Organic &
Biomolecular
Chemistry

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 5005

www.rsc.org/obc

PERSPECTIVE

Putting the 'N' in ACENE: Pyrazinacenes and their structural relatives

Gary J. Richards,*[a,b] **Jonathan P. Hill,***[a,c] **Toshiyuki Mori**[b] **and Katsuhiko Ariga**[a,c]

Received 22nd March 2011, Accepted 27th April 2011
DOI: 10.1039/c1ob05454f

Acenes have emerged as an important class of organic electronic material. Related heteroatom-substituted compounds, or heteroacenes, introduce an important means for modulating properties and improving materials' stability. In this perspective, we will review the historical origins of the heteroacenes and discuss recent progress in the field of acene and related compounds containing fused 1,4-diazabenzene units, *i.e.* pyrazine, also known as the 'pyrazinacenes'. We focus not only on the types of materials that have been prepared but also on their chemical and physical properties, including synthetic procedures, electronic properties, self-assembly characteristics, and we also introduce some of the computational studies aimed at understanding the more unusual behaviours of this group of compounds, such as protic tautomerism and aromaticity/antiaromaticity.

Introduction

Acenes[1] are a class of organic materials consisting of laterally annelated five- or six-membered aromatic rings. Recently, larger acenes, in particular, pentacene,[2] have attracted significant interest as a result of their solid state semi-conducting properties.[3] Development of these materials is expected to realise cheap, flexible, lightweight and printable electronic devices including displays,[4] memories[5] and solar cells.[6] Unfortunately, acenes become increasingly unstable with increasing size and whereas tetracene is a relatively stable compound, pentacene is both unstable in air and light sensitive.[7] Higher acenes such as hexacene, heptacene and nonacene are so unstable that they can only be studied using matrix isolation techniques.[8] One approach to the stabilization of higher acenes involves their substitution with alkyl or aryl derivatives at selected peripheral positions. For example, Kuar and co-workers synthesised a persistent nonacene derivative through lateral expansion of the π-electronic system at reactive positions using arylthio substituents.[9]

A different route towards more stable compounds involves the exchange of CH atoms with heteroatoms such as nitrogen. This approach offers several important advantages since *N*-substituted oligoacenes are expected to be less susceptible to degradation through oxidation or dimerization than their non-*N*-substituted equivalents. Also, synthesis of acenes is often complex involving the formation of numerous C–C bonds while synthesis of heteroacenes sometimes permits the use of simpler synthetic strategies such as simple condensations of 1,2-phenylenediamines with 1,2-diketones (see Scheme 1) or 1,2-dichlorides. Nitrogen-substituted oligoacenes are of particular interest since they possess different electronic and physical properties, and they also introduce new possibilities for chemical modification at the nitrogen atoms including, but not limited to, acid/base reactions, hydrogenation (*i.e.* reduction to amine), *N*-oxidation or alkylation. The better chemical stability of the pyrazinacenes is especially against oxidative processes since the molecules are generally less electron rich with an accompanying resistance to oxidation. A specific aspect of pyrazinacenes lies at the central benzene ring of azapentacenes (*i.e.* 6,13 positions) since *N*-substitution at these points effectively precludes formation of the corresponding 6,13-pentacenequinone.

In this brief review we will describe the history and recent progress in the field of acene compounds containing fused 1,4-diazabenzene units, *i.e.* pyrazine. For convenience, we have applied the term 'pyrazinacenes' as in 'pyrazine-containing-acenes' for this family of compounds, which arbitrarily includes all acenes containing a fused pyrazine or fused dihydropyrazine group since this is one of the important features of pyrazine chemistry which affects the properties of pyrazinacenes. We have also included several compounds bearing pyreno moieties which, while at the same time as being not strictly acene in character, have obvious structural similarities with extended acenes and have given rise to some of the highest order fused pyrazinacene-type compounds. The aim of this review is to demonstrate how substitution of methine groups with N atoms in acenes can lead not only to compounds with isostructural and isoelectronic properties but also to materials possessing different and unique properties, which may find application in a variety of nascent technologies. With this aim in mind, we focus not only on the types of materials which have been prepared, but also on their chemical and physical properties, together with some of the more recent computational

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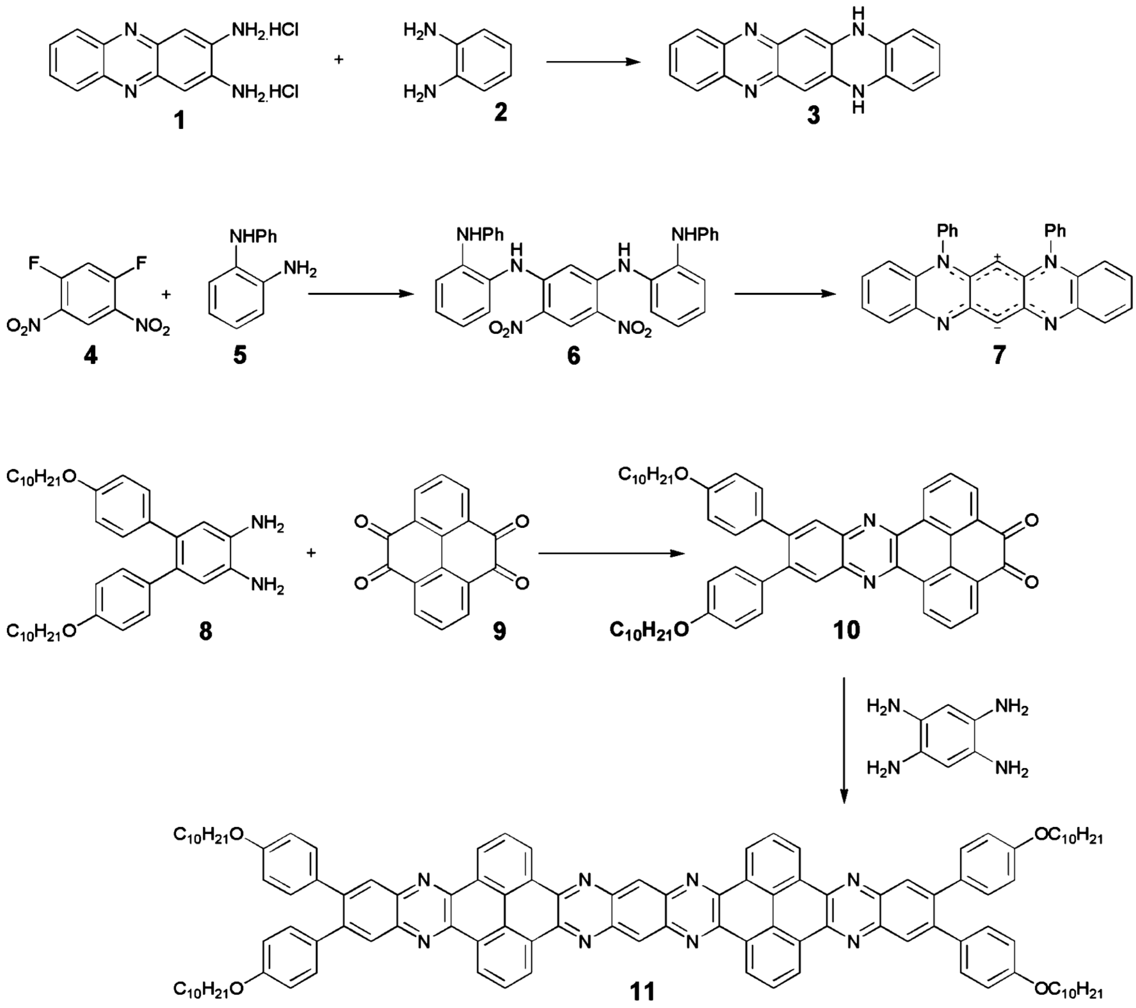
[a] *Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Japan. E-mail: Richards.Gary@nims.go.jp, Jonathan.Hill@nims.go.jp; Fax: +81 29 860 4832; Tel: +81 29 860 4399*
[b] *Fuel Cell Materials Center, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, 305-0044, Japan*
[c] *JST-CREST, Namiki 1-1, Tsukuba, Japan*



