

Pyrene-fused Pyrazaacenes: From Small Molecules to Nanoribbons

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Aurelio Mateo-Alonso obtained his BSc (1999) and MSc (2000) degrees in Organic Chemistry at Universidad Autónoma de Madrid (Spain). In 2004, he completed his PhD at Queen Mary, University of London (UK). Between 2004 and 2009, he was a Postdoctoral Researcher at Università di Trieste (Italy). In 2009, he joined the Freiburg Institute for Advanced Studies (Germany) as a Group Leader. Since 2012, he is an Ikerbasque Research Professor and Group Leader at POLYMAT in Donostia-San Sebastian (Spain). He has been awarded with the Young Investigator Prize of Università di Trieste (Italy 2007), the Eugen-Graetz Prize of Universität Freiburg (Germany 2009), the RSEQ-Sigma-Aldrich Young Investigator Prize of the Spanish Royal Chemical Society (Spain 2011), and the Young Investigator Award of the Nanocarbons Division of the Electrochemical Society (USA 2012).

Abstract

Linear and ribbon-like polycyclic aromatic hydrocarbons such as acenes and graphene nanoribbons are at the forefront of current investigations, as these graphene “cut outs” possess discrete energy gaps that can be tailored with the number of rings and their arrangements. Pyrene-fused pyrazaacenes are a type of nitrogenated ribbon-like polycyclic aromatic hydrocarbons with a very high stability. As a matter of fact, ribbon-like pyrene-fused pyrazaacenes with as many as 85 linearly fused aromatic rings have been synthesised with thermal stabilities over 500°C in air. This review covers most of the synthetic and application aspects of pyrene-fused pyrazaacenes from 1937 to our days, illustrating that pyrene-fused pyrazaacenes are a widely tuneable and a highly stable platform for developing ribbon-like nitrogenated polycyclic aromatic hydrocarbons for a broad spectrum of applications.

Dedication

Dedicated to Prof. James H.P. Utley.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are receiving a great deal of attention because of their increasing performance as semiconductors. Among these, linear and ribbon-like PAHs (e.g. acenes and graphene nanoribbons) are at the forefront of current investigations as these graphene “cut outs” possess discrete energy gaps that can be tailored with the number of rings and their arrangements.¹

The introduction of heteroatoms in the aromatic framework of PAHs can vary drastically their properties. For instance, the introduction of more electronegative nitrogen atoms in hole transporting *n*-acenes results in ambipolar and electron transporting *n*-azaacenes.² In addition, by varying the number and position of N atoms and the substitution on the aromatic core along the π -framework, it is possible to modulate the electronic structure, stability, solubility, and supramolecular organisation.³

Pyrene-fused pyrazaacenes (PPAs) are among these nitrogenated ribbon-like structures (Figure 1). This oversimplified name includes the term *pyrazaacene* that indicates both the presence of pyrazine rings on the framework and their elongated nature, while the term *pyrene-fused* refers to the presence of couples of lateral rings that correspond to the pyrene residues on the conjugated framework. Such cross conjugation increases the number of aromatic sextets on the electronic structure of PPAs, which provides them a high stability. As a matter of fact, PPA ribbon-like polymers with molecular weights that provide ~85 linearly-fused aromatic rings have shown no decomposition in air until 545°C.⁴

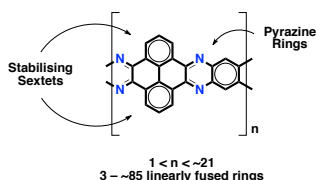


Figure 1. General structure of PPAs.

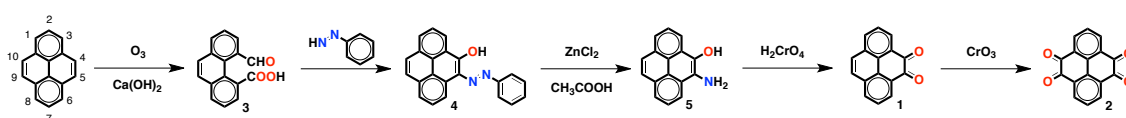
To the best of this author's knowledge, the first report on PPAs dates back to 1937,⁵ and their polymers received a lot of attention in the 1960's.^{4, 6} In 2005, several key building blocks necessary to prepare PPAs were made synthetically accessible through a one-step procedure,⁷ which has resulted in a substantial increase in their interest.

This review covers most of the work published on PPAs from 1937 to our days. Since the literature spans broadly over the time with very diverse structures and applications, it is impossible to arrange the work available following chronological order. For this reason, this review has been organised from a structural perspective from small building blocks to PPAs with increasing size and complexity of its conjugated core. To avoid redundancies the term "acene" has been used to refer of "pyrene-fused acene" throughout the review.

2. Synthesis of building blocks

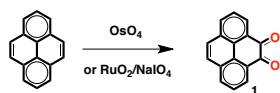
PPAs are generally synthesised from derivatives of pyrene-4,5-diketone and/or pyrene-4,5,9,10-tetraketone. Therefore, this whole section is dedicated to the different routes reported to prepare these building blocks.

The first report⁵ on the synthesis of pyrene-4,5-diketone (**1**) and pyrene-4,5,9,10-tetraketone (**2**) is also the first report of the synthesis of PPAs (Scheme 1). In this seminal work, entitled *Beträge zur Kenntnis des Pyrens und Seiner Derivate* (*In English: Contribution to the knowledge of Pyrene and its Derivatives*), the synthesis of **1** and **2** was carried out following a multistep route from pyrene. Ozonolysis was directly performed on pyrene to obtain **3** that was allowed to react with phenylhydrazine. The intermediate **4** was hydrolysed to the corresponding pyreneaminol **5** that was subsequently oxidised to diketone **1** using chromic acid. Finally, diketone **1** was further oxidised to the tetraketone **2** with chromic oxide.



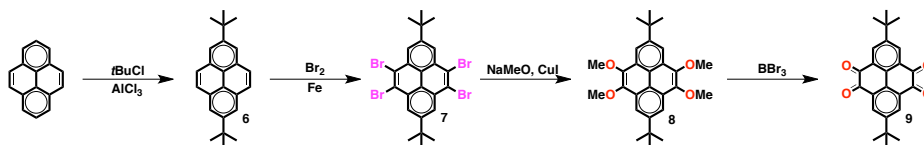
Scheme 1. Early synthesis of **1** and **2**.

In the 1950's two methodologies were developed to prepare pyrene diketone **1** directly from pyrene using OsO₄ and RuO₂ catalysed oxidations (Scheme 2).⁸ The latter evolved as a way to avoid the use of the toxic OsO₄. Another report from the 1970 described the synthesis of **1** by oxidation with Na₂Cr₂O₇ from 4,5-dihydropyrene that is achieved one step by hydrogenation from pyrene.⁹



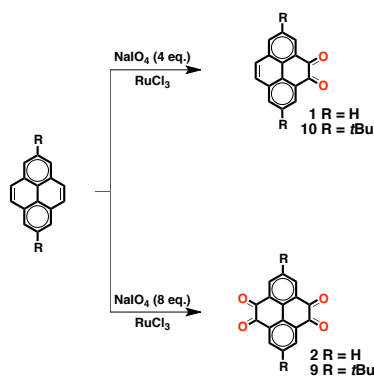
Scheme 2. Synthesis of **1** by direct oxidation of pyrene.

In the 1990's, a method was described to prepare pyrene tetraketone **9** with two *tert*-butyl groups in the 2,7 positions (Scheme 3).¹⁰ Pyrene was first functionalised with two *tert*-butyl groups by Friedel-Crafts alkylation. Bromination of **6** in the presence of Fe led to tetrabromopyrene **7**. Nucleophilic substitution with sodium methoxide yielded tetramethoxypyrene **8**, which upon demethylation followed by air oxidation led to the desired tetraketone **9**.



