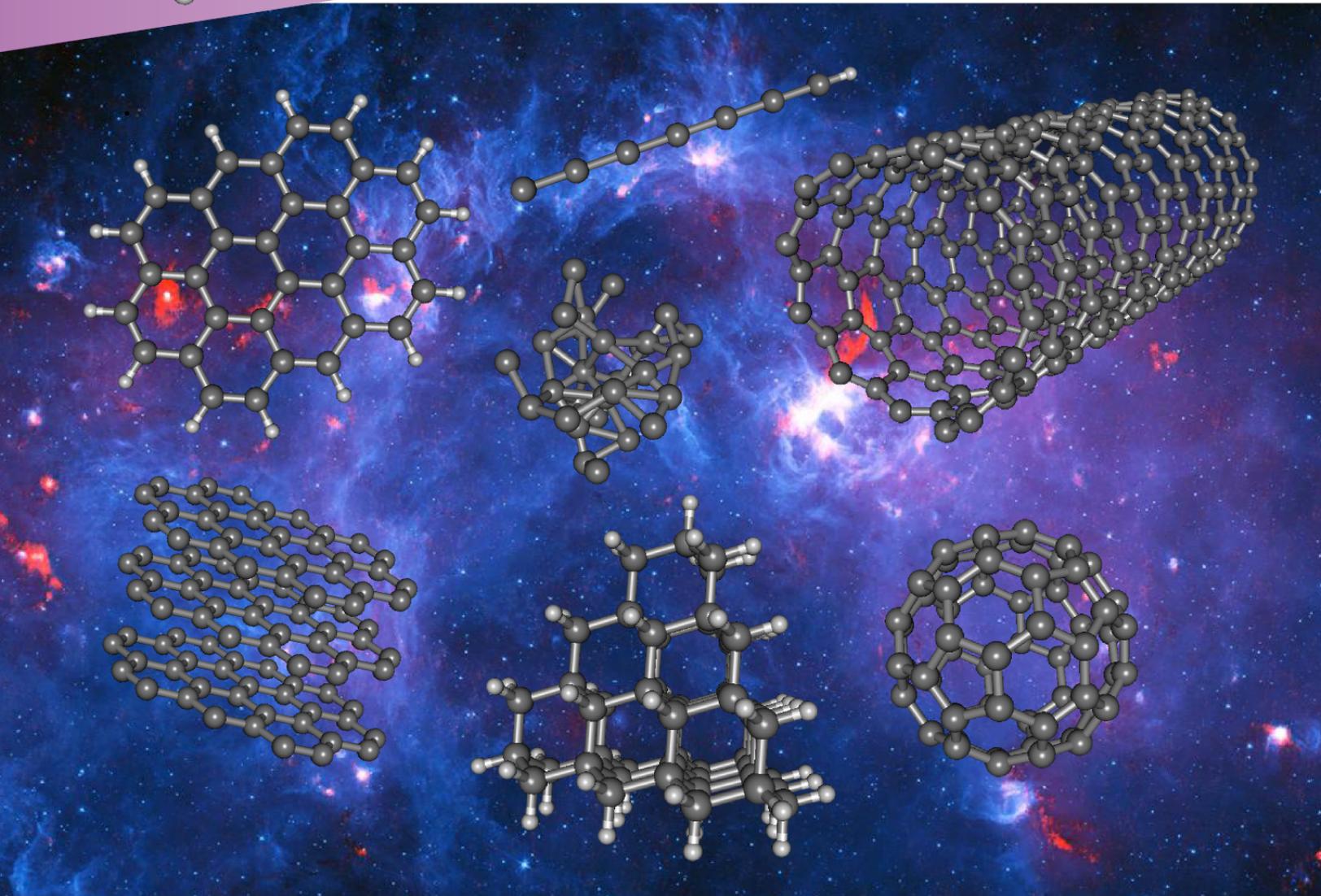


AstropAH

A Newsletter on Astronomical PAHs

Issue 47 | Apr 2018



FAMILY PORTRAIT

Editorial

Dear Colleagues,

Our April cover is illustrated with a collage of different hydrocarbon structures, in light of the diverse species presented in this issue. The In Focus section, presented by Xiao-Ye Wang, Akimitsu Narita and Klaus Müllen, introduces us to multiple new synthetic pathways for the production of large PAHs.

This month's collection of abstracts presents both PAH research and a broader look into the periphery of PAH research with theory on the treatment of out-of-plane motions, experiments on unimolecular reaction energies, predictions of adsorption and ionization energies of PAHs on water ice, ion implementation in nanodiamonds, study of photon flux in photochemical aerosol experiments, dust in supernovae and their remnants, and PAHs with straight edges and their band intensity ratios in reflection nebulae.

We would like to take this opportunity to repeat the news that the JWST cycle 1 proposal deadline has been postponed to early 2019. For those who ran out of time, you have another chance! Other news is the kick-off of the Dutch Astrochemistry Network II on Monday 23 April. We are happy with this follow-up of the successful DAN-I programme and look forward to new exciting studies.

Do you want to highlight your research, a facility or another topic, please contact us for a possible In Focus. Of course, do not forget to send us your abstracts! We also encourage you to send in your vacancies, conference announcements and more. For publication in the next AstroPAH, see the deadlines below.

The Editorial Team

**Next issue: 17 May 2018.
Submission deadline: 4 May 2018.**

AstroPAH Newsletter

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PAH Picture of the Month

Thanks to its valence, carbon can form many allotropes, and the cover celebrates some of them. Starting from the top left to the bottom right: polycyclic aromatic hydrocarbons, carbon chains, amorphous carbon, nanotubes, graphite, nanodiamonds and fullerenes. All of these allotropes, with the exception of nanotubes, are of interest to astronomy since they are detected in meteorites and or in the interstellar medium. Background: Composition of Galactic plane images as seen by APEX (the Atacama Pathfinder EXperiment), Spitzer Space Telescope, and Planck Space Telescope .

Credits: ESO/APEX/ATLASGAL consortium/
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A New Synthetic World of Large Polycyclic Aromatic Hydrocarbons

by Xiao-Ye Wang, Akimitsu Narita and Klaus Müllen

In this piece, we present new synthetic pathways to the production of PAHs, which have been developed and used in our laboratory since the mid 1990s.

1. Our entry into the PAH field

The chemistry of polycyclic aromatic hydrocarbons (PAHs) dates back to the 19th century, and it saw a remarkable peak in the middle of the 20th century due to the pioneering works of Erich Clar.¹ PAHs played a crucial role in the rise of modern organic chemistry and served as test cases for spectroscopy and molecular orbital theory methods. PAHs are regarded as somewhat “non-natural” and have often been considered from the angle of health risks. However, they have been deemed to be carriers of the infrared (IR) emission features that are observed from space, and have thus been attracting intense interest from the astronomical community.² At the beginning of the 21st century, PAHs also attracted renewed attention for their role in the studies of small cut-outs of graphene.³