Scheme 1 Synthesis of pyrazinacenes by condensation of amines ($\mathbf{3}^{10}$ and $\mathbf{7}^{16}$) or by condensation of *o*-phenylenediamines with diketones ($\mathbf{11}^{17}$).

studies used to understand the behaviour of this fascinating group of compounds. For other reviews on the subject of heteroacenes we direct the reader to comprehensive reviews from Anthony[1a] and Bunz.[1b,c] Bunz gives accounts of properties of azaacenes including thiadiazoles and non-pyrazine N-heteroacenes, especially in regard to their properties which give them potential as molecular electronic materials. Our attention has been focussed on self-assembly and exploitation of tautomeric properties leading to this overview of the pyrazinacenes.

History

The first available report of a pyrazine-containing-acene derivative appeared in the late 19th century when Hepp and Fischer described the synthesis of 5,14-dihydro-5,7,12,14-tetraazapentacene (homofluorindine) **3**.[10] This work was later extended by Hinsberg,[11] who investigated a series of linearly and angularly fused pyrazinacenes, and also by Badger and Pettit who, in their 1951 publication, studied 5,14-dihydro-5,7,12,14-tetraazapentacene **3**, together with some of its oxidation and acylation products.[12] Of course, those early studies of these materials were concerned mostly with their preparation and fundamental chemical properties, and for some time, pyrazinacenes received little scientific attention other than for their use in some simple applications such as as dyestuffs.[13] More recently, several azaacenes have attracted renewed interest from researchers because of their potential in advanced electronic applications.

Synthesis of pyrazinacenes

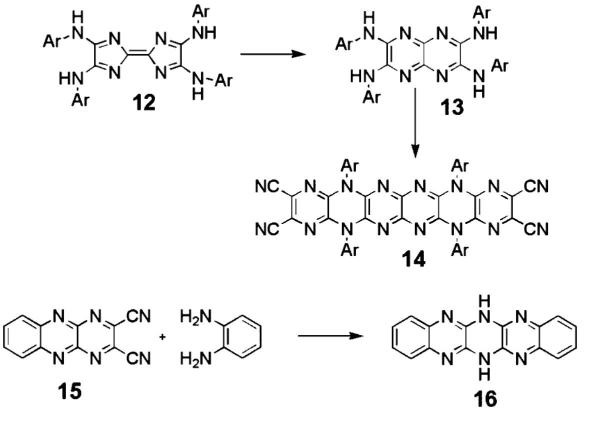
Hepp and Fischer first prepared 5,14-dihydro-5,7,12,14-tetraazapentacene **3** by direct condensation of 2,3-diaminophenazine hydrochloride **1** with *o*-phenylenediamine **2** (Scheme 1).[10] Badger and Petit prepared **3** by condensing 2,3-diaminophenazine with *o*-benzoquinone in benzyl alcohol.[12]

The same authors also found that **3** could be prepared by heating *o*-phenylenediamine or its hydrochloride salt in naphthalene under a stream of O_2. More recently, Siri and coworkers reported an alternative synthesis involving condensation of *o*-phenylenediamines with 2,5-dihydroxy-*p*-benzoquinone to afford high yields of substituted 2,3-dihydroxyphenazines.[14] The phenazine intermediates were then reacted individually with excesses of substituted *o*-phenylenediamines in the presence of glacial acetic acid yielding substituted 5,14-dihydro-5,7,12,14-tetraazapentacene derivatives. Palladium catalysts have recently proved useful in the synthesis of tetraazapentacenes.[15]

Wudl and co-workers developed a strategy for the synthesis of *syn*-substituted zwitterionic tetraazapentacenes.[16] The preparation involved a double nucleophilic aromatic substitution of 1,5-difluoro-2,4-dinitrobenzene **4** with *N*-substituted-1,2- phenylenediamines **5** to give 2,4-dinitrobenzene-1,5-diamines **6** in good yield. Hydrogenation of compounds **6** followed by heating in ethanol in air gave the zwitterionic tetraazapentacenes **7** (Scheme 1).