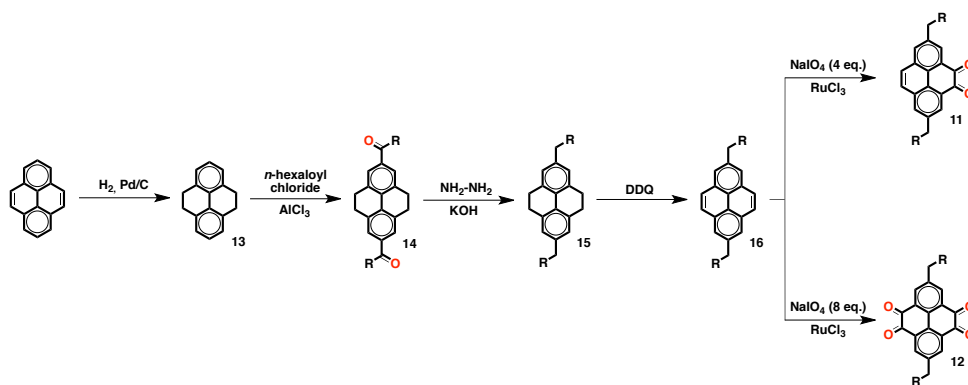
Scheme 3. Synthesis of tetraketone **9**.

The multigram methodology reported by Harris and co-workers allows preparing pyrene diketones and tetraketones in one step directly from pyrene by oxidation with NaIO_4 catalysed by RuCl_3 (Scheme 4).⁷ Pyrene diketone **1** and tetraketone **2** are readily obtained by varying the stoichiometry of NaIO_4 . The reaction also proceeds with *tert*-butyl groups in the 2,7 positions to yield diketone **10** and tetraketone **9**.⁷



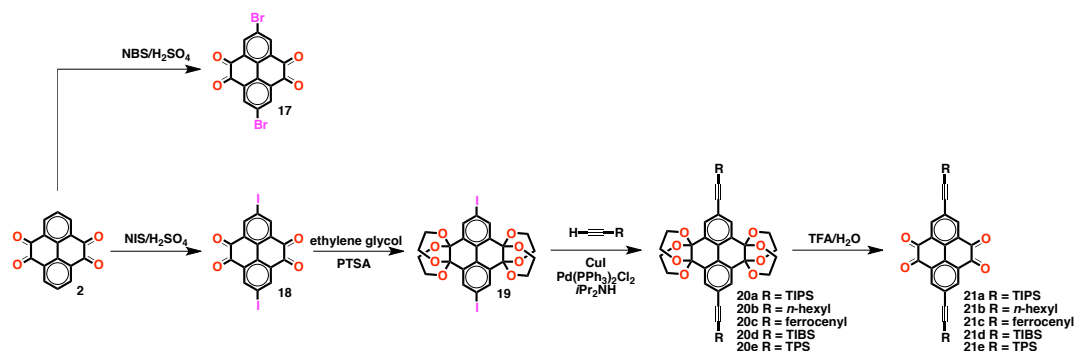
Scheme 4. Direct synthesis of pyrene diketones and tetraketones.

Harris' oxidation procedure has proven to be general and compatible with many substitution patterns and functional groups. In fact, this methodology has opened the door to the synthesis of more sophisticated pyrene building blocks, since the oxidation step is reduced to one single step. This is illustrated by the synthesis of di-*n*-hexyl diketone **11** and tetraketone **12** (Scheme 5). The first step is hydrogenation of pyrene into 4,5,9,10-tetrahydropyrene **13**. On the contrary to pyrene in which electrophilic substitutions take place preferentially on positions 1,3,6,8 – with the exception of *tert*-butyl alkylation that takes place on positions 2,7 because of the steric hindrance with hydrogens on positions 4,5,9,10 – Friedel-Crafts acylation on hydrogenated pyrene **13** takes place on the 2,7 positions.⁷ The ketones on **14** are transformed to methylenes by Wolff-Kishner reduction. Rearomatisation of **15** provides di-*n*-hexyl-pyrene **16**, which upon oxidation provides either di-*n*-hexyl-pyrene diketone **11** or tetraketone **12**, depending on the stoichiometry of NaIO_4 .



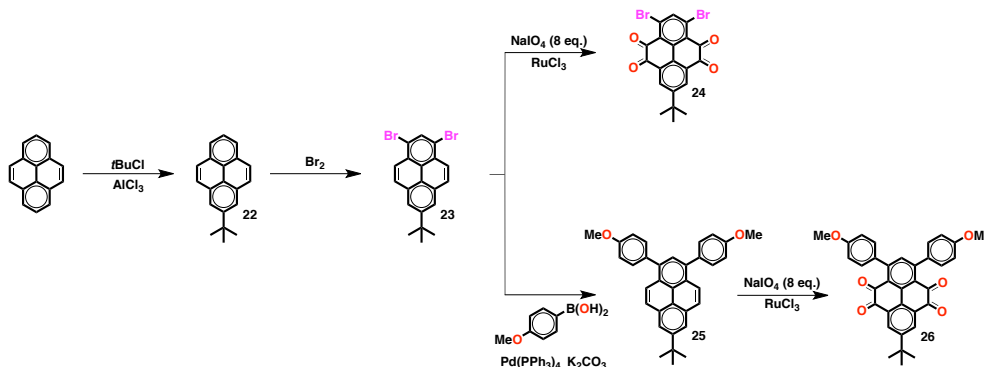
Scheme 5. Synthesis of **11** and **12**.

Tetraketones **17**¹¹ and **18**^{11a} functionalised with bromides or iodides, respectively, in the 2,7-positions have been obtained by halogenation of pyrene tetraketone **2** with *N*-bromosuccinamide (NBS) and *N*-iodosuccinamide (NIS) in acid media (Scheme 6). A recent and versatile synthetic route¹² that allows preparing tetraketones with a wide variety of groups in the 2,7 positions is based on tetraketone **18**. The iodides in tetraketone **18** are completely unreactive in Suzuki or Sonogashira conditions.^{11a, 12} On the contrary, Sonogashira reactions proceeded successfully on **19** that was obtained by protecting the ketones into diketals with ethylene glycol and *p*-toluenesulfonic acid (PTSA). Good yields were obtained for **20** with a wide variety of acetylenes displaying bulky triisopropylsilyl (TIPS) groups, alkyl chains, and ferrocenyl electron-donating moieties. The deprotection of the diketals is straightforward, and the desired tetraketones **21a-c** were obtained in the presence of trifluoroacetic acid (TFA) and water. On a second report,¹³ this procedure was used to prepare triisobutylsilyl (TIBS) and triphenylsilyl (TPS) substituted tetraketones **21d** and **21e**, respectively.



Scheme 6. Synthesis of pyrene tetraketones with substituents on the 2,7 positions.

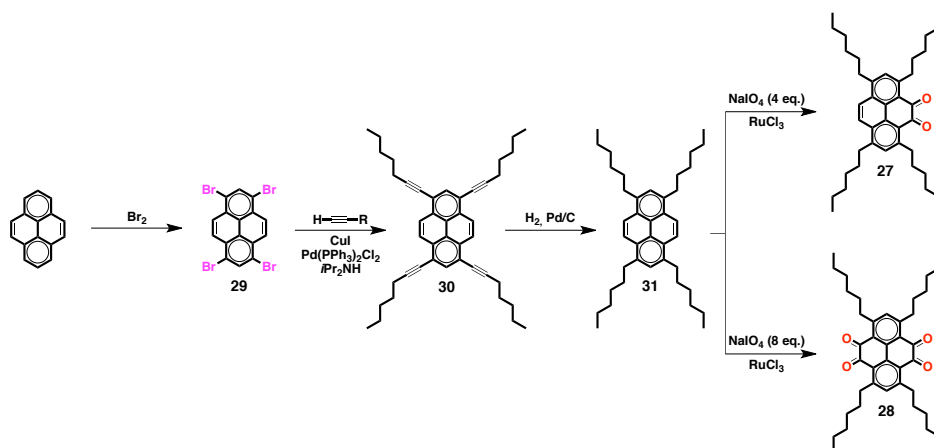
A methodology to prepare trisubstituted diketones has been described (Scheme 7).¹⁴ First, a *tert*-butyl group was introduced in pyrene in position 2 by Friedel-Crafts alkylation. Bromination of *tert*-butyl-pyrene **22** provided 1,3-dibromo-7-*tert*-butylpyrene **23**, which was subsequently oxidised to tetraketone **24**. In addition, the arylation of dibromide **23** by Suzuki coupling and subsequent oxidation of **25** led to trisubstituted tetraketone **26**.



