannulated pyrans and oxepines.

To gain additional data, we have exposed the model substrate **23a** to the following reaction conditions. Thus, we have found that in the presence of 3 equiv. of *t*-BuOK, the reaction terminates at the formation of the 2-(tert-butoxy)-1,1'-biphenyl **23b**, which was isolated in 60% yield. Meanwhile, using 6 equiv. of *t*-BuOK, we isolated [1,1'-biphenyl]-2-ol in 93% yield (Scheme 1, A). These facts confirm that the transformation occurs via *tert*-butyl ethers. However, the mechanism of de-*tert*-butylation remained uncertain. Capturing the volatile products with bromine water, we have observed exclusively brominated acetone's derivatives. Since acetone is a typical product of *tert*-butoxyl radical degradation (Scheme 1, B)[64] and *t*-BuOK is a suitable reagent for single electron transfer (SET) reactions[65], we conclude the radical nature of de-*tert*-butylation. Presumably, *tert*-butoxyl radical abstracts hydrogen from the -$C(CH_3)_3$. In the absence of hydrogen donors the formed radical **1f** undergoes β-scission releasing isobutylene and radical **1g** which is reduced by the following SET. Isobutylene was not detected apparently due to the fast radical polymerization, which leads to the increased viscosity of the obtained reaction mixture.

The initiation step including the substitution of fluorine with *tert*-butoxide anion is the most crucial and at the same time intricate step. Despite low nucleophilicity of *t*-BuOK and its high basicity, aryne mechanism of the substitution is excluded due to the successful transformations of *ortho*-substituted substrates e.g. **3b** and **7b**. As mentioned earlier, *t*-BuOK can undergo SET and initiate $S_{RN}1$ type of reactions[66]. However, the absence of defluorinated products and dimers evidences against this mechanism. Meanwhile, deiodination and partial demethylation (in the cases of **4b**-**8b**) indicate the radical character of the reaction. The possibility of the alternative radical $S_{RN}2$ mechanism has been discussed elsewhere and is considered as an unlikely event due to charge repulsion and orbital arguments[67].

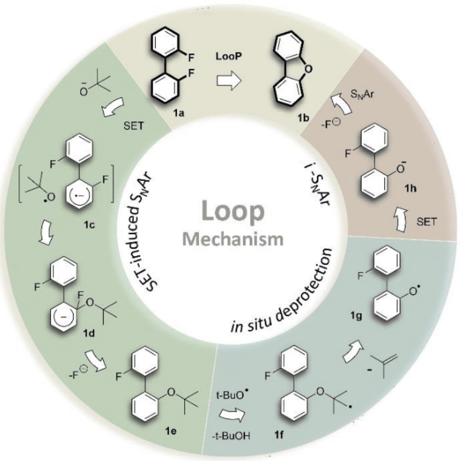
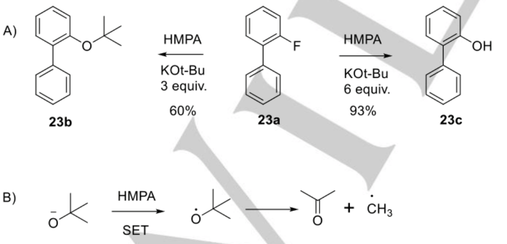


Figure 4. Suggested mechanism of dibenzofuran formation..

Having excluded these mechanisms we end up with the last possible radical pathway (See SI). SET to **1a** generates radical-anion **1c** that rapidly interacts with the formed *tert*-butoxyl radical within the solvent cage[68]. Although it is rather problematic to distinct this mechanism from classic S$_N$Ar, the successful substitution of fluorine in electron-rich molecules (**9a**), low nucleophilicity of *t*-BuOK, and stability of fluoroarene radical-anions [69] prove at least partial participation of the SET-induced S$_N$Ar pathway[70]. Moreover, it is impossible to exclude that both mechanisms occur independently since unlike common radical processes the intermediates cannot be quenched with common radical traps such as TEMPO[71]. This outcome was indeed observed in our experiment.



Scheme 1. A) Nucleophilic substitution of 2-fluorobiphenyl with *t*-BuOK. B) Radical degradation of *tert*-butoxyl radical.