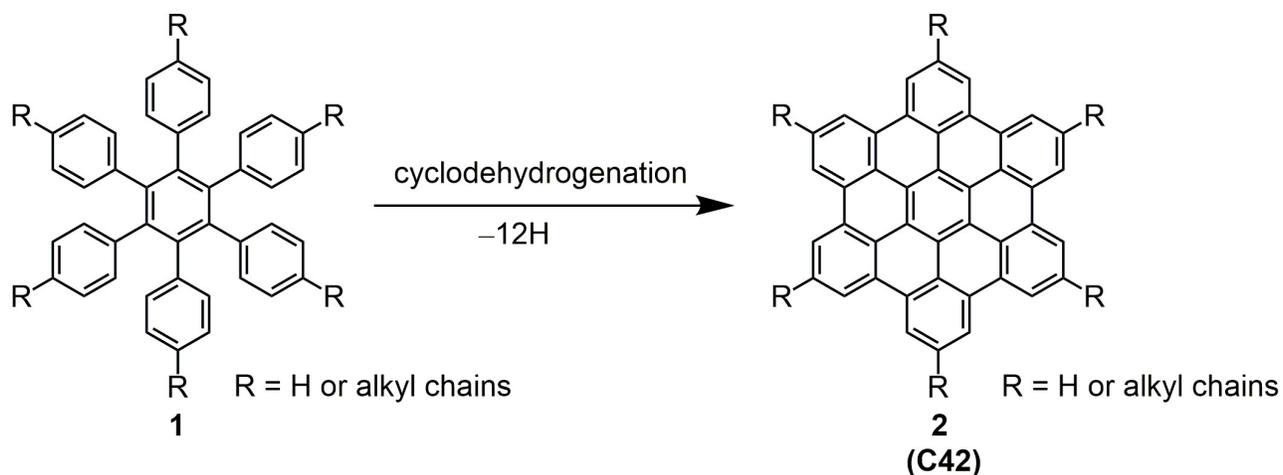
Graphene, as a monolayer of graphite, is a 2D π -system with unique electronic properties, and it is presently considered as a wonder material for various applications. As far as the electronic features of graphene are concerned, a major advantage is its high charge-carrier mobility, which makes graphene an attractive material for electronic applications. This advantage is somewhat obstructed by the lack of an electronic bandgap. Indeed, because a bandgap is necessary for the off-behavior of a field-effect transistor (FET), graphene cannot be used as an active component of FETs. To open the bandgap, a geometric confinement of graphene's 2D sheet structure as it occurs in the so-called graphene nanoribbons (GNRs) has been considered. These semiconductors are promising alternatives to silicon used in CMOS-technologies and can be made by top-down techniques. However, only the “reverse” procedure, their “bottom-up” synthesis from benzenoid precursors, offers the required structural precision, including defined edges and widths of the ribbons. This is where PAHs come into play.

Over the last decades, our group has been synthesizing larger and larger PAHs, beyond the classical cases of pyrene, coronene and triphenylene, for example, giving rise to PAHs that can now be called nanographenes. We have also been paving the way to the urgently sought GNRs.⁴ With the renaissance of PAH chemistry and physics in recent years, we and other organic chemists have not only provided impressively large PAHs, but we have also enriched the toolbox of classical PAHs between C₂₀ and C₆₀. We are continuously seeking the synthesis of novel PAHs and GNRs with unique structures, bringing about new optical, magnetic and charge transport properties by changing the sizes and topologies of the polycycles.

2. From “superbenzene” to small and large PAHs using mild graphitization

2.1. Hexa-*peri*-hexabenzocoronene (HBC or superbenzene)

Our own PAH story started in 1995 when we described the synthesis of hexa-*peri*-hexabenzocoronene (HBC), which consists of 42 sp² carbon atoms (thus also called C₄₂), as a hexaalkyl derivative (molecule **2** in Scheme 1).⁵ The resulting HBC (or C₄₂) molecule can be regarded as “superbenzene” due to its 6-fold symmetry axis. At the time, making larger and larger PAHs was difficult to achieve by the fusion of smaller disc-type structures. Instead, we introduced a kind of precursor route, in which we start from 3D-polyphenylenes with a twisted arrangement of benzenes. These are then subjected to a cyclodehydrogenation process with various chemical oxidants to flatten the precursor toward the targeted PAH. The readily available precursor here is hexaphenylbenzene (molecule **1** in Scheme 1) with a propeller arrangement of the phenyl groups, which can easily be converted to HBC (molecule **2** in Scheme 1) with high efficiency. This process can be considered as a kind of “graphitization” at room temperature.



Scheme 1: Synthetic route from hexaphenylbenzene (molecule **1**) to hexa-*peri*-hexabenzocoronene (HBC, C₄₂, or molecule **2**).

HBC molecules without substituents can be sublimed, but they are hardly soluble in organic solvents. Solubility can be brought about by attaching alkyl chains, which has two important consequences:

1. The resulting sheet gives rise to liquid crystalline phases with columnar supramolecular structures consisting of stacks of discs. Such columns can then serve as a channel for the transport of charges for which a regular order is particularly favorable.
2. The physisorption of alkyl-substituted HBC from solution onto graphite or other substrates becomes possible. This produces ordered monolayers from which single molecules can be visualized in real space by Scanning Tunneling Microscopy (STM). The alkyl chains deposited along the symmetry axes of graphite serve as a kind of adhesive. The ability to “see” the actual shape of a nm-sized molecule without working in reciprocal space and without demanding ultrahigh-vacuum (UHV) techniques is a remarkable and enlightening step for a chemist. Further, modification of the experiment has allowed Scanning Tunneling Spectroscopy (STS) to be used, providing current-potential curves for a single molecule and thus offering an entry into nanoelectronics.

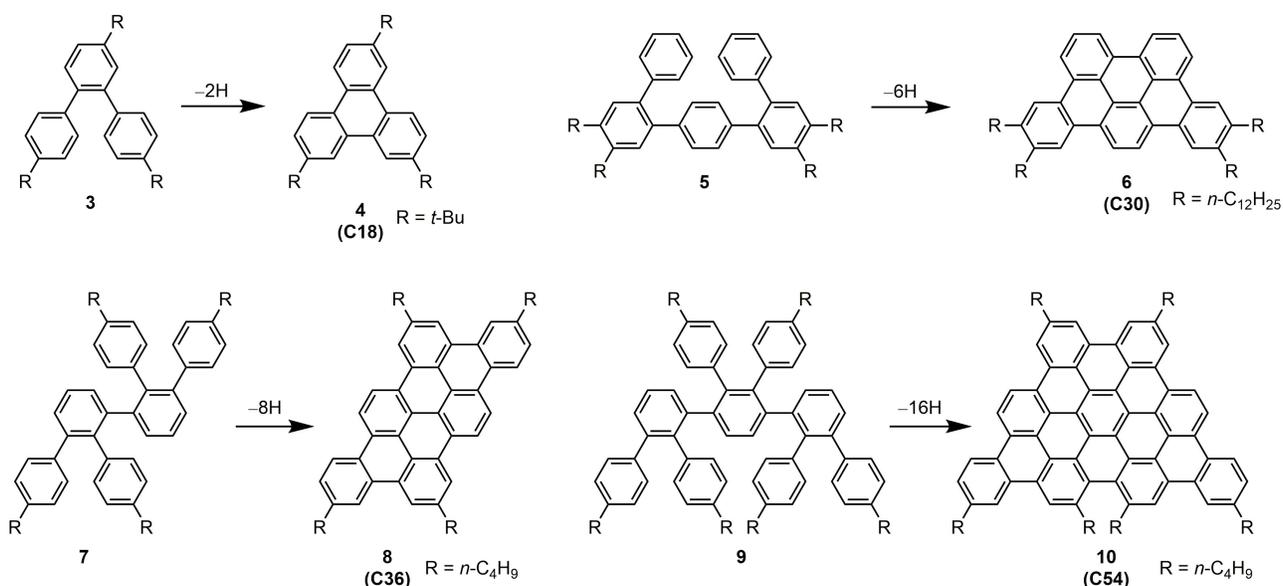
Processable HBCs have played a key role in the development of bulk heterojunction solar cells. They have showed the crucial role of supramolecular order and nanophase separation between donor and acceptor components. There are other cases where the casting of films from solution is used without the need for any supramolecular order. This technique has led to a cheap and non-invasive method of diagnosing lung tumors or neurological diseases from respiration.⁶