Pyrazinacenes based on the pyrene moiety have also been prepared. Synthetic methods usually involve oxidation of pyrene to give either a di- or tetraketone which is then condensed with the required phenylenediamine to give a phenazine or bisphenazine containing a pyrene unit. Using similar procedures Wang and co-workers synthesised a series of molecular ribbons with up to 16 linearly fused aromatic rings.[17] A typical synthesis is shown in Scheme 1. Phenylenediamine **8** was condensed with pyrene-4,5,9,10-tetrone **9** to give **10**. A double condensation reaction between benzene tetramine and **10** gives **11** containing 11 linearly fused rings (Scheme 1). However, it should be pointed out that the energy gaps of such molecular ribbons are saturated rapidly as the molecular length increases, in contrast to those of previously reported hydrocarbon acenes. This is probably due to the pyrene moiety which interrupts mesomeric delocalization on the acene backbone.

Until quite recently examples of pyrazinacenes containing adjacently fused pyrazine groups had been limited to compounds containing the 1,2,5,6-tetraazanapthalene unit, *i.e.* two fused pyrazine rings. However, Stöckner, Beckert and co-workers presented an attractive strategy for the synthesis of pyrazinacenes containing up to six fused pyrazine rings (Scheme 2).[18] The key step was the synthesis of tetrasubstituted pyrazino[2,3-*b*]pyrazines **13** through a dyotropic rearrangement of 1,4,5,8-tetraazafulvalenes **12**. Compound **13** was used to prepare a series of substituted pyrazinacene compounds. For example, compound **14** was prepared through a nucleophilic aromatic substitution with 2,3-dichloro-5,6-dicyanopyrazine. Stöckner's compounds can be considered the first extended pyrazinacenes and the compounds had the added benefit of high solubilities enabling full structural characterizations of some derivatives.



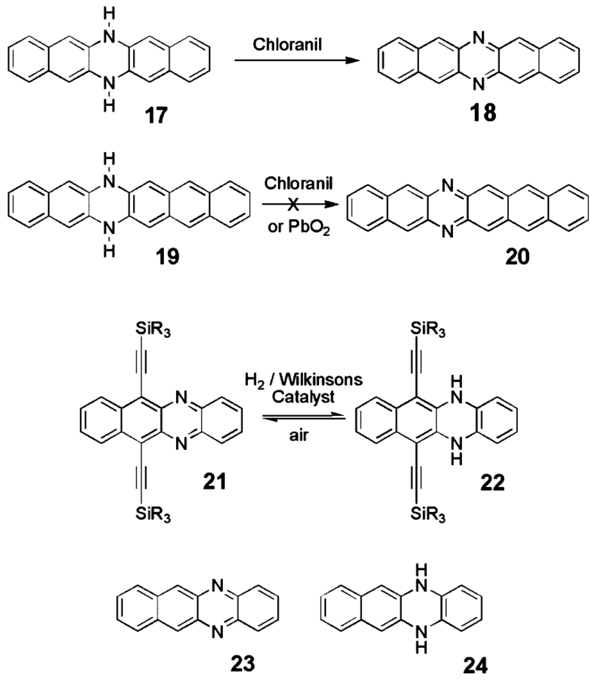
Scheme 2 Synthesis of pyrazinacenes through a dyotropic rearrangement of 1,4,5,8-tetraazafulvalenes (**14**[18]) or by nucleophilic aromatic substitution of 2,3-dicyanopyrazino[2,3-*b*]pyrazine derivatives (**16**[19,20]).

More recently, a new procedure for the synthesis of unsubstituted pyrazinacene derivatives has been reported.[19,20] The approach involves a double nucleophilic attack at the 2,3 positions of 2,3-dicyanopyrazino[2,3-*b*]pyrazine derivatives, which ultimately results in substitution of nitrile groups during the formation of an *N*,*N*′-dihydropyrazine ring. Nucleophilic substitution of nitriles has also been used in the synthesis of some dicyanoquinodimethane derivatives from 7,7,8,8-tetracyanoquinodimethane and amines or alcohols.[21,22]

Substitution of 2,3-dicyanopyrazino[2,3-*b*]pyrazine came about initially during attempts to use it to prepare phthalocyanines, which however resulted only in substitution of its nitrile groups by the available nucleophile (in that case hexanolate anion) giving aromatic ethers.[19] Later, *ortho*-substituted aromatic amines were also applied as nucleophiles. We realized that this reaction (Scheme 2) presents a useful method for preparation of discrete oligoacenes, especially pyrazinacenes, but should also be available for application in the synthesis of other heteroatom-substituted acenes. For example, 2,3-dicyano-1,4,5,10-tetraazaanthracenes **15** are substituted by phenylenediamines to give 6,13-dihydro-5,6,7,12,13,14-hexaazapentacenes **16**. One advantage of this method is that the pyrazinacenes obtained are unsubstituted and the reduced moiety is available for further chemical modification such as *N*-alkylation, oxidation or acid/base reactions. Thus, pyrazinacenes prepared by this method are complementary to those described by Stöckner and coworkers since they can be seen as unsubstituted analogues. The lack of *N*-substituents implies different uses for these compounds. While the *N*-alkylated derivatives of Stöckner and coworkers are highly fluorescent with great potential as dyestuffs and biochemical markers, the unsubstituted compounds have structures more appropriate for investigation as organic semi-conducting materials although they may be also developed as dyes and fluorescent markers since they also possess similar physicochemical characteristics to the *N*-substituted compounds. An additional unique feature which is due to a lack of substituents in a reduced pyrazinacene derivative is that protic tautomerism may occur. This is a potentially useful property which will be discussed in more detail later in this review.

Aromaticity/antiaromaticity

One point of interest which was largely unrecognised in the early days of pyrazinacene chemistry was the unusual redox behaviour of acene compounds containing the pyrazine unit. 6,13-Dihydro-6,13-diazapentacene **17** can be oxidized to the fully aromatic form **18** using *p*-chloranil (Scheme 3).[23] However, the fact that the reduced form is stable at all is somewhat surprising given that the dihydropyrazine unit contains $4n$ π electrons and is thus formally antiaromatic. As the length of the pyrazinacene is increased the fully oxidized form becomes even less favoured; for example, the reduced dihydrodiazahexacene **19**, cannot be oxidized either with *p*-chloranil or lead(IV) oxide (Scheme 3).[24] Also, as the number of fused pyrazine rings increases, the reduced form is increasingly favoured. This is exemplified by 5,14-dihydro-5,7,12,14-tetraazapentacene **3** which cannot be oxidized to the tetraazapentacene.[12] The somewhat unusual stability of the antiaromatic compounds compared to their fully aromatic counterparts was investigated using computational techniques by Bunz and Schleyer.[25] They synthesised two dialkynylated diazatetracenes (**21**, **22**), which could be reversibly reduced/oxidized



Scheme 3 Aromatic acenes containing the pyrazine moiety together with their antiaromatic reduced congeners.