Scheme 7. Synthesis of trisubstituted tetraketones.

Pyrene diketone **27** and tetraketone **28** with four *n*-alkyl chains on the 1,3,6,8 positions have been reported (Scheme 8).¹⁵ The starting point of this route is the bromination of pyrene that yields 1,3,6,8-tetrabromopyrene **29**, which can be functionalised with four

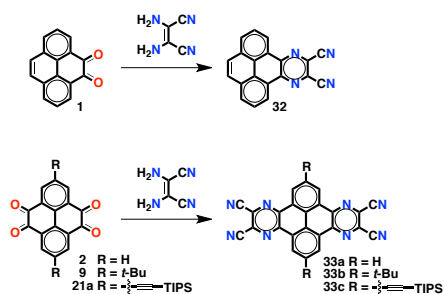
acetylenes by Sonogashira coupling with 1-octyne. The reduction of the acetylenes of **30** is necessary to ensure that the oxidation proceeds and is achieved by hydrogenation over Pd/C. The oxidation of the resulting tetraoctylpyrene **31** with NaIO₄/RuCl₃ yielded either diketone **27** or tetraketone **28** by varying the stoichiometry of the reagents.



Scheme 8. Synthesis of tetrasubstituted pyrene diketone **27** and tetraketone **28**.

3. Short Pyrene-fused Pyrazaacenes

The smallest pyrene-fused azaacenes are those obtained by cyclocondensation between pyrene diketone **1** and pyrene tetraketone **2**, **9** and **21a** with diaminomaleonitrile,¹⁶ which yield, respectively, diazatriacene **32**,¹⁷ and tetraazatetracenes **33** (Scheme 9).¹⁷⁻¹⁸ In particular, tetracenes **33** have remarkably low LUMO levels for its size (~ -3.7 eV) that make them eligible for electronic applications where n-type materials are needed.



Scheme 9. Synthesis of triacine **32** and tetracenes **33**.

Another type of tetracenes are those synthesised by reaction between pyrene diketones **1** and **10** with the corresponding *o*-phenylenediamine, which gives rise to a wide variety of compounds and applications (Figure 2). The simplest diazatetracene **34** was reported in 1937,⁵ but there is also later report describing its synthesis from 1959.⁸ Recently, tetracene **35** functionalised with TIPS-acetynyl substituents in the *o*-phenylenediamine residue has been prepared as part of a series of derivatives for light-emitting diode applications, since it exhibits enhanced solubility and strong fluorescence.¹⁹

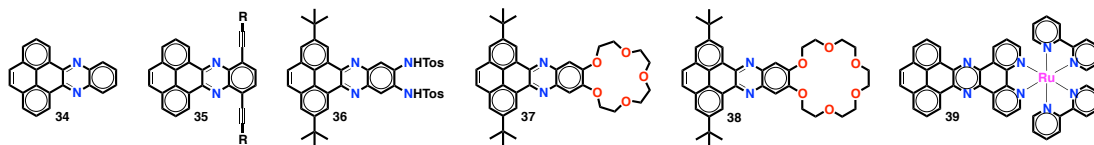


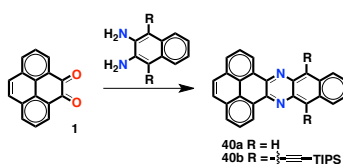
Figure 2. Tetracenes obtained from pyrene diketones.

The introduction of functional groups in this type tetracenes such as sulphonamides (**36**)²⁰ and crown ethers (**37**, **38**)²¹ provides sensors for anions and cations, respectively (Figure 2). In the case of **36**,²⁰ binding constants in between 10^4 - 10^6 have been observed for anions such as acetate, benzyloxy, cyanide and fluoride, while it showed a small binding constant with other anions such as chloride, bromide, iodide, nitrate and perchlorate. In the case of the crown ethers,²¹ sensor **37** forms 1:1 complexes with small ions (sodium and calcium), while in the case of sensor **38**, 1:2 complexes are formed with large ions (potassium, rubidium, cesium and barium) that are accompanied by absorption, emission and NMR changes.

Ru (II) complexes are known to intercalate in DNA, an approach that has been used to inhibit DNA transcription and to design diagnostic probes. The introduction of a phenanthroline on the tetracene core allowed the preparation of complex **39** (Figure 2) that displayed a much higher binding ability to DNA in comparison of the standard quinoxalinephenanthrolines complexes because of the extended conjugated plane.²² Also, complex **39** has been used to probe DNA defects by exploiting their luminescence response to base pair mismatches or abasic sites.²³

Pyrene-fused diazapentacenes can be obtained by cyclocondensation between pyrene diketone **1** and 2,3-diaminonaphthalene derivatives (Scheme 10).^{19, 24} The first pyrene-

fused pentacene **40** was synthesised as a π -extended surfactant in order to facilitate the dispersion of carbon nanotubes.²⁴ As a matter of fact, single walled carbon nanotubes were easily dispersed in the presence of diazapentacene **40a** by mild sonication (Figure 3). More importantly, the properties of carbon nanotubes were left virtually unaffected, as observed by a wide variety of steady-state and time-dependent photophysical measurements. Such a low level of disruption makes this approach very attractive for the manipulation and processing of carbon nanotubes for electronic applications. Pyrene-fused pentacenes have been also synthesised as potential emitters for light-emitting diodes. The introduction of two TIPS-acetylene substituents in the pentacene core (**40b**) resulted in strongly emitting chromophores with quantum yields in the range of 0.341.¹⁹



Scheme 10. Synthesis of diazapentacenes **40**.

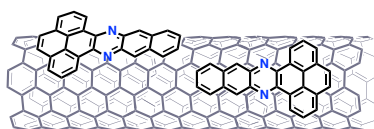
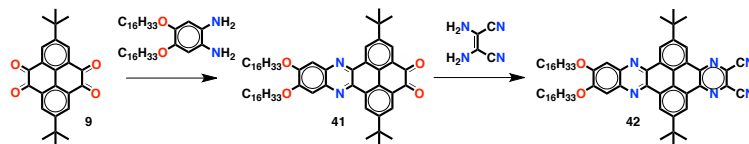


Figure 3. Supramolecular ensembles of carbon nanotubes with **40a**.

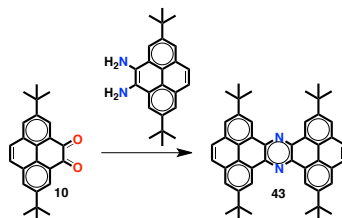
Asymmetric pyrene fused pentacenes can be prepared by a methodology developed by Lee and co-workers (Scheme 11).²⁵ The reaction of pyrene tetraketone **9** with one equivalent of the corresponding diamine yields tetracene diketone **41** that upon reaction with diaminomaleonitrile provides the asymmetric pyrene-fused tetraazapentacene **42**. This type of asymmetric pentacenes self-assembles readily by means of the phase

transfer method in $\text{CHCl}_3/\text{MeOH}$ to induce the formation of 1D nanometric fibers that can be observed by optical and atomic force micrographs.