From the chemistry point of view, alkyl-substituted PAHs are more often preferred than the unsubstituted ones, as the former have a higher solubility, which is important for purification and characterizations, and allows for broader applications. **In the astronomical context, PAH models often consider unsubstituted PAHs as the carriers for the unidentified IR emission bands. However, recent studies have also suggested that astronomical PAHs might have aliphatic components.⁷ In this regard, synthetic PAHs with alkyl substitutions are potentially valuable for astrophysical investigations.**

2.2. Variations from HBC to smaller or larger PAHs

Starting from HBC, synthetic variations are possible by the oxidative flattening of polyphenylene precursors to make PAHs both smaller and larger than HBC, as shown in Scheme 2. Thus, *ortho*-terphenyl (molecule **3**) can be transformed into triphenylene (molecule **4**).⁸ Likewise, a slight modification of the precursor molecules produces C30 (**6**),⁹ as well as the dimerized and trimerized products C36 (**8**) and C54 (**10**), as shown in Scheme 2.¹⁰

The fabrication of HBC, or superbene, has led to the synthesis of “superacenes”, e.g. “supernaphthalene” C72 (PAH molecule **12**), and “supertriphenylene” C132 (PAH molecule **14**), via cyclodehydrogenation of their corresponding twisted precursors, as shown in Scheme 3.¹¹ Even more remarkable has been the extension in size via the D_{6h} -manifold which enabled the synthesis of C222 (PAH molecule **16**).¹² It is noteworthy to mention here that the precursor molecule **15** is nothing else but a dendrimer, a 3D-macromolecule only consisting of benzene

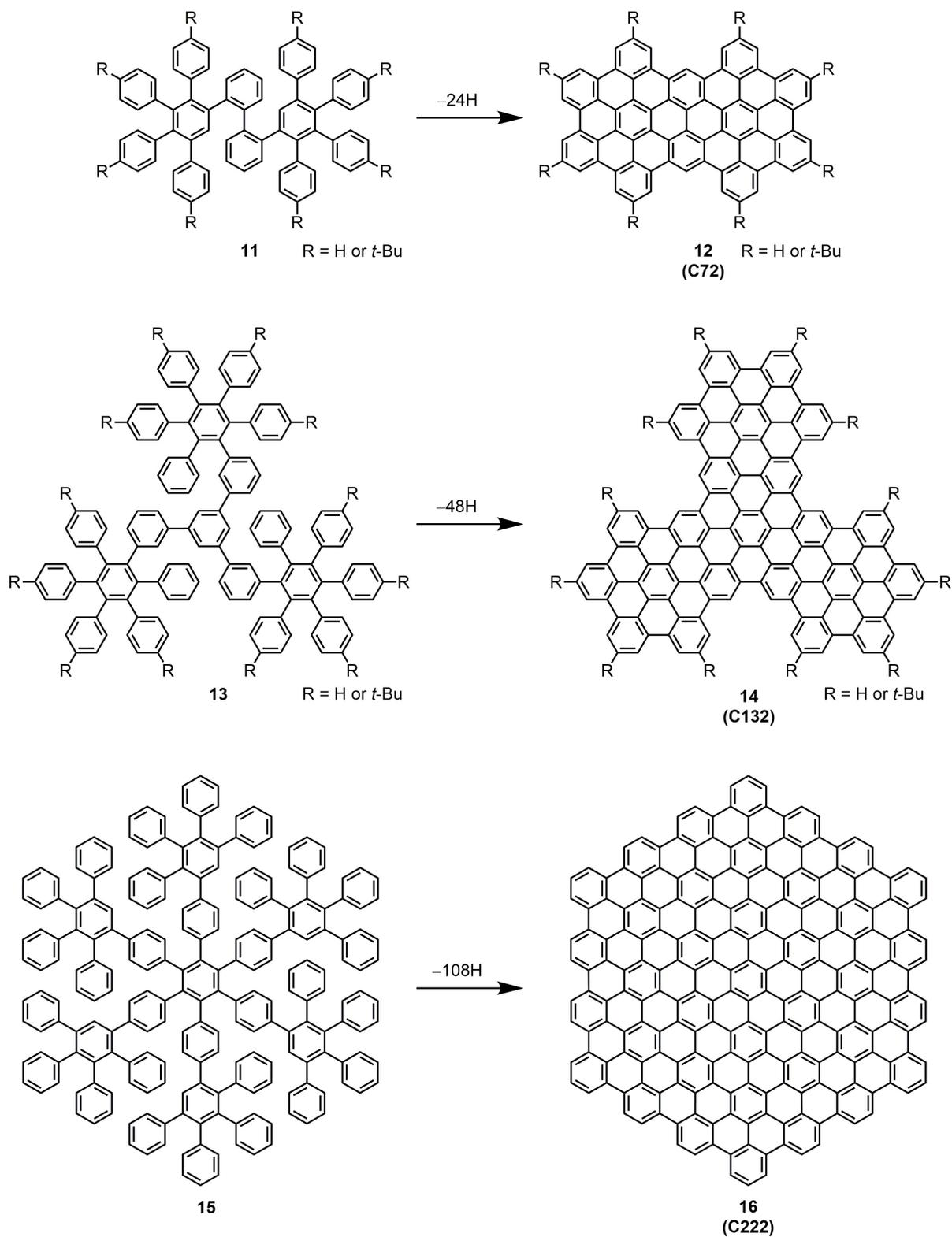


Scheme 2: Synthesis of triphenylene-based PAHs from tailor-made polyphenylenes.

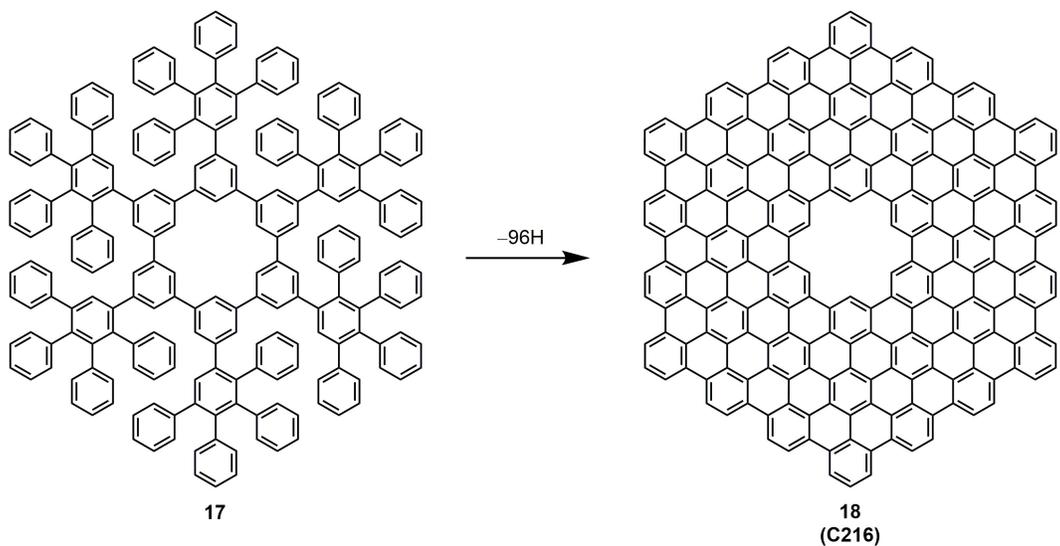
rings. Its single-crystal structure provides firm evidence for the twisted arrangement of its benzene moieties.¹³