In summary, we have developed a synthetic tool allowing the direct transformation of 2,2'-difluorinated biphenyl moiety into dibenzofuran fragment.. The reaction enables multiple annulations providing a facile pathway towards various ladder-type oxygen heteroacenes and dibenzofurans oligomers. Besides oxygen-containing pentagons, the possibility to obtain xanthene's and oxepine's derivatives has also been shown.

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Keywords: Ladderization• O-heteroacenes • dibenzofurans• xathenes • oxepins

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7. Summary

The main objective of this thesis was to develop new methods of synthesis of PAHs and hetero PAHs containing zigzag periphery. State of the art before starting the thesis was that synthesis of pristine 2D acenes did not have any achievements since the explorations of e. Clar in the middle of the 20th century, but his methods often can not be reproduced due to substantial amount of inseparable side products. Also, in the case of oxygen heteroacenes, no method could incorporate oxygen from an external source. In contrast, the simultaneous formation of a heterocycle could simplify the overall synthesis of complex carbon nanostructures. This summary briefly describes our achievements and observations made during the thesis fulfilment.

First of all, we developed a new technique called DPEX (dehydrative π-extension), which allows the formation of pristine zigzag periphery directly from the aldehyde group. The reaction proceeds in very mild conditions and turns into usefulness the biggest flaw of all pristine PAHs: low solubility. The starting material and all side products can be easily separated from the product via simple precipitation of the PAH. Simple preparation of precursors via Suzuki reaction allows the design of a big library of two-dimension angularly fused acenes, and the ability to carry out n-fold cyclizations does not have any foreseeable end. We have shown this approach, which we called modular, on the synthesis of 13 known and unknown 2D acenes and described the longest known example dianthra[2,1,9-jkl:2′,1′,9′-uva]pentacene. We described all molecules from the theoretical point of view and found a linear correlation between the experimental optical gap and diradical character. This finding will help to design another super interesting zigzag nanographenes.

Also, this reaction allows synthesizing PAHs with high biradical character, which leads to the low stability of the compounds. Nevertheless, we turned this ability to a useful tool for further π-extension. We developed the synthesis of violanthrenes and extended 5-helicenes via domino reaction consisting of DPEX and oxidative electrocyclization. During DPEX, we generated molecules with high biradical character (extended bisphenaneles) and, if the radicals are placed in the right spot, room temperature forbidden 6-π thermal electrocyclization occurred. Using Clar sexter theory, we were able to predict the outcome of the reaction and supported our predictions with DFT calculations.

Also, we developed a novel catalyst-free approach for O-heteroacenes from fluorinated oligophenylenes (ladderization of oligophenylenes, Loop). This reaction is relied on the external source of oxygen, i.e. potassium *tert* -butoxide, which served as an O^{2-} synthon. We showed the applicability of the method on 21 examples of O-heteroacenes, containing five-, six- and seven-member rings. Also, the reaction allows multiple annulations at once and opens the synthetic path to ladder-type O-heteroacenes and oligodibenzofurans. The reaction mechanism involves extremely rare SET-induced S_NAr on the first step and previously unknown radical cleavage of *tert*-butyl ethers, which allows to carry out the substitution even in the presence of strong electron-donating groups.

Overall, newly developed reactions (DPEX and LooP) open path to novel organic materials, have unusual mechanisms and show much room for the modification toward the synthesis of other zigzag nanographenes and heteroacenes.

8. Zusammenfassung

Das Hauptziel dieser Arbeit war die Entwicklung neuer Synthesemethoden für PAK und Hetero-PAK mit Zick-Zack-Peripherie. Stand der Technik vor Beginn der Arbeit war, dass die Synthese von unberührten 2D-Acenen seit den Untersuchungen von keine Erfolge hatte. Clar in der Mitte des 20 Jahrhunderts, aber seine Methoden können oft aufgrund der erheblichen Menge an untrennbaren Nebenprodukten nicht reproduziert werden. Auch im Fall von Sauerstoffheteroacenen konnte kein Verfahren Sauerstoff von einer externen Quelle einbauen. Im Gegensatz dazu könnte die gleichzeitige Bildung eines Hetero-PAK die Gesamtsynthese komplexer Kohlenstoffnanostrukturen vereinfachen. Diese Zusammenfassung beschreibt kurz unsere Erfolge und Beobachtungen, die während der Erfüllung der Arbeit gemacht wurden.