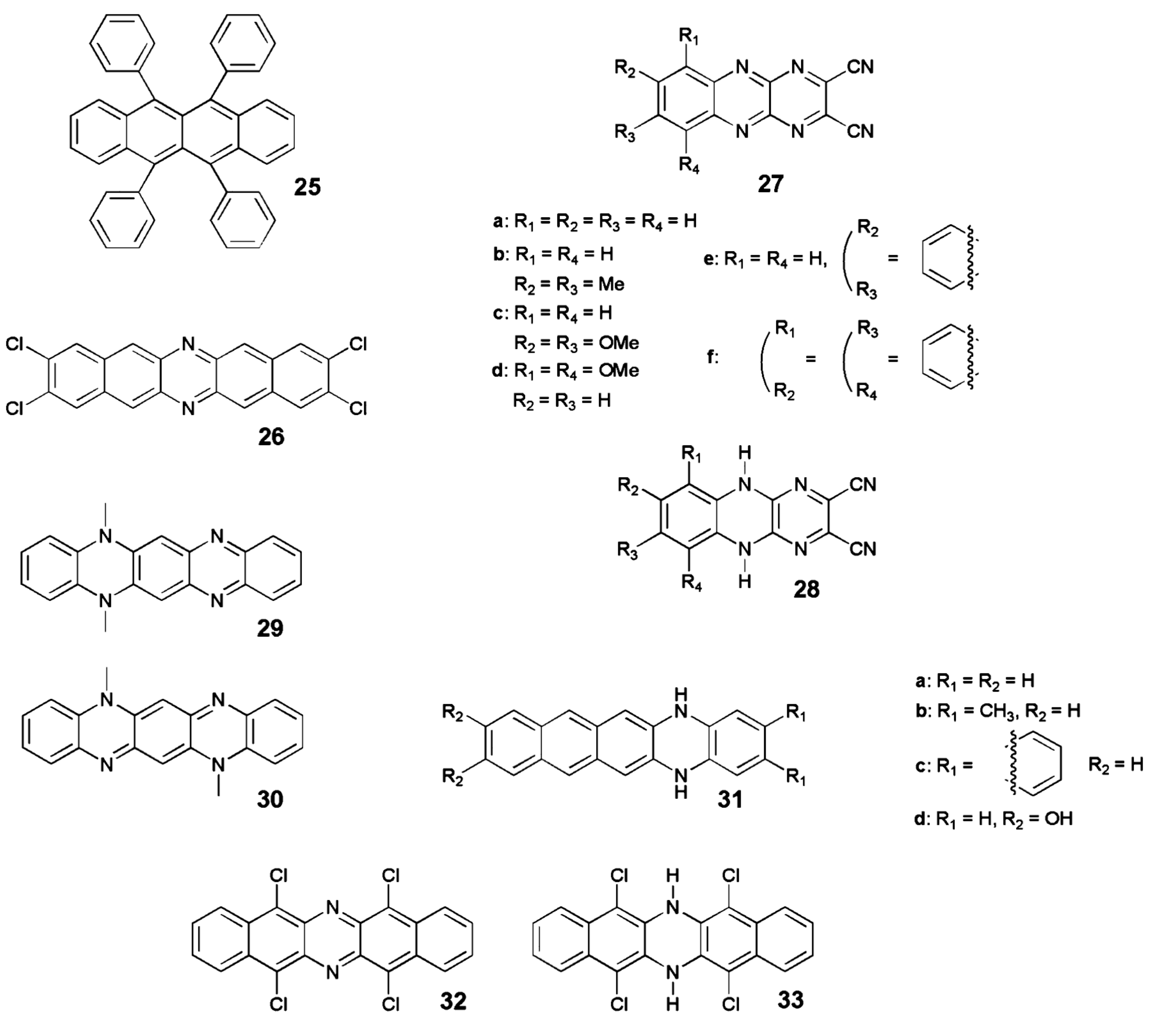
between the antiaromatic and aromatic forms (Scheme 3). Nucleus Independent Chemical Shift (NICS) calculations were used to estimate the aromatic and antiaromatic contributions for each six-membered ring in the two model compounds, diazatetracene and the reduced derivative dihydrodiazatetracene. As expected, the NICS calculations for the fully oxidized compound **21** showed that each of the rings were diatropic (diamagnetic). The remote π contribution from other rings was found to be rather small. These findings were almost identical to the simple acene, tetracene. For the reduced compound **22**, the findings were somewhat different. Despite containing 4*n* π electrons, **22** was found to be weakly aromatic. The reduced pyrazine ring was found to be locally paratropic (paramagnetic) and the remaining rings locally diatropic; however, the remote π contributions for each of the rings were found to be distinctly paratropic. In other words, **22** can be viewed as globally aromatic, yet the central dihydropyrazine ring is strongly (locally) antiaromatic. These ideas were further developed by Bunz and Schleyer.[26] Resonance energy (RE) and extra cyclic resonance energy (ECRE) calculations for a series of dihydrodiazapentacenes revealed that the compounds are stabilized by a combination of aromaticity and ethenamine conjugations of their dihydropyrazine rings. Stability is increased in the case of dihydrodiazapentacenes with "inner" dihydropyrazine moieties which can have two Clar sextet rings and are thus more aromatic than those with an outer dihydropyrazine ring as well as the 4*n* + 2 π electron diazapentacenes. As a result of the unusual electronic interactions in the dihydropyrazine-containing derivatives, the acene skeleton maintains a planar configuration maintaining their interest as molecular electronic materials (since planar acene forms favour herringbone-type or long-range stacked structures which in turn are favorable for the semi-conducting properties).