It should be emphasized that these PAHs, while becoming readily available due to the elegant and straightforward precursor routes, are pure and structurally defined compounds. This is important since nanostructured carbon materials, in particular when fabricated by rather harsh “cook-and-bake” procedures, often lack structural precision. The power of this synthetic protocol is supported nicely by the synthesis of C216 (PAH molecule **18**) (cf. Scheme 4).¹⁴ C216 is formally derived from C222 (PAH molecule **16**) by cutting a hole in the middle of the molecule. Holey graphenes have acquired a great significance in graphene research for tuning electronic and mechanical properties. While Raman spectroscopy is generally of great value to assess the quality of graphene materials, in the case of holey C216, the analysis by means of IR spectroscopy allows one to discriminate between inner and outer hydrogens.

Not surprisingly, such large PAHs without substitutions are insoluble in organic solvents. A simple chemical chlorination of the PAHs with iodine chloride affords perchlorinated derivatives. Due to their ring puckering, a result of steric hindrance between chloro substituents, they are soluble and can be subjected to single-crystal growth.¹⁵ From the crystal structures of the colorful nanographene derivatives one not only learns about the characteristic bond length alternation of graphenic species but also about their packing in the solid state (cf. Figure 1).



Scheme 3: Synthesis of large PAHs (C72, C132, and C222) via cyclodehydrogenation of corresponding polyphenylene precursors.



Scheme 4: Synthesis of a structurally defined holey PAH C216 via the precursor route.

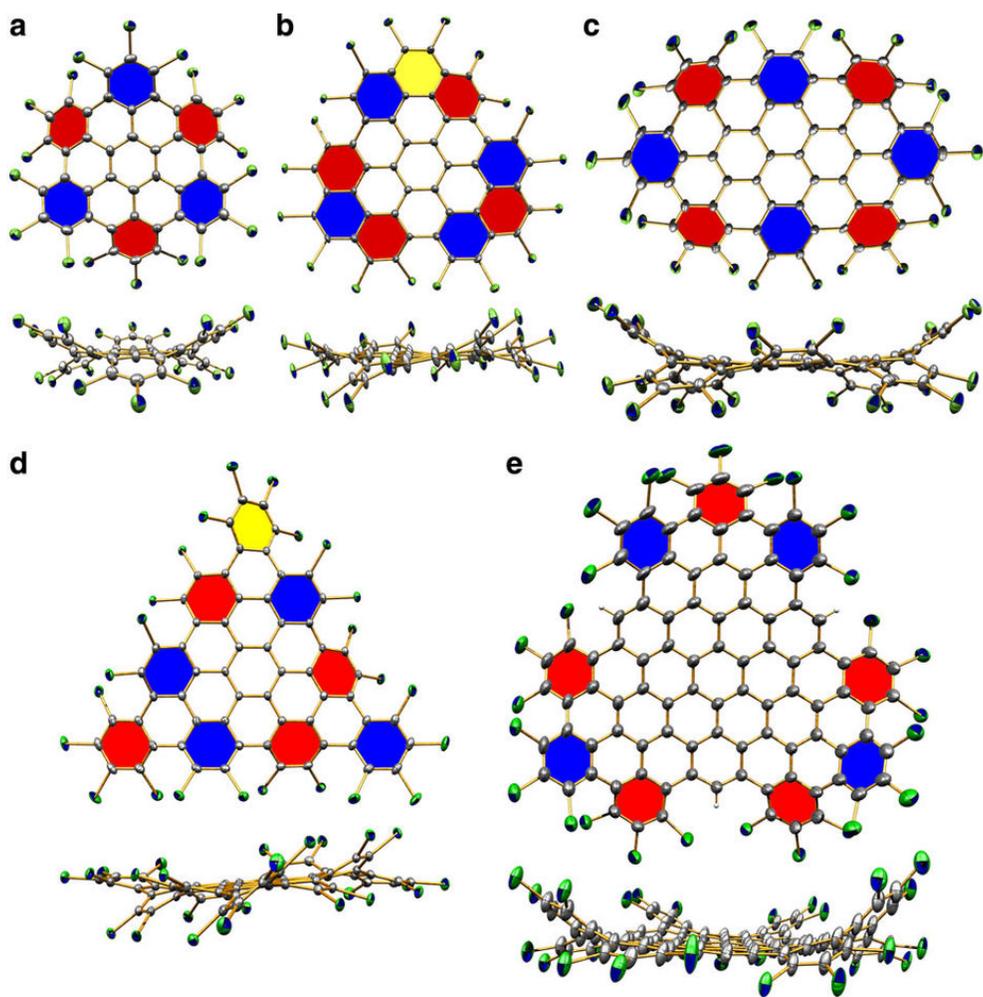
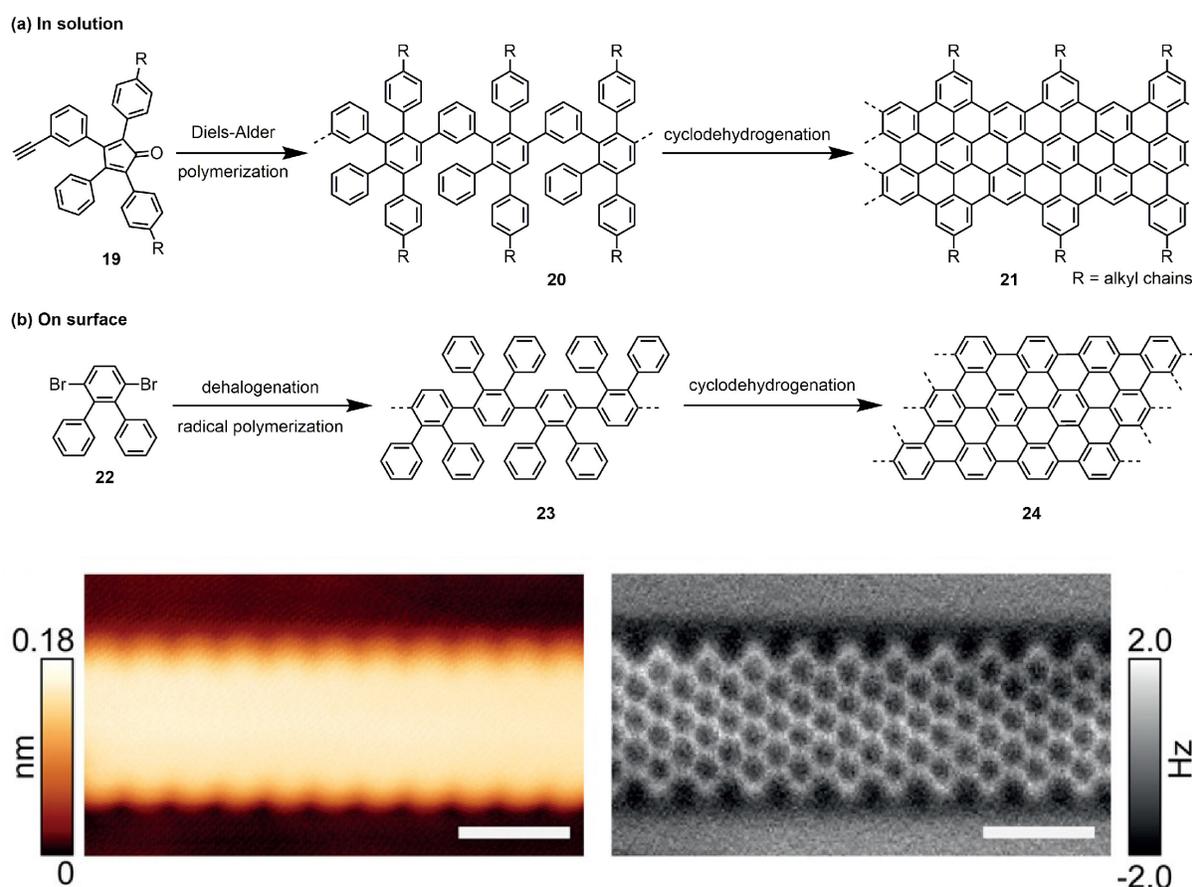