Scheme 11. Synthesis of asymmetric pentacene **42**.

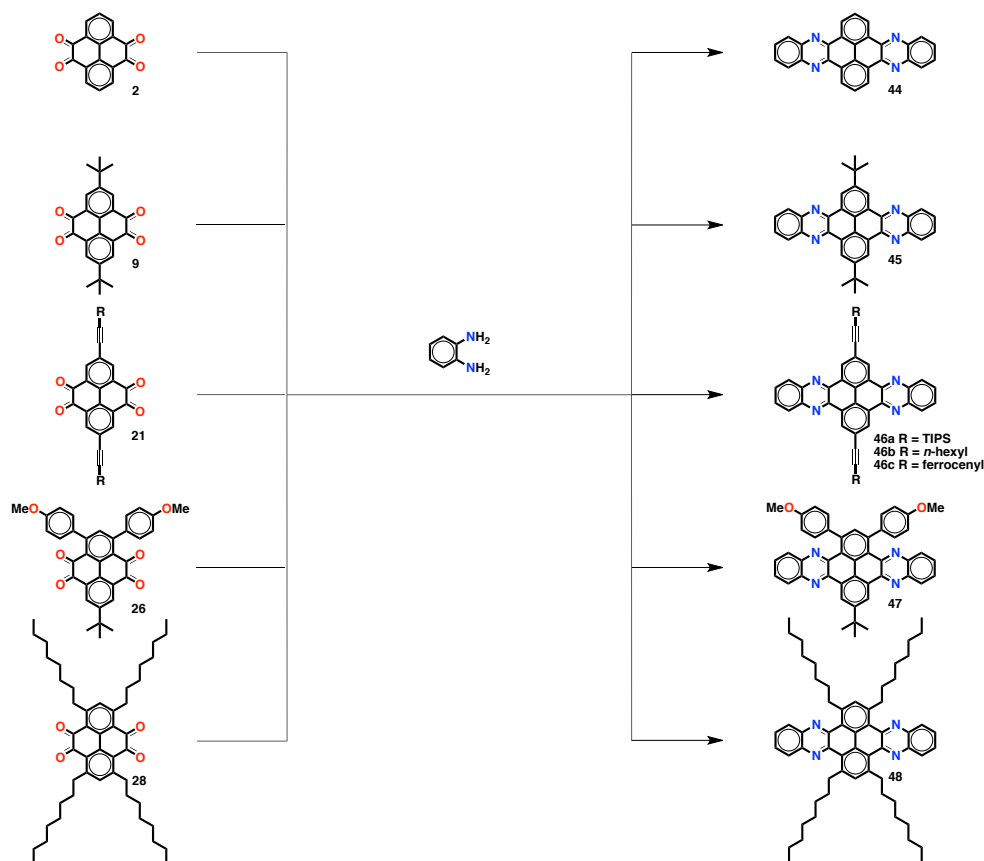
A different type of pentacene with two fused pyrene units has been synthesised and used as an emitter in light-emitting diodes. Pentacene **43** is obtained by cyclocondensation between pyrenediketone **10** and 4,5-diamino-pyrene (Scheme 12).⁶ An interesting aspect of this compound is that its photoluminescence in solution and electroluminescence in the solid state remain almost invariable, even in the presence of high percentages of dopants.



Scheme 12. Synthesis of pentacene **43**.

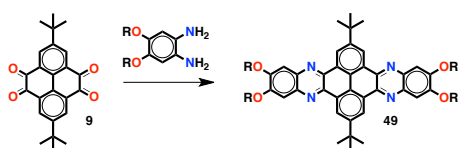
4. Pyrene-fused Pyrazahexacenes

This whole section is dedicated to pyrene-fused hexacenes due to the large number of examples available in the literature. The first pyrene-fused hexacene (**44**) was reported in 1937 in the seminal paper by Vollmann et al.,⁵ which was synthesised by a double cyclocondensation from pyrene tetraketone **2** and *o*-phenylenediamine (Scheme 13). Following this route, hexacenes with different functionalisation in the pyrene core have been reported with almost all the different pyrene tetraketones described in section 2. There are reports of hexacenes disubstituted in the 2,7 positions of the pyrene core with *tert*-butyls (**45**),¹⁰ and acetylenes with different pending groups (**46**).¹² Also trisubstituted hexacenes¹⁴ in the 1,3,7 positions of the pyrene core (**47**) and tetrasubstituted hexacenes with octyl substituents in the 1,3,6,8 positions of the pyrene core (**48**),¹⁵ have been described.



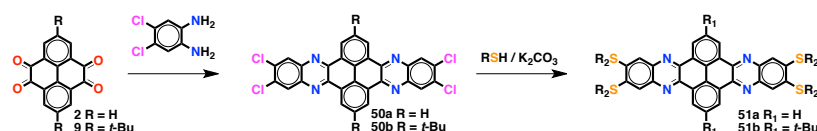
Scheme 13. Synthesis of symmetric hexacenes.

In 2004, Harris reported a series of hexacenes by modifying the diamine precursor with different alkylethers (Scheme 14).²⁶ The tetraalkyloxy hexacenes **49** with *n*-decanyl and *n*-undecanyl chains displayed liquid crystalline phases with π - π overlap between molecules above 200°C. In a different work, liquid crystalline phases were also observed for *n*-hexadecacenyl and *n*-icosanyl substitution.²⁷ In addition, a detailed spectroscopic study illustrates the effects of different concentrations,²⁸ solvents,²⁸ and chain lengths²⁹ in their photophysical properties.



Scheme 14. Synthesis of hexacenes with alkylethers.

Other pyrene discotics have been synthesised with thioethers. The first synthetic reports from Kaafarani and Jabbour described the synthesis of these derivatives from tetrachlorohexacene **50**. This is obtained by a double cyclocondensation of tetraketones **2** and **9** with 1,2-dichloro-4,5-diamino-benzene. Tetrachlorohexacene **50** was transformed in the corresponding tetrathioethers **51** with alkyl chains ranging from *n*-butyl to *n*-dodecyl by nucleophilic aromatic substitution with the corresponding thiol in the presence of a base (Scheme 15).³⁰ Average saturation hole mobilities were in the range of $10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Thin film microstructure studies of hexacene **51** ($R_2 = n$ -dodecyl) showed that temperature had a minimal effect on the overall structure.³¹ A nearly complete crystal packing mode was determined that showed that the hexacene molecules are arranged in segregated vertical layers with a cofacial packing of their tilted core planes. A complementary study showed that hexacenes **51** ($R_2 =$ even chains from *n*-hexyl to *n*-dodecyl) can also show four crystalline phases, which are crystal-crystal transitions with increasing conformation defects in the alkyl chains.³² Also the effects of different concentrations,²⁸ solvents,²⁸ and chain lengths²⁹ in the photophysical properties of hexacenes **51** ($R_2 =$ even chains from *n*-butyl to *n*-dodecyl) were investigated in detail. In a different study, hybrids between hexacene **51** ($R_2 = n$ -butyl) and butylamine-modified graphene sheets have been described, which are able of promoting the generation of charge carriers under illumination.³³



Scheme 15. Synthesis of hexacenes with alkylthioethers.

Columnar mesomorphism has been also observed from hexacene **52** functionalised with dialkoxyphenyl substituents (Figure 4), which has been obtained by cyclocondensation of tetraketone **9** with the corresponding amine.³⁴ In fact, hexacene **52** displays crystalline phases, rectangular mesophases, columnar hexagonal mesophase and an isotropic liquid phase. In addition, fluorescence has been observed both in its crystalline and columnar liquid phases, which is unusual for π - π stacking materials.

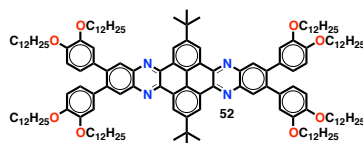


Figure 4. Hexacene with dialkoxyphenyl substituents.