Zunächst entwickelten wir eine neue Technik namens DPEX (dehydrative π-extension), die die Bildung einer unberührten Zick-Zack-Peripherie direkt aus der Aldehydgruppe ermöglicht. Die Reaktion läuft unter sehr milden Bedingungen ab und wird zur Nützlichkeit des größten Fehlers aller unberührten PAK: geringe Löslichkeit. Das Ausgangsmaterial und alle Nebenprodukte können durch einfaches Ausfällen des PAK leicht vom Produkt getrennt werden. Die einfache Herstellung von Vorläufern über die Suzuki-Reaktion ermöglicht den Entwurf einer großen Bibliothek zweidimensionaler, eckig kondensierter Acene, und die Fähigkeit, n-fache Cyclisierungen durchzuführen, hat kein vorhersehbares Ende. Wir haben diesen Ansatz, den wir als modular bezeichneten, an der Synthese von 13 bekannten und unbekannten 2D-Acenen gezeigt und das längste bekannte Beispiel für Dianthra [2,1,9-jkl: 2 ', 1', 9'-uva] pentacen beschrieben. Wir haben alle Moleküle vom theoretischen Standpunkt aus beschrieben und eine lineare Korrelation zwischen der experimentellen optischen Lücke und dem diradikalen Charakter gefunden. Dieser Befund wird dazu beitragen, weitere super interessante Zick-Zack-Nanographene zu entwerfen.

Diese Reaktion ermöglicht auch die Synthese von PAK mit hohem biradikalischem Charakter, was zu einer geringen Stabilität der Verbindungen führt. Trotzdem haben wir diese Fähigkeit zu einem nützlichen Werkzeug für die weitere π-Erweiterung gemacht. Wir entwickelten die Synthese von Violanthrenen und verlängerten 5-Helicenen über eine Dominoreaktion, die aus DPEX und oxidativer Elektrocyclisierung besteht. Während der DPEX erzeugten wir Moleküle mit hohem biradikalischen Charakter (verlängerte Bisphenanele), und wenn die Radikale an der richtigen Stelle platziert wurden, trat bei

Raumtemperatur eine verbotene thermische 6-π-Elektrocyclisierung auf. Mithilfe der Clar-Sexter-Theorie konnten wir das Ergebnis der Reaktion vorhersagen und unsere Vorhersagen mit DFT-Berechnungen unterstützen.

Außerdem haben wir einen neuartigen katalysatorfreien Ansatz für O-Heteroacene aus fluorierten Oligophenylenen entwickelt (Ladderisierung von Oligophenylenen, Loop). Diese Reaktion beruht auf der externen Sauerstoffquelle, d. H. Kalium-tert.-butoxid, das als O2-Synthon diente. Wir haben die Anwendbarkeit der Methode an 21 Beispielen von O-Heteroacenen gezeigt, die fünf-, sechs- und siebengliedrige Ringe enthalten. Die Reaktion ermöglicht auch mehrere Annulationen gleichzeitig und eröffnet den Syntheseweg zu O-Heteroacenen und Oligodibenzofuranen vom Leitertyp. Der Reaktionsmechanismus beinhaltet extrem seltene SET-induzierte SNAr im ersten Schritt und eine bisher unbekannte radikalische Spaltung von tert-Butylethern, wodurch die Substitution auch in Gegenwart starker elektronenspendender Gruppen durchgeführt werden kann.

Insgesamt eröffnen neu entwickelte Reaktionen (DPEX und LooP) den Weg zu neuartigen organischen Materialien, weisen ungewöhnliche Mechanismen auf und zeigen viel Raum für Modifikationen zur Synthese anderer Zick-Zack-Nanographene und -Heteroacene.

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Eidesstattliche Erklärung

Hiermit erkläre ich, Mikhail Feofanov, die vorliegende Arbeit Rationale *Synthese von konjugierte Moleküle mit Zickzack-Peripherie* selbständig und ohne fremde Hilfe verfasst zu haben. Es wurden keine anderen als die von mir angegebenen Quellen und Hilfsmittel benutzt. Die den benutzten Werken wörtlich oder inhaltlich entnommenen Stellen sind als solche kenntlich gemacht worden. Ich erkläre, die Angaben wahrheitsgemäß gemacht, keine vergeblichen Promotionsversuche unternommen und keine Dissertation an einer anderen wissenschaftlichen Einrichtung zur Erlangung eines akademischen Grades eingereicht zu haben. Ich bin weder vorbestraft noch sind gegen mich Ermittlungsverfahren anhängig.

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