Figure 1: Single-crystal structures of (a) $C_{42}Cl_{18}$; (b) $C_{48}Cl_{18}$; (c) $C_{60}Cl_{22}$; (d) $C_{60}Cl_{24}$; and (e) $C_{96}Cl_{27}H_3$. Reprinted with permission from ref.15.

2.3. Synthesizing graphene nanoribbons (GNRs)

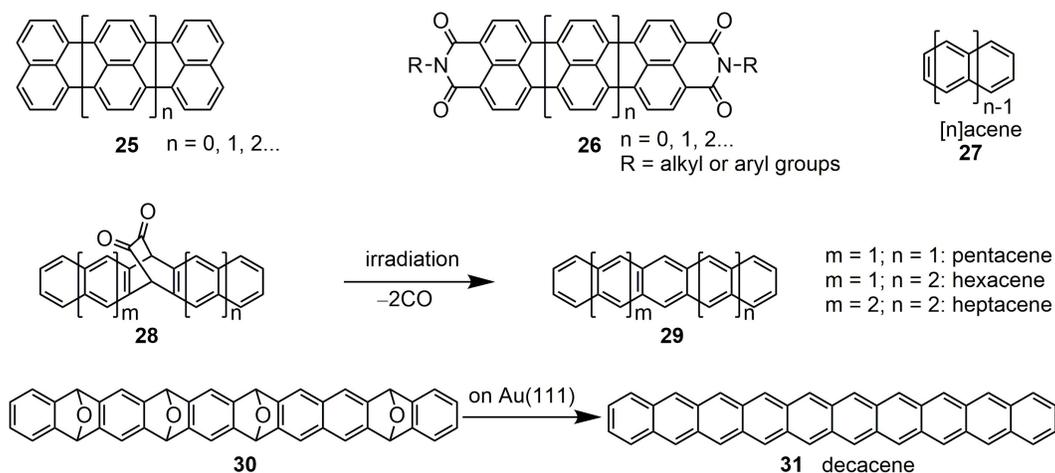
The readers might welcome information on the synthesis of new PAHs and the underlying chemistry, but they still tend to restrict their attention to the molecules that might exist in the interstellar space. The exercise of covering different sizes of PAHs and the bottom-up synthesis of graphenes cannot be concluded, however, without mentioning graphene nanoribbons (GNRs) like GNR **21** (cf. Scheme 5). GNR **21** is made using the same synthetic concepts as above and comes as solution processable ribbons up to 600 nm in length.¹⁶ Even more remarkable is the fact that GNRs are not only accessible by classical solution synthesis but also by immobilizing suitable aromatic precursor monomers (e.g. **22**) on metal surfaces, followed by heat-induced polymerization and cyclodehydrogenation (cf. Scheme 5).¹⁷ Remarkably enough, by designing the right monomers, the bandgaps of the semiconductor GNRs can be precisely tuned. Further, it now becomes possible to monitor the progress of the reaction, the perfection of the GNRs and their electronic characteristics by STM and STS.¹⁸



Scheme 5: Top: In-solution (a) and on-surface (b) synthesis of graphene nanoribbons (GNRs). Bottom: Scanning Tunneling Microscopy (STM) images (left), and non-contact Atomic Force Microscopy (nc-AFM) images (right) of GNR **24**. Scale bar: 1 nm. Reprinted with permission from ref.17.

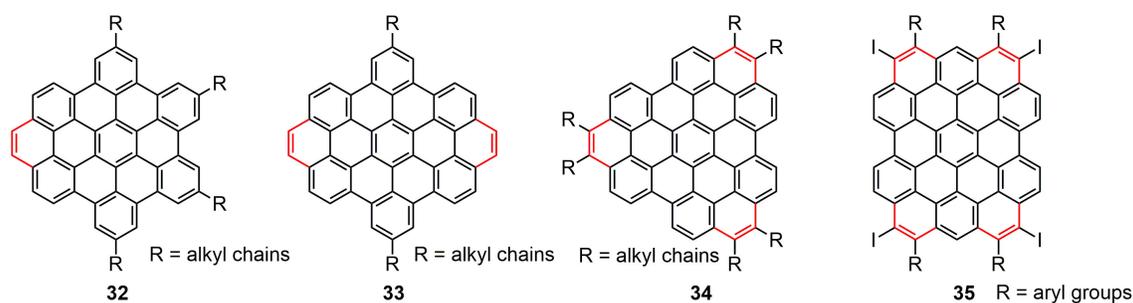
3. Varying the topologies and edge structures of PAHs

Beyond his other contributions, Erich Clar developed the classification of PAHs according to their topology, that is, the fusion mode of the benzenoid subunits. Triphenylene (molecule **4** in Scheme 2) and HBC (molecule **2** in Scheme 1) belong to the group of PAHs with “Clar’s aromatic π -sextets” (defined as six π -electrons localized in a single benzene-like ring separated from adjacent rings by formal CC single bonds), which are characterized by high chemical stability and large energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Other topologies, such as that of “rylenes” (molecule **25**) and of [n]acenes (molecule **27**), are characterized by reduced chemical stability and smaller HOMO-LUMO gaps (cf. Scheme 6). For both families, much effort has been made on varying their sizes and building up homologous series. It should be noted that rylene hydrocarbons can be stabilized by attaching auxochromic groups at their *peri*-positions yielding a whole new class of chromophores (molecule **26** in Scheme 6) which have not only served as industrial colorants but also as unique chromophores for bioimaging, organic optoelectronic devices, and single-molecule spectroscopy. Pentacene (PAH molecule **27**, $n = 5$) is an intensively studied semiconductor whose application greatly suffers from its high sensitivity to oxidation. Another type of precursor route has therefore been introduced, in which a series of higher acenes (**29**) are obtained in matrices by photochemical extrusion of bridging groups from molecules **28**.¹⁹ In a similar way, octacene (**27**, $n = 8$) and nonacene (**27**, $n = 9$) have been achieved.²⁰ This concept has even been used for the synthesis of the highest homologue decacene (**31**) where, as an additional concept, surface-bound chemical reactions have been employed.²¹



Scheme 6: Structures of rylene diimides, as well as acenes, and a generation of higher acenes via extrusion of bridging units in the precursors.⁷