As described for the tetracenes above, hexacenes functionalised with sulfonic amides²⁰ or with crown ethers^{21b, 35} are also suitable for sensing ions in solution (Figure 5). Hexacenes **53** and **54** are obtained by reaction of tetraketones **2** and **10** with their respective diamines. A high sensitivity for acetoxy, benzyloxy, cyano and fluoride ions was observed for hexacene **53** by absorption and emission spectroscopy that also demonstrated their ability to bind two anions.²⁰ In the same way, the crown-ether functionalised hexacene **54** was able to bind a metal cation in each binding site with a higher sensitivity for Ca^{2+} and Ba^{2+} ions.^{21b, 35}

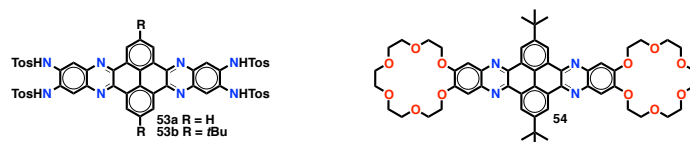


Figure 5. Hexacene-based sensors for ions in solution.

The synthesis and characterisation of a series of hexacenes that possess LUMO levels between -3.4 and -4.3 eV has been reported.^{12, 18b} These values are remarkably lower than those typically observed for pyrene-fused hexacenes and comparable to those of state-of-the-art n-type semiconductors such as [6,6]-phenyl-C₆₁-butyric acid methyl ester and rylene dyes. Hexacenes **55-58** were obtained by cyclocondensation of tetraketone **21a** with their corresponding diamine. Hexacene **55** with eight fluorine atoms displays a lower LUMO level (-3.4 eV) than that of unsubstituted hexacene **46a** (-3.2 eV).¹² The presence of four nitro groups **56** (-3.7 eV) or four cyano groups in **57** (-3.6 eV) also results in a significant reduction of the LUMO level.^{18b} A much lower LUMO was observed for **58** (-4.3 eV) as a result of the combination of the four nitriles and the two additional pyrazine rings.^{18b}

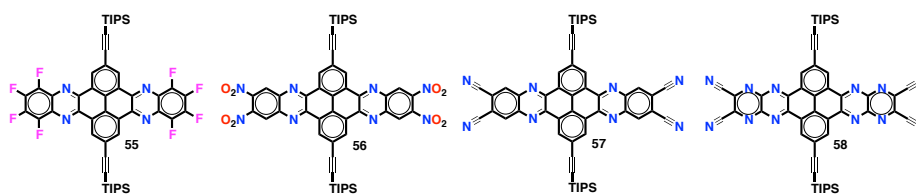


Figure 6. Low-LUMO hexacenes.

A synthetic strategy that allows distorting the π -system of planar pyrene-fused azaacenes has been described.¹³ Hexacenes **59** have been obtained by reaction of tetraketones **21a**, **21d** and **21e**, with their parent diamine. Depending on the volume and the rigidity of the silyl groups, different-sized twist angles are induced along the longitudinal conjugated backbone. The larger twists are obtained as a compromise between volume and rigidity, as evidenced by X-ray crystallography. TIPS-substituted hexacene **59a** showed a twist angle of 6° . Changing the size of the side groups to bulkier TIBS groups resulted in hexacene **59b** with smaller twist angles of 4° because of the

enhanced flexibility of the substituents. The introduction of bulky and rigid TPS groups distorts the hexacene core of **59c** and twist angles of 24° were observed. In addition, hexacenes **59** present completely different packing motifs.

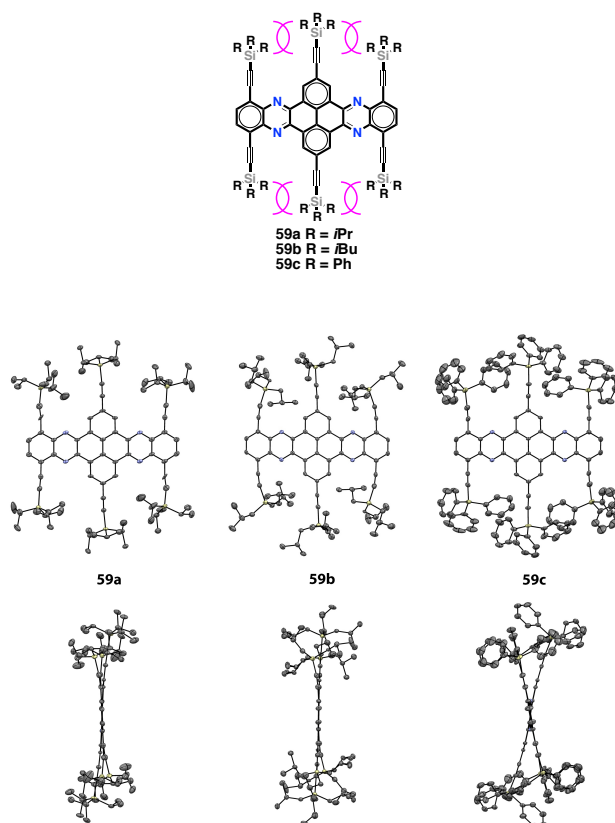


Figure 7. Twisted hexacenes.

Hexacene derivatives **60** (Figure 8) functionalised with dicarboximide groups equipped with branched alkyl chains ($R_2 = 2\text{-decyl-tetradecyl}$ and $3,7\text{-dimethyl-octyl}$) have been synthesised from tetraketones **2** and **9**.³⁶ From the four systems synthesised, only compound **60a** ($R_2 = 2\text{-decyl-tetradecyl}$) displayed three different phase transitions. Upon cooling, textures consistent with a columnar liquid crystalline phase were observed. Due to the electron withdrawing nature of the substituents, electron mobilities in the range of $10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ were measured for **60** *via* space-charge limited-current measurements.

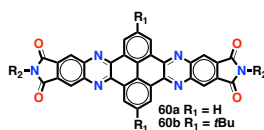


Figure 8. Dicarboximide hexacenes.

Molecular rulers based on pyrene-fused hexacenes equipped with pyrrolidine biradicals (**61**) have been synthesised as model compounds to measure nanometer distances between paramagnetic centers (Figure 9). In the same way as similar compounds, hexacene **61** was synthesised from tetraketone **9** with the corresponding pyrrolidine hydroxylamine followed by oxidation with *m*-chloroperbenzoic acid. Pulsed electron double resonance (PELDOR) experiments showed that it is possible to make high sensitivity distance and orientation measurements with hexacene **61**.³⁷

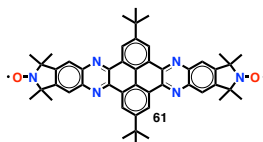
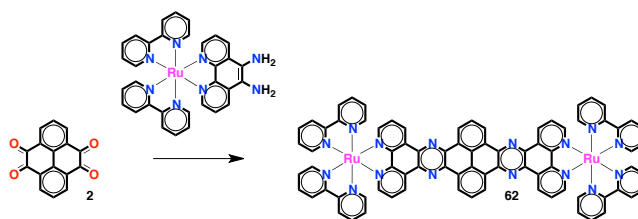


Figure 9. Hexacene biradicals.

Hexacenes fused to phenanthrolines have been synthesised with the aim of preparing their corresponding Ru(II) complexes (Scheme 16).³⁸ Such complexes are very attractive for studying electron- and energy transfer processes and electronic communication between metal atoms. The most intuitive synthetic route to achieve these complexes, which is based on the synthesis of the hexacene followed by metalation, failed as the cyclocondensation between tetraketone **2** and 5,6-diamino-5,10-phenanthroline did not yield the desired hexacene. The synthesis of the complex was elegantly achieved by metalation of the phenanthrolinediamine precursor, which

upon cyclocondensation yielded the desired biscomplex **62** that is soluble in a variety of solvents (Scheme 16). In addition, supramolecular dimers of complex **62** were described.