Pyrazinacenes as organic electronic materials

Acenes have attracted significant interest as a result of their excellent solid state electronic properties.[3] For example, pentacene has a hole mobility of up to 5.5 $cm^2\ V^{-1}\ s^{-1}$, greater than that of amorphous silicon.[27,28] Rubrene **25** (Scheme 4), a tetracene derivative, has the highest recorded charge carrier mobility for an organic semiconductor at 40 $cm^2\ V^{-1}\ s^{-1}$.[29,30] Unfortunately, pentacene as well as some other acene derivatives are susceptible to oxidative degradation. Also, most acenes are p-type semiconductors. Realisation of new types of molecular electronic devices utilizing complementary circuits requires both n-type and p-type materials. Replacing carbon with nitrogen atoms in acenes not only produces materials which are more stable, but also results in materials which are more electron deficient. Houk and Winkler used DFT methods to calculate the electron affinities of a series of azapentacenes.[31] As expected, electron affinities increase with the number of nitrogen atoms contained in the azapentacene. Calculations suggest that a minimum of 7–8 nitrogen atoms need to be incorporated into pentacene to give a sufficiently high electron affinity (3 eV) for n-type behavior. By comparing the calculated electron affinities of a series of azapentacenes with that of the known n-type compound, perfluoropentacene, Chen and Chao suggested that as few as 5 nitrogen atoms were necessary for a change of polarity of charge transport.[32] Their calculations also showed that the frontier orbital energy levels can be tuned not only by the number of heteroatoms in the acene backbone, but also by introducing additional electronegative substituents such as chlorine or fluorine at the acene periphery. For example, they calculated that tetrachlorodiazapentacene **26** (Scheme 4), would have a larger electron affinity than perfluoropentacene.

Yamashita and co-workers reported on the preparation and OFET properties of a series of dicyanotetraazaanthracene derivatives, **27a–f** and reduced congeners **28** (Scheme 4).[33] The electron accepting properties of these materials were investigated using cyclic voltammetry, which revealed that the compounds are all strong electron acceptors. The combination of the electron deficient pyrazinoquinoxaline moiety together with the electron withdrawing cyano substituents results in compounds with large electron affinities. In organic field effect transistor (OFET) devices, clean n-type transistor behaviors were observed, although the charge mobilities were somewhat low (up to $3.6 \times 10^{-6}\ cm^2\ V^{-1}\ s^{-1}$). The authors suggested improvements in charge mobility may be realized through the use of more symmetrical compounds and by optimization of device fabrication conditions. Some very recent results have suggested N-heteropentacenes can exhibit ambipolar and n-type OFET properties with charge mobilities as high as 3.3 $cm^2\ V^{-1}\ s^{-1}$, which are among the highest reported for n-channel organic semicondutors.[34]

Because of their higher stabilities than their acene congeners, azaacenes have also been investigated as p-type semiconductors. For example, Miao and co-workers synthesized *N*-alkylated derivatives of 5,14-dihydro-5,7,12,14-tetraazapentacene by deprotonation and subsequent reaction with methyl iodide to give compounds **29** and **30** (Scheme 4).[35] Both alkylated compounds showed p-type OFET behaviour, with mobilities of $5 \times 10^{-4}\ cm^2\ V^{-1}\ s^{-1}$ and $1 \times 10^{-4}\ cm^2\ V^{-1}\ s^{-1}$ for **29** and **30**, respectively. Nuckolls and co-workers investigated the thin film transistor properties of a series of dihydrodiazapentacene derivatives **17**