Returning to the prototypic HBC (molecule **2**), a fine-tuning of the electronic structure becomes possible by going beyond the Clar-sextet case and fusing additional benzene rings such as in PAH molecules **32**, **33** and **34**. An exemplary case is HBC with four additional K-regions (molecule **35**), namely isolated C2 units that do not belong to the Clar sextet (highlighted in red in Scheme 7). Here again, the last step of its synthesis is a dehydrogenation of a twisted polyphenylene precursor, the synthesis of which cannot be described in detail here.²²

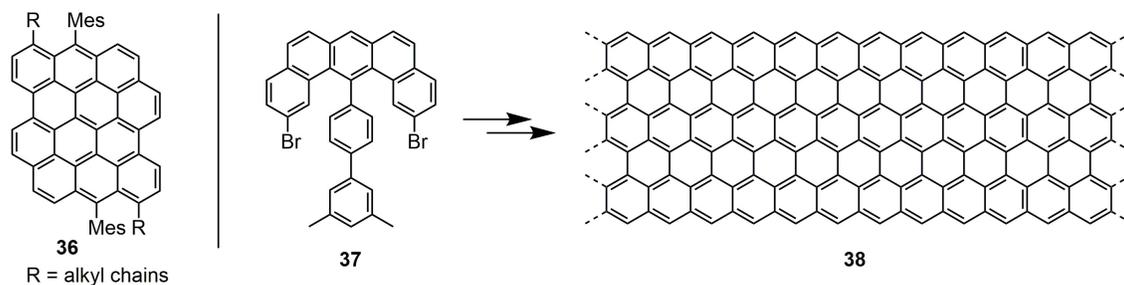


Scheme 7: Chemical structures of HBC derivatives with additional K-regions (marked in red).

There are synthetic schemes available which combine CC-bond formation via ring closure of phenyl groups, so-called electrocyclic reactions, with another type of bond formation, namely that between (functionalized) methyl groups and neighboring phenyl rings. This combined approach has made available unique PAHs such as PAH molecule **36** (cf. Scheme 8).²³ The latter product is a useful chromophore demonstrating stimulated emission upon laser excitation and thus holding promise for organic lasing. Such ring closure has also been employed in a remarkable synthesis of GNRs such as zigzag GNR **38** (Scheme 8). It must be noted that this ribbon possesses zigzag peripheries which lead to edge-localized electronic states with associated spins.²⁴ While the dramatic consequences of this mode of PAH synthesis cannot be further described here, it should also be noted that the edge structure of GNRs such as **24** is called armchair. The armchair GNRs possess quite large bandgaps, contrary to zigzag GNRs. This characteristic is also different from carbon nanotubes where armchair edges give rise to metallic behaviors.

Reported examples of PAHs and GNRs featuring long zigzag edges are scarcer than their armchair-edged counterparts. The reason not only lies in the synthetic challenges but also relates to the high instability of zigzag-edged structures, which may only survive under UHV conditions and need bulky protecting groups under ambient environments. Thus, the availability of such compounds from synthetic chemists is strongly limited, although zigzag-edged PAHs are more often targets of theoretical studies and are apparently attracting greater interests in the astronomical community.²⁵ **This situation calls for a close collaboration between synthetic chemists and astrophysicists to tackle the challenge together.** For example, generation of such ambient-unstable PAHs from stable precursors under the experimental setup of astrophysicists and in situ characterization of the spectroscopic properties could be a solution to this problem. On the other hand, synthetic chemists can provide a larger variety of PAH structures that have never been considered in the astronomical community, but might still be relevant for the interstellar compounds.

Screening further exciting PAH structures, many conventional PAHs exist with fused five-membered rings, so-called cyclopenta derivatives. The five-membered ring can have a $-\text{CH}_2-\text{CH}_2-$ or a $-\text{CH}=\text{CH}-$ unit, whereby the latter provides a fully unsaturated but non-benzenoid hydrocarbon. The isomeric C₁₀ pair of (non-colored) naphthalene (**39**) and (blue) azulene (**40**) is a classical case. Also characteristic is the group of pyrene (**41**) and its three isomers dicyclohepta[*cd,gh*]pentalene (**42**), dicyclopenta[*ef,kl*]heptalene (**43**), and acepleiadylene (**44**) (cf. Figure 2), the latter of which is a deep-red chromophore as opposed to the non-colored benzenoid pyrene. This situation is depicted by the notion of alternating vs. non-alternating



Scheme 8: The structure of zigzag-edged PAH **36** and synthesis of zigzag GNR **38** from carefully designed precursor **37**.

PAHs. Yet another structure is formed when five- (or seven-) membered rings are located inside the polycycle and thus surrounded by benzene rings. This mode of fusion can lead to bowl-shaped structures, with corannulene (molecule **45**) probably being the most instructive case. We have made a number of PAHs with incorporated five-membered rings such as **46**.²⁶ These can not only lead to pronounced deviations from flat disc structures but also deeply change the electronic situations.

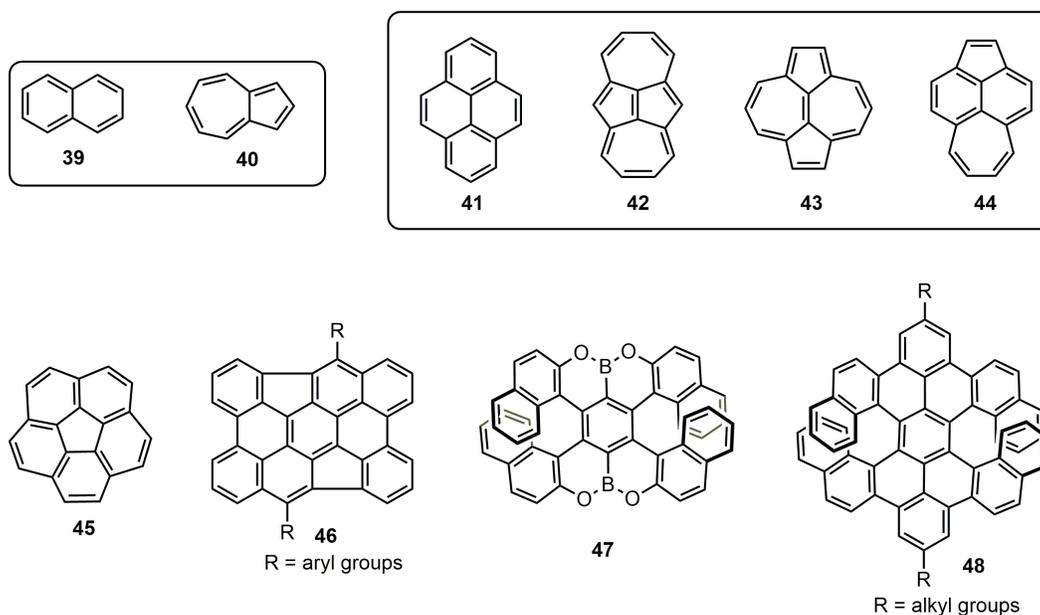


Figure 2: PAHs containing non-benzenoid rings and chirality resulting in double (hetero)helicenes.