Scheme 16. Synthesis of hexacene-base Ru(II) complexes.

Hexacenes fused to thiadiazol and equipped with triphenyl and thiophene-fluorene electron donors, **63a** and **63b** respectively (Figure 10), have been synthesised from pyrene tetraketone **2**.³⁹ Hexacenes **63** have shown absorption in the NIR, attributed to charge transfer transitions from the donors to the hexacene acceptor. Moreover, NIR photoluminescence at wavelengths over 1000 nm has been observed both in solution and remarkably in thin films, enabling a variety of potential applications for these materials that include photovoltaics, light emitting-diodes and bioimaging.

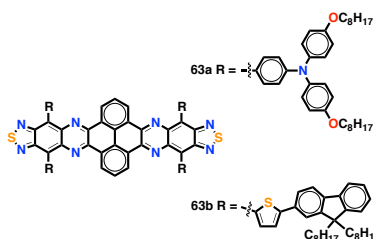
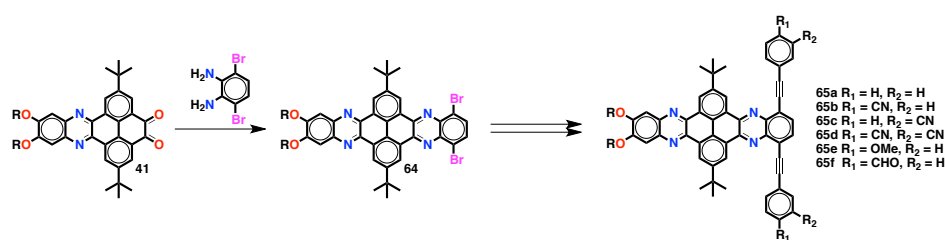


Figure 10. Hexacenes fused to thiadiazols.

Asymmetric hexacenes have been synthesised by Lee⁴⁰ from hexacene **64** that is obtained by cyclocondensation between the above-mentioned diketone **41** and 1,4-

dibromo-2,3-diamino-benzene (Scheme 17). A group of T-shaped hexacenes with varying peripheral substitution has been prepared through this strategy. Besides the changes in the electronic properties, the substituents have a profound effect on the morphologies of their self-assembled structures. One-dimensional assemblies can be obtained for **65a** ($R_1 = H$, $R_2 = H$) and **65b** ($R_1 = CN$, $R_2 = H$) in the form of microstrands and nanofibers, respectively.^{40a} In addition, the morphology of the assemblies of **65b** can be further tuned by controlling the concentration.^{40b} Modification of the length of the alkyl chains (from *n*-hexadecyl to *n*-decyl) and the nature and number of the peripheral groups on **65** provides organogels with tunable morphologies and gelation temperatures.^{40c}



Scheme 17. T-shaped hexacenes.

Asymmetric hexacenes **66** generate organogels through the growth of nanofibers with acid sensing properties (Figure 11).^{25, 41} These are obtained in a similar way by reaction between **41** with the corresponding diamine. Different fibre morphologies can be obtained by changing the peripheral substituents. For instance, long flexible nanofibres (**66b**), straight nanofibres (**66c**), thin and short nanofibres (**66d**) and nanobelts (**66e**) were clearly observed by scanning electron microscopy.

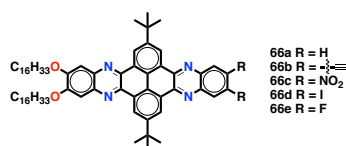


Figure 11. Asymmetric hexacenes.

A much more in-depth study of the structure and self-assembly relationship has been carried out,^{25, 42} in which a series of asymmetric hexacenes **67-70** were synthesised from compound **64** with different substituents and a different number of heteroatoms were synthesised and studied (Figure 12). Hexacenes **68** and **69** were able to form xerogels, while **70** formed a partial gel.

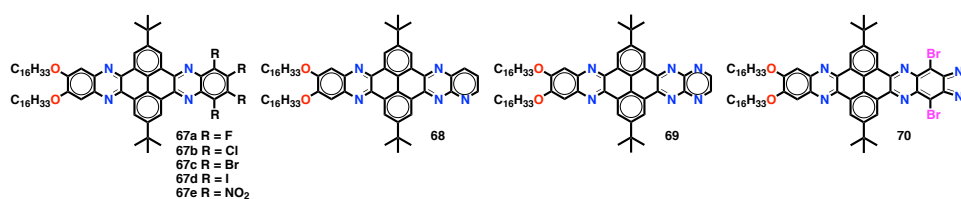
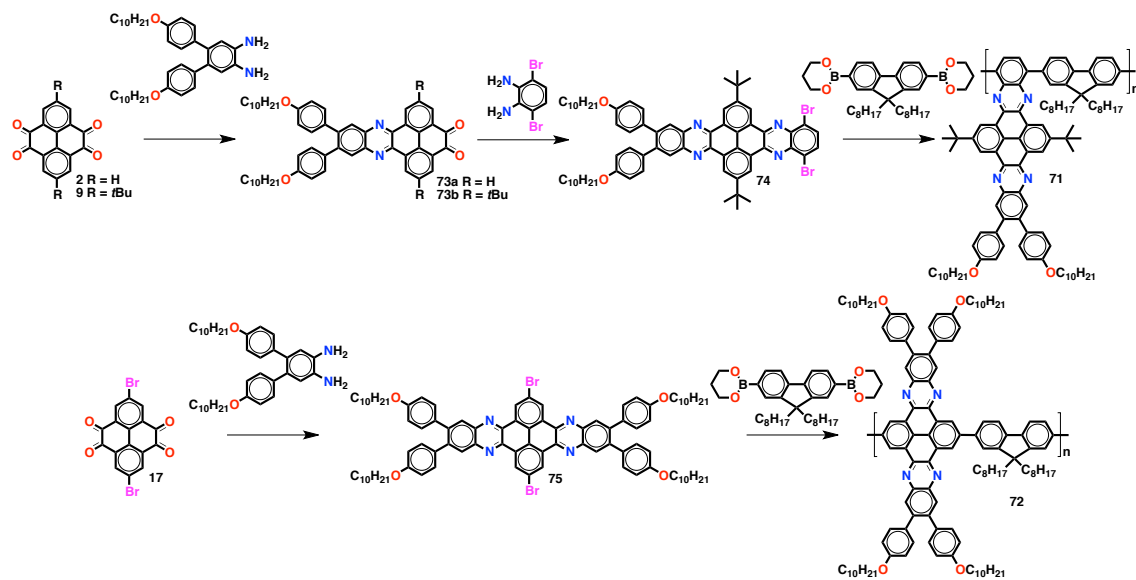


Figure 12. Complex asymmetric hexacenes.

Two types of copolymers (**71** and **72**)⁴³ based on hexacenes and fluorene have been described by Wang and co-workers by Suzuki polymerisation that have been used as novel emitters in light-emitting diodes (Scheme 18). The presence of the hexacene monomers favours electron injection in both cases. In addition, the brightness and efficiency of **71** and **72** surpassed those of the fluorene homopolymer. Copolymer **71** was synthesised from diketone **73** that is obtained by monocyclocondensation of tetraketone **9** with a diamine with *n*-decyloxyphenyl substituents. Reaction of **73** with 1,4-dibromo-2,3-diamino-benzene yields hexacene monomer **74**, which upon polymerisation with 9,9-dioctylfluorene-2,7-diboronic acid ester provides copolymer **71**. Copolymer **72** was synthesised from similar building blocks. Cyclocondensation of

tetraketone **17** with the same diamine yields dibromohexacene **75** that polymerises in the presence of 9,9-dioctylfluorene-2,7-diboronic acid ester into copolymer **72**.