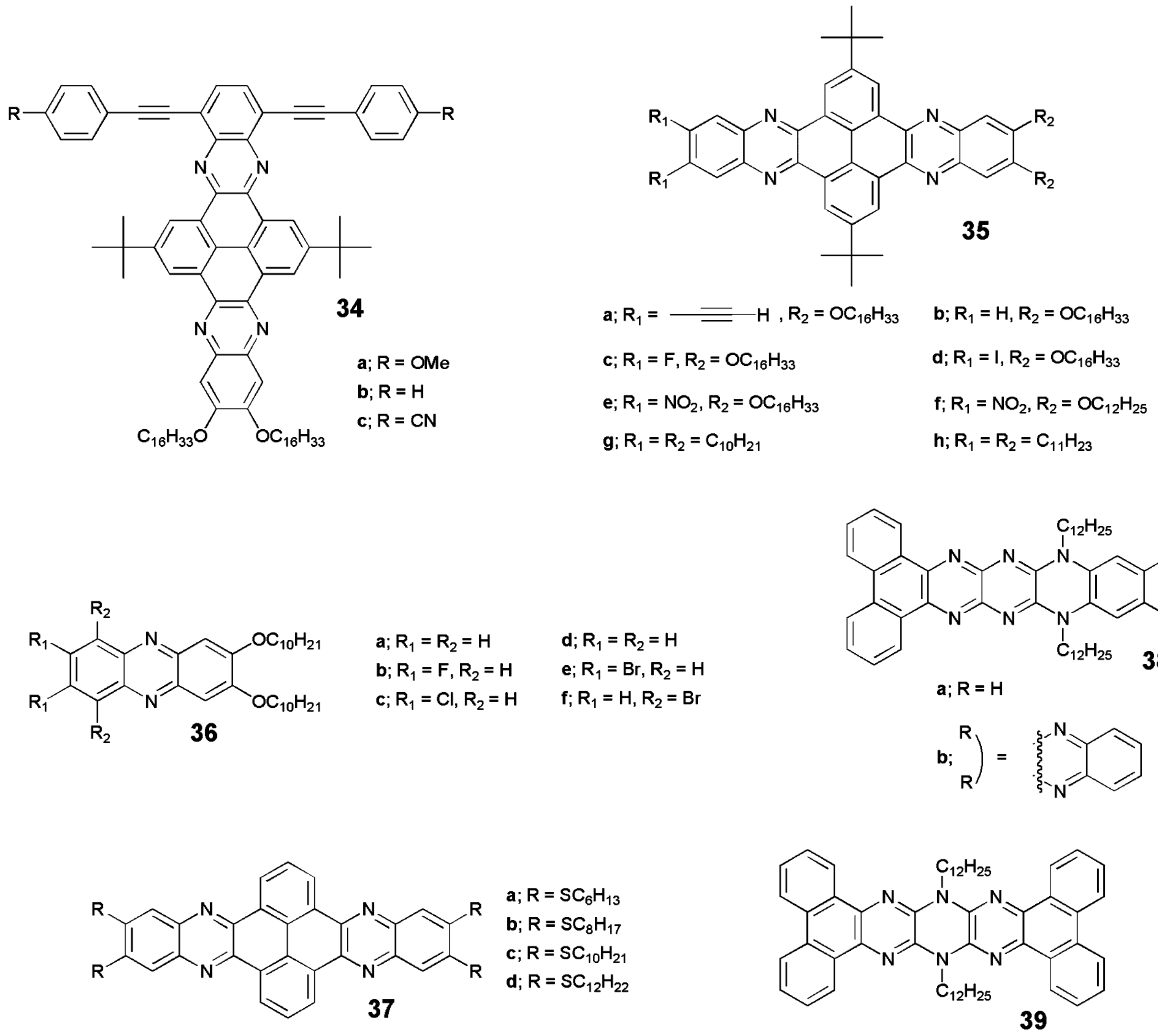


Scheme 4 Acene and azaacene derivatives which have been investigated as candidates for organic electronic applications. Azaacenes such as **32** have shown charge mobilities approaching those exhibited by some pentacene-based devices.[37]

(Scheme 2), **31a–d** (Scheme 4).[36] Although OFET properties were modest with mobilities approaching 10^{-2} cm^2 V^{-1} s^{-1} and on/off ratios up to 8 × 10^4, the devices were found to be remarkably stable; when operated periodically over several days, open to the atmosphere, they showed no significant deterioration of operation. The OFET performance of dihydrodiazapentacene **17** was later found to be significantly dependent on the crystalline polymorph of the deposited film.[37] Deposition of dihydrodiazapentacene on an octadecyltrichlorosilane (OTS) treated SiO_2 on silicon substrate resulted in OFET mobilities over 5000 times greater than those obtained using non-treated SiO_2 on silicon substrates. The difference was due to the formation of a different crystalline polymorph of dihydrodiazapentacene on the OTS treated surface. Thin film morphology was also found to play a significant role in the performance of azaacene-based OFET devices. For example, the tetrachlorodiazapentacene **32** and its reduced congener **33** (Scheme 4) were synthesized and assessed as active channel materials for thin film transistors. Deposition onto SiO_2/Si substrate resulted in amorphous films, and no OFET properties could be observed. However, the use of a pentacene buffer layer resulted in formation of crystalline films with a very high mobility of 1.4 cm^2 V^{-1} s^{-1} measured for **33** and a respectable 0.13 cm^2 V^{-1} s^{-1} for the oxidized derivative **32**.[38] Although the performance of nitrogen-containing organic electronic materials is not quite as high as some of the best materials available, these latest results demonstrate that high performance is possible. Heteroatom substitution provides a new means of altering not just the intrinsic molecular electronic properties of materials, but also a means to control thin film, crystalline and aggregated morphologies which play a key role in the performance of bulk materials. This is discussed further in the following section.

Self assembly

In the previous section, we discussed how the performance of materials in organic electronic devices depends not only on the molecular identity, but also on the supramolecular structure of the active materials. Self assembly can be achieved through crystallization,[39] self aggregation in solution,[40] Langmuir Blodgett techniques,[41] layer-by-layer (LbL) methods[42] or through liquid crystalline properties.[43] In the case of conventional acenes, self assembly has yielded nanostructures with novel properties and advantages over their microcrystalline counterparts. For example, self assembly of solution-processable substituted



Scheme 5 Pyrazinacenes showing self assembling properties: bisphenazine compounds can self assemble through self aggregation in solution (**34b–c**[43] and **35a–f**[14]), crystallisation (**37a–d**[45,46]) and liquid crystalline properties (**35g–h**[50]). Pyrazinacene derivatives **38**[19] and **39**[20] can also show self assembly through self aggregation.

pentacenes has produced microribbons exhibiting excellent OFET characteristics,[44] self-assembled gel fibers of substituted anthracene and tetracene have been shown to exhibit efficient energy transfer,[45] and end-functionalized acenes with a static dipole can self-assemble to form co-facially stacked columnar superstructures which exhibit very good OFET properties.[46] We now introduce some of the latest developments regarding nitrogen-containing acenes and structural relatives which exhibit self-assembling properties. With respect to the relative self-assembly properties of acenes and azaacenes, it is important to note that introduction of several nitrogen atoms to acenes increases the polarity and potential for hydrogen-bonding interactions so that azaacenes may be better suited for aggregation studies due to their greater amphiphilicity (especially if substituted with appropriate hydrophobic groups). With this in mind we will describe several excellent examples of aggregated pyrazinacenes and we highlight one example of a hierarchic nanotubular assembly of pyrazinacenes.

Lee and co-workers reported on the synthesis and self-assembling properties of a series of T-shaped molecules based on unsymmetrical bisphenazines, **34a–c** (Scheme 5).[47] Variation of the peripheral substituent groups resulted not only in tunability of the HOMO and LUMO levels of the molecules, but also influenced the 1D self assembly and morphologies of the aggregated molecules. **34a** did not undergo self assembly probably due to free rotation of its methoxy group, which interferes with molecular packing. However, compound **34b** formed high aspect ratio straight strand-like structures on self assembly using a phase transfer method. In contrast, **34c** formed flexible 1D nanofibres with a homogeneous thickness distribution (Fig. 1). The self-assembling properties of the bisphenazine compounds **35a–f** (Scheme 5) were also reported in a follow-up publication.[48] Bisphenazine was substituted asymmetrically and the effect of the various substituents on the self-assembling and electronic properties of the compounds studied. Using a phase transfer precipitation method, the compounds self assembled into nanofibres, the size and shape of which were found