Another interesting type of PAH is helicenes, which comprise *ortho*-fused benzene rings and possess helical chirality. There is abundant literature and accumulated knowledge for the chemistry of helicenes, but as far as we know, they are seldom considered in the astronomical context. We have recently pursued the synthesis of unprecedented double [7]helicenes, which have two fused monohelicenes sharing a common ring. We have achieved the first double [7]heterohelicene (**47**) by incorporation of oxygen-boron-oxygen (OBO) units at the peripheries²⁷ and the first purely hydrocarbon double [7]helicene (**48**) as new synthetic records in the field of helicenes (cf. Figure 2).²⁸ They are potential candidates for chiroptical applications. One may ask

if helicenes and/or other PAHs with chirality, which is important to life on earth, also exist in space. In this sense, the helical PAHs might prove valuable for experimentally looking into this interesting aspect.

4. Future perspectives

The present overview over recent advances in PAH chemistry and their newly derived physical properties was intended to demonstrate the unbelievable breadth of the field and the existing challenges that remain. It is exciting to see that methods of synthesis have been improved and the characterization techniques have largely advanced. **It is imperative to emphasize the importance of collaboration between the organic chemistry and astronomical communities that are necessary to tackle the highly interdisciplinary question about the interstellar PAHs.** The synthetic world of PAHs is rapidly growing, continuously providing various types of new structures. Recently, chemists have been focusing more on the materials aspects of PAHs, but it might be that now is the time when organic chemistry can again contribute to the development of astrophysics.



Xiao-Ye Wang received his Bachelor's degree in Chemistry from Nankai University in 2009. Then he became a graduate student in Professor Jian Pei's group at Peking University and obtained his PhD degree in Organic Materials Chemistry in July 2014. Afterwards he joined the group of Professor Klaus Müllen at the Max Planck Institute for Polymer Research (MPIP) for postdoctoral research, during which he was supported by the Alexander von Humboldt Foundation for two years. His research interests include organic electronic materials and devices as well as bottom-up synthesis of heteroatom-doped graphene molecules and graphene nanoribbons.

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Akimitsu Narita received his Bachelor's (2008) and Master's (2010) degrees in Chemistry at the University of Tokyo under the supervision of Professor Eiichi Nakamura. In March 2014, he obtained his PhD in the group of Professor Klaus Müllen at the Max Planck Institute for Polymer Research (MPIP) in Mainz. He was an Early-Stage Researcher in the Marie-Curie Initial Training Network (ITN) "SUPERIOR" for three years starting in May 2010. Beginning in August 2014, he became a project leader at MPIP. His current research focuses on the bottom-up synthesis of functional graphene molecules and graphene nanoribbons.

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Klaus Müllen received his PhD in 1972 at the University of Basel (Professor F. Garson) after completing his Diploma in Chemistry at the University of Cologne (Professor E. Vogel) in 1969. He pursued postdoctoral research in the group of J. F. M. Oth at ETH Zurich, where he received his habilitation in 1977 and was appointed a Privatdozent. In 1979, he became a Professor in Organic Chemistry at the University of Cologne and accepted an offer to become a chair in Organic Chemistry at the University of Mainz in 1983. In 1989, he became a scientific member of the Max Planck Society and the director of the Synthetic Chemistry Department at the Max Planck Institute for Polymer Research (MPIP). Since 2016, he has been the leader of an emeritus group at MPIP. His current research focuses on synthetic macromolecular chemistry, supramolecular chemistry, and materials science.

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Abstracts

Overcoming the Failure of Correlation for Out-of-Plane Motions in a Simple Aromatic: Rovibrational Quantum Chemical Analysis of $c\text{-C}_3\text{H}_2$

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Truncated, correlated, wave function methods either produce imaginary frequencies (in the extreme case) or non-physically low frequencies in out-of-plane motions for carbon and adjacent atoms when the carbon atoms engage in π bonding. Cyclopropenylidene is viewed as the simplest aromatic hydrocarbon, and the present as well as previous theoretical studies have shown that this simple molecule exhibits this behavior in the two out-of-plane bends (OPBs). This non-physical behavior has been treated by removing nearly linear dependent basis functions according to eigenvalues of the overlap matrix, by employing basis sets where the *spd* space saturation is balanced with higher angular momentum functions, by including basis set superposition/incompleteness error (BSSE/BSIE) corrections, or by combining standard correlation methods with explicitly-correlated methods to produce hybrid potential surfaces. However, this work supports the recently described hypothesis that the OPB problem is both a method and a basis set effect. The correlated wavefunction's largest higher-order substitution term comes from a $\pi \rightarrow \pi^*$ excitation where constructive interference of both orbitals artificially stabilizes OPB. By employing schema to overcome this issue, the symmetric OPB ν_9 is predicted to be the second-brightest transition, and it will be observed very close to 775 cm^{-1} . However, more work from the community is required to formulate better how carbon atoms interact with their adjacent atoms in π -bonded systems. Such bonds are ubiquitous in all of chemistry and beyond.

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Unimolecular Reaction Energies for Polycyclic Aromatic Hydrocarbon Ions

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Imaging photoelectron photoion coincidence spectroscopy was employed to explore the unimolecular dissociation of the ionized polycyclic aromatic hydrocarbons (PAHs) acenaphthylene, fluorene, cyclopenta[*d, e, f*]phenanthrene, pyrene, perylene, fluoranthene, dibenzo[*a, e*]pyrene, dibenzo[*a, l*]pyrene, coronene and corannulene. The primary reaction is always hydrogen atom loss, with the smaller species also exhibiting loss of C₂H₂ to varying extents. Combined with previous work on smaller PAH ions, trends in the reaction energies (E_0) for loss of H from sp²-C and sp³-C centres, along with hydrocarbon molecule loss were found as a function of the number of carbon atoms in the ionized PAHs ranging in size from naphthalene to coronene. In the case of molecules which possessed at least one sp³-C centre, the activation energy for the loss of an H atom from this site was 2.34 eV, with the exception of cyclopenta[*d, e, f*]phenanthrene (CPP) ions, for which the E_0 was 3.44 ± 0.86 eV due to steric constraints. The hydrogen loss from PAH cations and from their H-loss fragments exhibits two trends, depending on the number of unpaired electrons. For the loss of the first hydrogen atom, the energy is consistently ca. 4.40 eV, while the threshold to lose the second hydrogen atom is much lower at ca. 3.16 eV. The only exception was for the dibenzo[*a, l*]pyrene cation, which has a unique structure due to steric constraints, resulting in a low H loss reaction energy of 2.85 eV. If C₂H₂ is lost directly from the precursor cation, the energy required for this dissociation is 4.16 eV. No other fragmentation channels were observed over a large enough sample set for trends to be extrapolated, though data on CH₃ and C₄H₂ loss obtained in previous studies is included for completeness. The dissociation reactions were also studied by collision induced dissociation after ionization by atmospheric pressure chemical ionization. When modeled with a simple temperature-based theory for the post-collision internal energy distribution, there was reasonable agreement between the two sets of data.

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Dust in Supernovae and Supernova Remnants I: Formation Scenarios

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Supernovae are considered as prime sources of dust in space. Observations of local supernovae over the past couple of decades have detected the presence of dust in supernova ejecta. The reddening of the high redshift quasars also indicate the presence of large masses of dust in early galaxies. Considering the top heavy IMF in the early galaxies, supernovae are assumed to be the major contributor to these large amounts of dust. However, the composition and morphology of dust grains formed in a supernova ejecta is yet to be understood with clarity. Moreover, the dust masses inferred from observations in mid-infrared and submillimeter wavelength regimes differ by two orders of magnitude or more. Therefore, the mechanism responsible for the synthesis of molecules and dust in such environments plays a crucial role in studying the evolution of cosmic dust in galaxies. This review summarises our current knowledge of dust formation in supernova ejecta and tries to quantify the role of supernovae as dust producers in a galaxy.