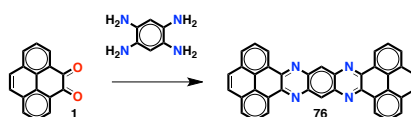


Scheme 18. Synthesis of hexacene-fluorene copolymers.

5. Higher Pyrene-fused Pyrazaacenes

The term higher pyrene-fused azaacenes is introduced to refer to pyrene-fused azaacenes with a number of linearly-fused aromatic rings higher than six, in analogy to acenes.

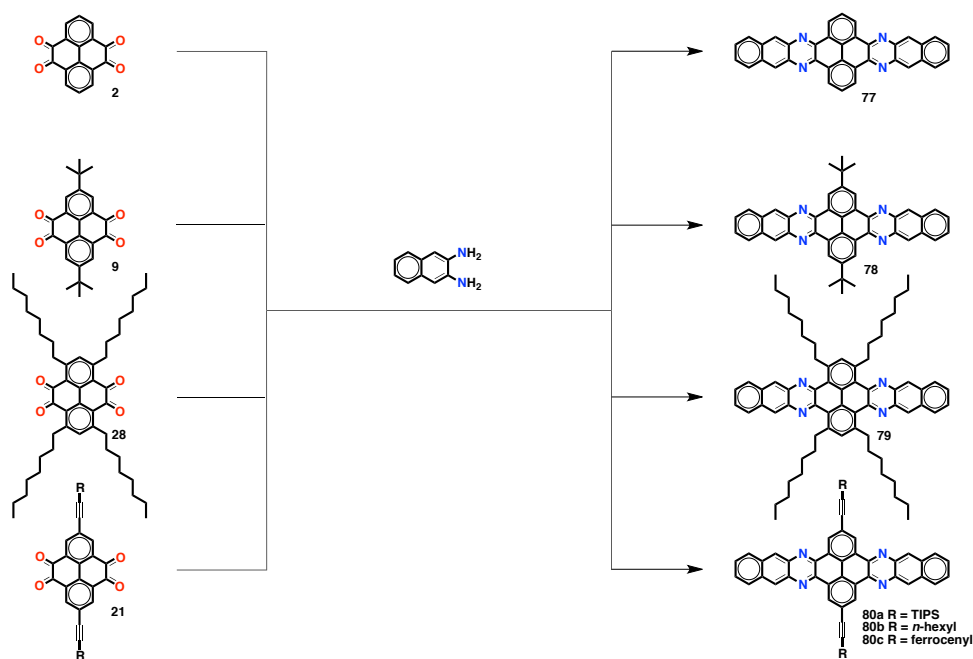
The synthesis of pyrene-fused tetraazaheptacene **76** has been described by Mateo-Alonso⁴⁴ by converging pyrene diketone **1** with 1,2,4,5-tetraaminobenzene (Scheme 19). The lack of solubilising groups resulted in a very insoluble material. However, it was possible to characterise **76** thoroughly by using 1,2,4-trichlorobenzene and deuterated trifluoroacetic acid. The neutral solutions of **76** displayed a grenadine colour of the solid material while in solvents like trifluoroacetic acid the solutions turned blue. A closer look at the absorption features evidenced that while absorption in the visible is observed in neutral solvents, in trifluoroacetic acid strong and well-resolved bands evolve in the NIR. The crystal structure of **76** and its photoconductive behaviour was reported later by Zhang.⁴⁵



Scheme 19. Synthesis of heptacene **76**.

The synthesis of octacene derivatives with different solubilising and functional groups has been described in a series of papers by Mateo-Alonso and co-workers (Scheme 20). Octacene **77** with no substituents was obtained by reaction between pyrene tetraketone **2** and 2,3-naphthalenediamine and was found to be very insoluble.⁴⁴ NMR

characterisation of **77** was only possible in a highly diluted [D₁]trifluoroacetic acid solution. The solubility of hexacene **78** increased substantially with the presence of two *tert*-butyl groups, nevertheless the addition of [D₁]trifluoroacetic acid was still necessary in order to obtain a well-resolved NMR.^{15b} Finally, the use of tetraketones **28**,^{15b} **21a**,¹² and **21b**¹² with four octyls, two TIPS or two *n*-hexyl, respectively, yielded octacenes **79**,^{15b} **80a**¹² and **80b**,¹² which were soluble over a wide variety of solvents and allowed a complete and precise optoelectronic characterisation. In addition, donor-acceptor octacenes with ferrocenyl substituents (**80c**) have been also described.¹²



Scheme 20. Synthesis of symmetric octacenes.

Octacene **81** (Figure 13) has been synthesised from triphenylenediamine precursors, which displays liquid crystalline columnar phases.³⁴ The larger planar core of the octacene increases the thermal stability of the crystalline and liquid crystalline phases in comparison to similar less conjugated azaacenes.

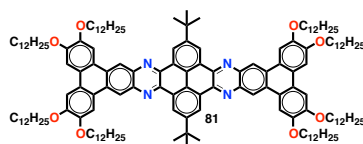


Figure 13. Triphenylene-fused octacene **81**.

A series of octaazaoctacene derivatives (Figure 14) has been reported by several authors from tetraketones **2** and **9**. Octacenes **82** have been reported by Wang,⁴⁶ which present terminal *n*-decyloxyphenyl substituents as solubilising groups and different substitution on the pyrene core (either unsubstituted or disubstituted with *tert*-butyls). A more recent work from Cheng²⁷ reports octacene derivative **83**, substituted with *n*-eicosyloxy substituents that displayed a high-order columnar phase at room temperature. Also tetrahydrododecaazadodecacene **84** (technically an octacene according to the number of conjugated rings) has been reported by Chi and co-workers.⁴⁷ Several attempts carried out to oxidise **84** to a fully conjugated dodecacene were unsuccessful. As expected, octacene **84a** with no substituents on the pyrene core showed a much higher packing order in the solid state than **84b**.

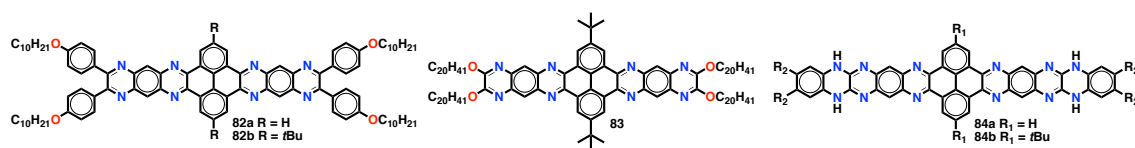
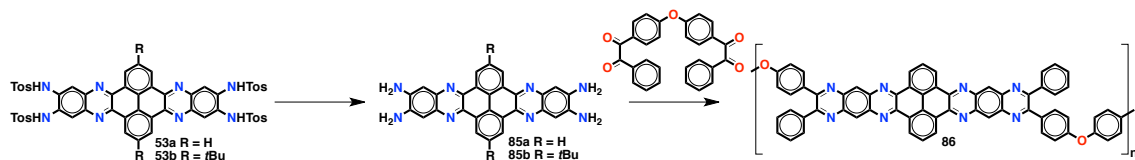


Figure 14. Symmetric octacenes.

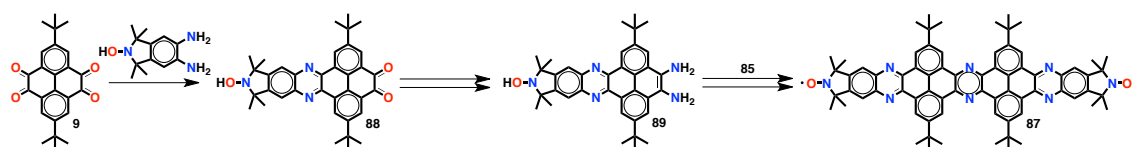
The deprotection of tosyl groups of **53** leads to the corresponding hexacene tetramines **85** that have proven to be a very useful building block in the synthesis of oligomers⁴⁶ and polymers (Scheme 21) by cyclocondensation with diketone building blocks.⁴⁸ Polymers based on octaazaoctacene **86**^{48c} have been synthesised on the search of

materials with glass transition temperatures over 400°C, therefore an enhanced thermal stability is strictly necessary. Polymer **86** has shown a very high thermal stability with no signs of decomposition after 600-650°C in N₂ and 400-450°C in air.