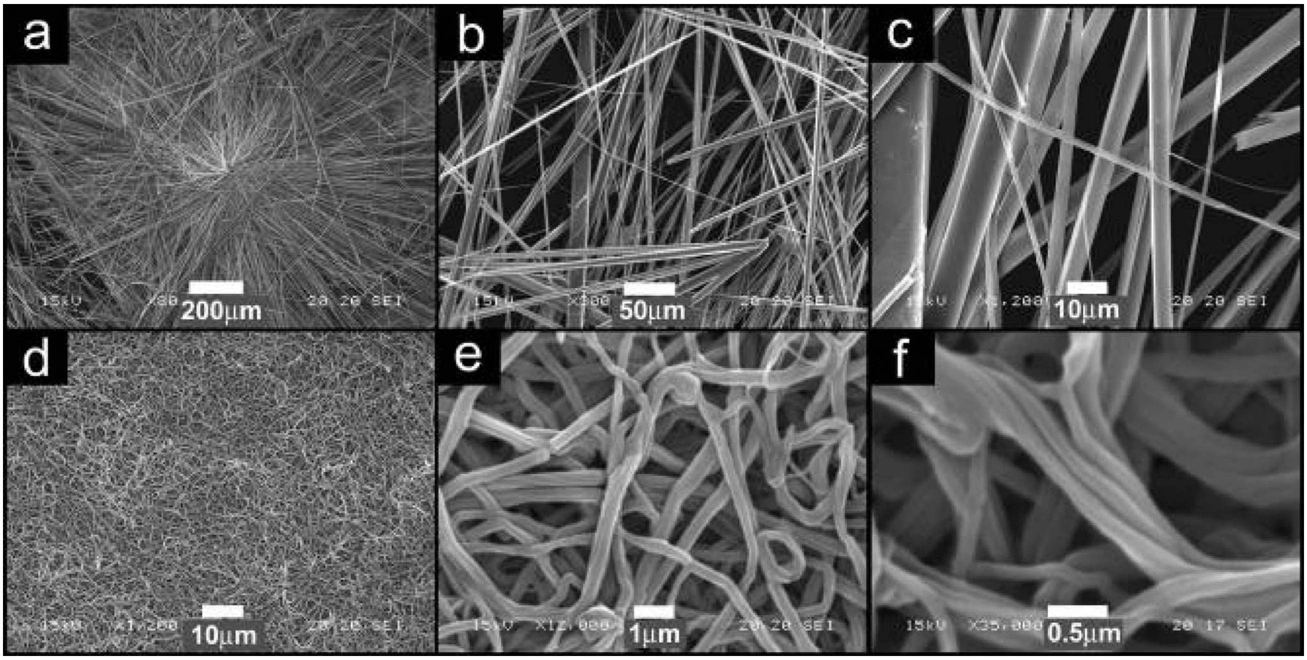


Fig. 1 SEM images of microstrands of **34b** (a–c) and nanofibers of **34c** (d–f). (Reprinted with permission from ref. 47. Copyright American Chemical Society).

to be dependent on the nature of the peripheral substituents. The substituents also played an important role in electronic properties of the compounds, for example, the nitro-substituted compounds **35e** and **35f** had the lowest LUMO energy levels as a result of the electron withdrawing effect of the nitro substituents. The authors suggested that these electron deficient compounds may find application as n-type materials in optoelectronic devices. Lee and co-workers also studied the effects of halogen substitution on the self-assembling properties of a series of alkyloxy terminated phenazines **36a–f** (Scheme 5).[49] Significant differences in morphology based on the type of halogen substituents were observed and were presumed to be due to the balance of intramolecular forces, including hydrogen bonding, between hydrogen atoms and the phenazine nitrogen atoms, π–π interactions, van der Waals interactions and possible halogen–halogen bonding in some compounds. When strong interactions such as hydrogen-bonding or halogen–halogen interactions are coupled with directionally orthogonal π–π interactions, unequal growth rates in two different directions lead more effectively to 1D assembly. The thin film microstructures of a series of symmetrical bisphenazines were studied in two separate publications.[50,51] Although the compounds did not exhibit liquid crystalline properties, a series of transitions was observed using differential scanning calorimetry corresponding to crystal–crystal phase transitions. Jabbour and co-workers combined lattice information from XRD analysis with orientation information from polarized photon absorption spectroscopy, Fourier transform infra-red (FTIR) spectroscopy, spectroscopic ellipsometry (SE), and near-edge X-ray absorption fine structure spectroscopy (NEXAFS) to confirm an almost complete crystal packing model for compound **37d** (Scheme 5).[50] Cheng and co-workers used wide-angle X-ray diffraction (WAXD) and selected area electron diffraction (SAED) to study the microstructure of the homologous compounds **37a–d** (Scheme 5) and confirmed a monoclinic structure for all the phases studied, the phase transitions corresponding to an increase in conformational defects in the alkyl chains with increasing temperature.[51] The authors suggested that these compounds may find use in photovoltaic applications.

A series of fused pyrazine derivatives which usually exist with one of the pyrazine rings in a reduced state has also been prepared **38a–b**, **39** (Scheme 5).[19,20] Reduced pyrazine rings can be *N*-alkylated to give amphiphilic molecules which self assemble under appropriate conditions. For example, **36a** tends to form sheet- or foam-like aggregates, probably as a result of the formation of mono- or bilayer lamellar architectures (Fig. 2).[19] In contrast, **38b** tends to form fibrous structures reminiscent of organogels and a π–π stacking aggregation mode based upon electronic spectroscopic measurements was proposed. **39** (Scheme 5) also shows very interesting self-assembling properties.[52] Dissolution in hot toluene followed by cooling to room temperature results in the formation of 130 nm wide 2D tape-like aggregates. Helical twisting of these structures leads to nanotubes 150–200 nm in diameter which can exceed 10 μm in length (Fig. 3). As with other assemblies of electro- and photoactive chromophores, we expect that these unusual structures of nitrogen-rich pentacenes will yield interesting properties that will depart significantly from the parent non-aggregated compounds.