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Dust in Supernovae and Supernova Remnants II: Processing and Survival

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Observations have recently shown that supernovae are efficient dust factories, as predicted for a long time by theoretical models. The rapid evolution of their stellar progenitors combined with their efficiency in precipitating refractory elements from the gas phase into dust grains make supernovae the major potential suppliers of dust in the early Universe, where more conventional sources like Asymptotic Giant Branch (AGB) stars did not have time to evolve. However, dust yields inferred from observations of young supernovae or derived from models do not reflect the net amount of supernova-condensed dust able to be expelled from the remnants and reach the interstellar medium. The cavity where the dust is formed and initially resides is crossed by the high velocity reverse shock which is generated by the pressure of the circumstellar material

shocked by the expanding supernova blast wave. Depending on grain composition and initial size, processing by the reverse shock may lead to substantial dust erosion and even complete destruction. The goal of this review is to present the state of the art about processing and survival of dust inside supernova remnants, in terms of theoretical modelling and comparison to observations.

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Theoretical determination of adsorption and ionisation energies of polycyclic aromatic hydrocarbons on water ice

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In dense interstellar environments, Polycyclic Aromatic Hydrocarbons (PAHs) are likely to condense onto or integrate into water ice mantles covering dust grains. Understanding the role of ice in the photo-induced processes involving adsorbed PAHs is therefore a key issue in astrochemistry. This requires -(i)- the knowledge of PAH-ice interactions, i.e. PAH-ice adsorption energies and local structures at the PAH-ice interface, as well as -(ii)- the understanding of the fate of electrons in the PAH-ice system upon excitation. Regarding -(i)-, in this work, we determined the lowest energy structures of PAH-ice systems for a variety of PAHs ranging from naphthalene to ovalene on three types of ice crystalline (Ih and Ic) and amorphous (low density) using an explicit description of the electrons and a finite-sized system. The electronic structure was determined using the Self Consistent Charge Density Functional based Tight Binding (SCC-DFTB) scheme with modified Mulliken charges in order to ensure a good description of the studied systems. Regarding -(ii)-, the influence of the interaction with ice on the Vertical Ionisation Potentials (VIPs) of the series of PAHs was determined using the constrained SCC-DFTB scheme benchmarked against correlated wavefunction results for PAH-(H₂O)_n (*n*=16,13) clusters. The results show a deviation equal, at most, to ~ 1.4 eV of the VIPs of PAHs adsorbed on ice with respect to the gas phase values. Our results are discussed in the light of experimental data and previous theoretical studies.

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Ion implantation in nanodiamonds: size effect and energy dependence

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Nanoparticles are ubiquitous in nature and are increasingly important for technology. They are subject to bombardment by ionizing radiation in a diverse range of environments. In particular, nanodiamonds represent a variety of nanoparticles of significant fundamental and applied interest. Here we present a combined experimental and computational study of the behaviour of nanodiamonds under irradiation by xenon ions. Unexpectedly, we observed a pronounced size effect on the radiation resistance of the nanodiamonds: particles larger than 8 nm behave similarly to macroscopic diamond (i.e. characterized by high radiation resistance) whereas smaller particles can be completely destroyed by a single impact from an ion in a defined energy range. This latter observation is explained by extreme heating of the nanodiamonds by the penetrating ion. The obtained results are not limited to nanodiamonds, making them of interest for several fields, putting constraints on processes for the controlled modification of nanodiamonds, on the survival of dust in astrophysical environments, and on the behaviour of actinides released from nuclear waste into the environment.

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Variation in photon flux during extended photochemical aerosol experiments: Implications for atmospheric laboratory simulations

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In order to simulate the interaction of sunlight with planetary atmospheres, including Pluto, Titan and the early Earth, many laboratory studies have used high-power broadband lamps with spectral features that extend into the vacuum-ultraviolet (VUV, <200nm) to initiate photochemistry relevant to the atmosphere of interest. In many cases, experiments are run on the order of hundreds of hours with no accounting for how the photon flux within the system may be evolving with lamp age or a possible buildup of films over optical surfaces when working with high-yield photochemical systems. Given that the nature of photochemistry depends on the ratio of photons to reactants, variations in flux must be taken into account if the system is to be fully understood. In this study, standard N₂O actinometry was used to measure the VUV flux of high-intensity deuterium lamps before, during, and after the photochemical synthesis of Titan analog aerosols made from methane or benzene precursors. It was found that VUV photon flux can be decreased by over 50% in under 10h at higher number densities, with recorded flux losses of over 75% during extended (>60h) photochemical experiments. While this is only one model system, it is apparent that changes in photon flux during simulations must be taken into account if adequate comparisons of the photochemical kinetics to their respective planetary environments are to be made.

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Polycyclic aromatic hydrocarbons with straight edges and the 7.6/6.2 and 8.6/6.2 intensity ratios in reflection nebulae

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We have investigated the mid-infrared spectral characteristics of a series of polycyclic aromatic hydrocarbons (PAHs) with straight edges and containing an even or odd number of carbons using density functional theory (DFT). For several even- and odd-carbon PAHs, the 8.6/6.2 and 7.6/6.2 intensity ratios computed in emission after the absorption of a 8 eV photon match the observed ratios obtained for three reflection nebulae (RNe), namely NGC 1333, NGC 7023,

and NGC 2023. Odd-carbon PAHs are favored, particularly for NGC 1333. Both cations and anions are present with the cations being predominant. Relevant PAHs span sizes ranging from 46 to 103-113 carbons for NGC 7023 and NGC 2023 and from 38 to 127 carbons for NGC 1333 and have symmetries ranging from D_{2h} to C_s . Our work suggests that even- and odd-carbon PAHs with straight edges are viable candidates for the PAH emission seen towards irradiated photo-dissociation regions (PDRs).

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Meetings

Hendrik van de Hulst Centennial Symposium The Interstellar Medium of Galaxies: Status and Future Perspectives

**Leiden, The Netherlands
5-9 November 2018**

The 100th birthday of Henk van de Hulst presents an opportune moment to take stock of our understanding of the structure, composition, origin and evolution of the interstellar medium of galaxies over cosmic times and chart the future of research in this area. The interstellar medium plays a central role in the evolution of galaxies as the repository of stellar ashes and the birth sites of new stars. Stars in their turn set their environment aglow through their radiation, and shape their surroundings with their powerful winds and explosions. This energetic interaction gives rise to multiple ionized, atomic, and molecular phases that interact and interchange material on rapid time scales. A variety of surveys have probed these phases over the years. At the microscopic level, small dust grains and large molecules play an important role in the physics and chemistry of the ISM. These species also provide convenient tracers of the structure of the ISM. Over the last two decades, the Spitzer Space Telescope and the Herschel Space Observatory have opened up the infrared sky to surveys of the ISM. With ALMA on line, JWST on the horizon, and SKA turning into reality, the ISM of galaxies can be probed out to high redshifts. This can be expected to provide much new insight in the evolution of the ISM over the history of the Universe.

Topics of the conference

- Components of the ISM
- Interstellar processes
- Stellar feedback on the ISM
- What have we learned from studies of the ISM in other galaxies?
- Theory of the ISM
- ISM over cosmic times
- Future observing opportunities

Deadline to submit abstracts for contributed talks and posters: **July 15, 2018**

For more information, please visit: <http://home.strw.leidenuniv.nl/~vdhulstcentennial/index.html>.

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