Scheme 21. Synthesis of an octacene-based polymer.

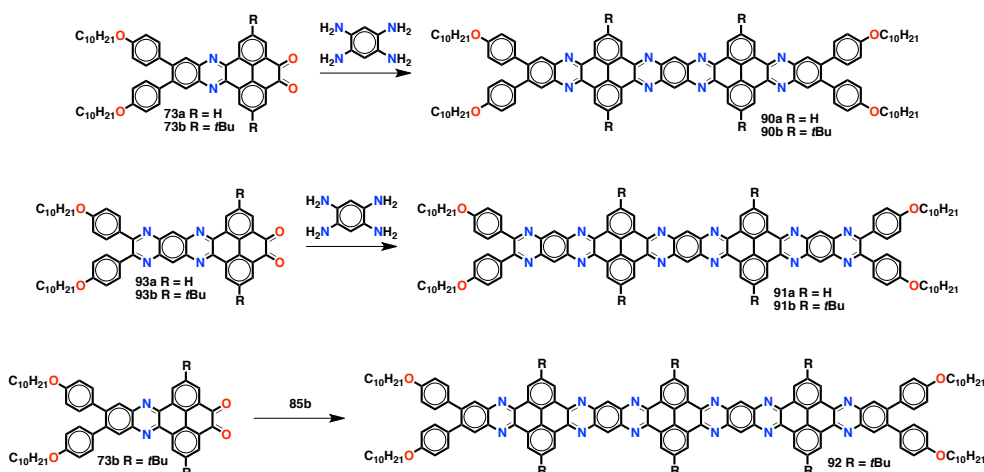
Nonacene **87** with terminal biradicals⁴⁹ has been used as a molecular ruler (Scheme 22). Pulsed electron-electron double resonance experiments allowed measuring distances and orientation between two spin labels in different DNA molecules. The synthesis of nonacene **87** proceeds through monocyclocondensation of tetraketone **9** with an aromatic diamine functionalised with a pyrrolidine hydroxyamine. Diketone **88** was then transformed into diamine **89** in two steps. Then **88** and **89** were condensed and the resulting product was oxidised in order to obtain nonacene **87**.



Scheme 22. Synthesis of nonacene biradicals.

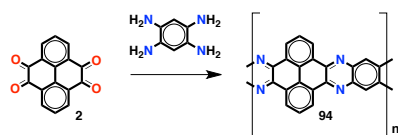
The longest oligoazaacenes reported to date have been described by Wang and co-workers.⁴⁶ Undecacene **90**, tridecacene **91**, and hexadecacene **92** have been synthesised by several convergent synthetic routes (Scheme 23). Undecacene **90** and tridecacene **91** are obtained by cyclocondensation of 1,2,4,5-tetraminobenzene with diketones **73** and

93, respectively. While hexadecacene **92** is obtained by cyclocondensation of hexacene tetraamine **85** with diketone **73**. Their strong tendency to aggregate in solution is illustrated by NMR characterisation in *o*-dichlorobenzene-*d*₄ at 120°C, in which mostly broad signals were observed. As a matter of fact, the structure of undecacene **90**, tridecacene **91**, and hexadecacene **92** was established by means of elemental analysis and MALDI. The optoelectronic properties illustrated decreasing bandgaps (2.25 - 2.18 eV) and decreasing LUMO levels (-3.7 - -3.8 eV) with increasing length of the oligoacenes.



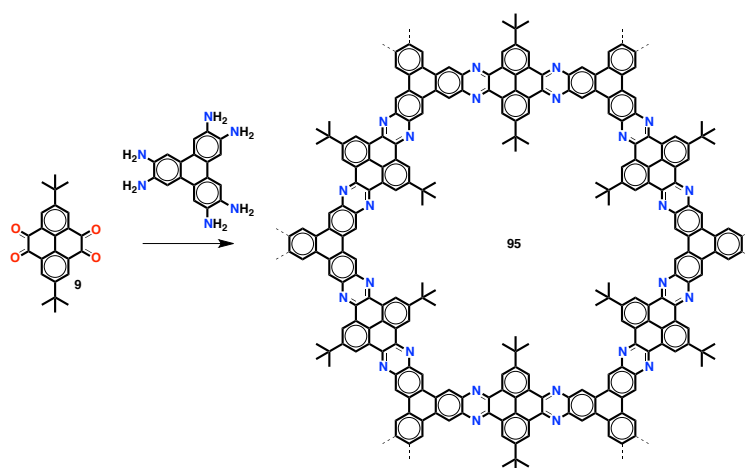
Scheme 23. Synthesis of nanoribbons.

Polyazaacenes **94**⁴ have been synthesised by reaction between tetraketone **2** and 1,2,4,5-tetraaminobenzene in solvents such as hexamethylphosphoramide, *m*-cresol and polyphosphoric acid (Scheme 24). Polymer **94** displayed a very high thermal stability up to 545°C in air and molecular weights around 7000 gr/mol that corresponds to ~85 linearly-fused aromatic rings.



Scheme 24. Polyazaacene ribbons.

Recently, the covalent organic framework **95**⁵⁰ has been described and synthesised from pyrene tetraketone **9** and triphenylene-2,3,6,7,10,11-hexamine (Scheme 25). The introduction of C₆₀ on the pores led to photocurrent generation with photon to current conversion of 0.9%. In addition, hole mobilities of 0.5 cm²V⁻¹s⁻¹ were measured by flash-photolysis time-resolved microwave conductivity measurements.



Scheme 25. Synthesis of covalent organic frameworks.

6. Conclusions

This review has highlighted the progress of the research on PPAs from 1937 to our days with a particular emphasis on the synthesis, properties and applications of PPAs. Among the several structures reported, ribbon-like PPAs with as many as 85 linearly fused aromatic rings have been synthesised with thermal stabilities over 500°C in air. Several examples illustrate that the LUMO level and the HOMO-LUMO gap of PPAs can be reduced by increasing (i) the length of the π -system, (ii) the number of N atoms in the framework and (iii) the number of strongly withdrawing groups.

The planar structure of PPAs can be constrained into exotic twisted conformations by means of congested substitution patterns that provide a playground to prepare new materials with unprecedented optoelectronic properties. In addition to their ability to self-assemble into liquid crystalline phases, gels and nanofibres, PPAs have shown charge mobilities ranging from 10^{-4} to $0.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, enhanced brightness and current efficiencies in light emitting diodes, photon-to-current energy conversions of 0.5% in photovoltaic cells, and NIR absorption, which evidence their potential in organic electronic applications.

Furthermore, examples of PPAs used as molecular rulers, molecular probes, sensors for cations and anions, and surfactants for nanocarbons have been described.

Overall, this review clearly shows that PPAs are a widely tuneable and a highly stable platform for developing ribbon-like nitrogenated PAHs for a broad spectrum of applications. The extraordinary progress made in the synthesis of PPAs during the last ten years has led to the production of a wide variety of compounds that have provided a general perspective of the potential of PPAs in several fields. Nevertheless, the synthesis of PPAs is still challenging and there is a need for better yielding and more

general protocols. As a matter of fact, even if pyrazine-type cyclocondensations are apparently straightforward reactions, every condensation is still a process of trial and error, driven by extensive labour, which could be solved by developing a truly general and clickable cyclocondensation procedure. Fortunately, this is only one of the many challenges and opportunities that lie ahead of this important field of research.

Acknowledgments

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