Liquid crystalline organic electronic materials have attracted considerable attention from researchers due to their unique properties. For example, although crystalline materials can exhibit very high charge mobilities, performance can be significantly reduced due to grain boundaries in polycrystalline films. Liquid crystalline materials still have sufficient ordering necessary to achieve high charge mobilities, but grain boundaries can be eliminated so that functional, easily processable devices can be realized. Liquid crystals have also found use as polarized light emitters in organic

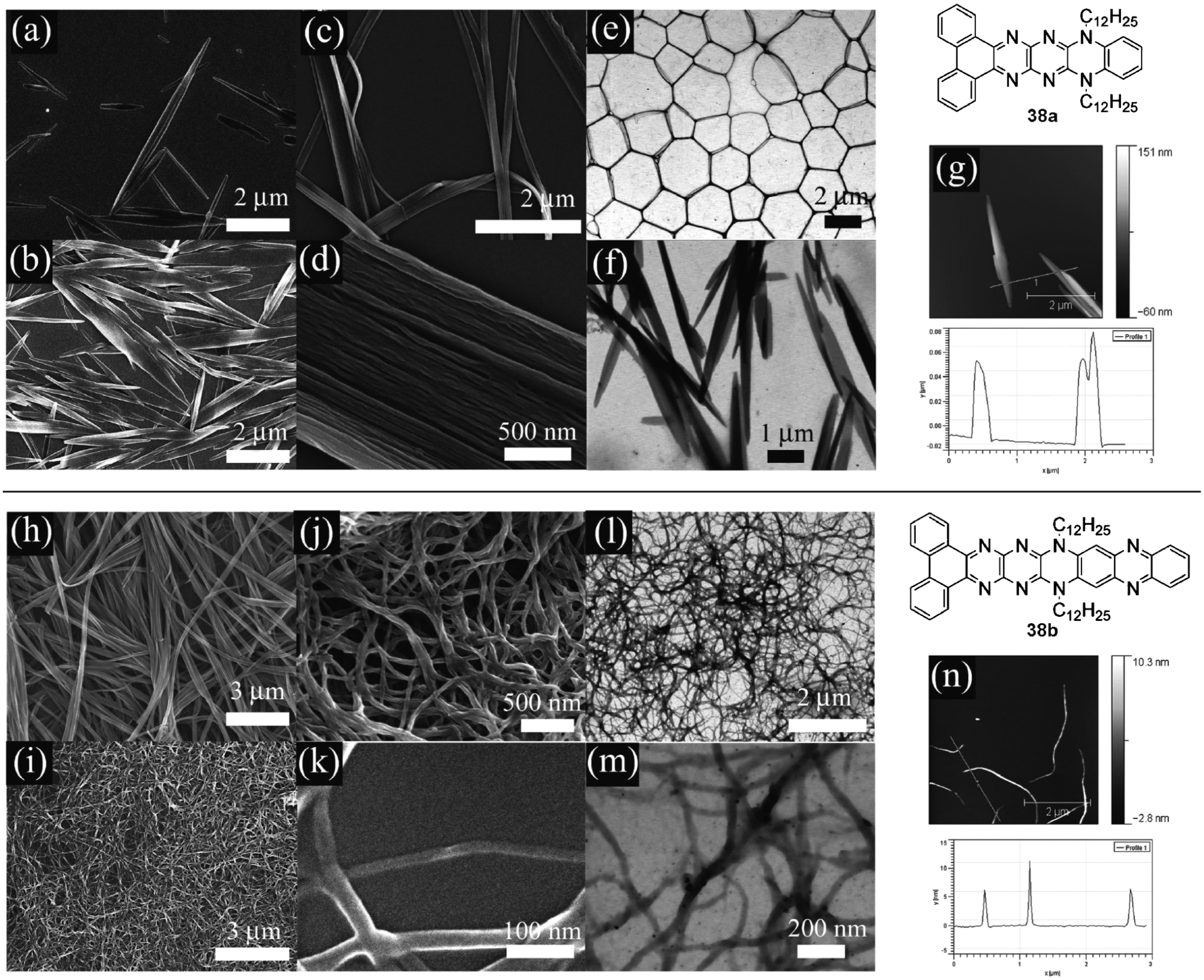
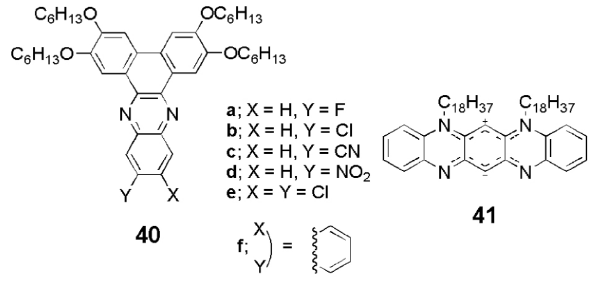


Fig. 2 Microscopic images of self-assembled structures of **38a** (upper) and **38b** (lower). **38a**: (a) SEM, from a dichloromethane suspension. (b) SEM, chloroform. (c, d) SEM, tetrahydrofuran/water suspension. (e) STEM, dichloromethane solution. (f) TEM, from a dichloromethane suspension. (g) AFM, from a dichloromethane suspension. **38b**: (h) SEM, tetrahydrofuran/methanol. (i–k) SEM, dichloromethane/methanol. (l, m) TEM, dichloromethane/methanol. (n) AFM, from a dichloromethane/methanol suspension. (Reprinted with permission from ref. 19. Copyright American Chemical Society).

LEDs[53] as well as in high performance organic photovoltaic devices.[54] Harris and co-workers reported that compounds **35g** and **35h** exhibited a liquid crystalline phase at higher temperatures. The exact phase structure was not fully characterized but XRD analysis confirmed π–π overlap in the liquid crystalline phase which, together with the two reduction processes observed using differential pulse voltammetry, suggested these materials have potential as electron transporting materials in organic photovoltaic or OLED applications.[55] Williams and co-workers utilized a simple modular approach involving the condensation of a range of *o*-phenylenediamines with a phenanthrene-9,10-dione to synthesize disk-shaped molecules **40a–f** (Scheme 6), many of which formed columnar phases.[56] Tolbert, Wudl and co-workers reported the synthesis of a zwitterionic tetraazapentacene derivative **41** (Scheme 6),[57] which exhibited several layered crystalline phases and, at higher temperatures, a lamellar liquid crystalline phase. The molecule has a very large dipole moment (calculated to be 9.1 D) due to its zwitterionic nature and the authors suggest that similar molecules may be interesting systems for optoelectronic switching devices.



Scheme 6 Liquid crystalline azaacene derivatives: a series of discotic azaacenes **40a–f**[56] and a zwitterionic azaacene (**41**[57]) exhibiting a lamellar liquid crystalline phase.

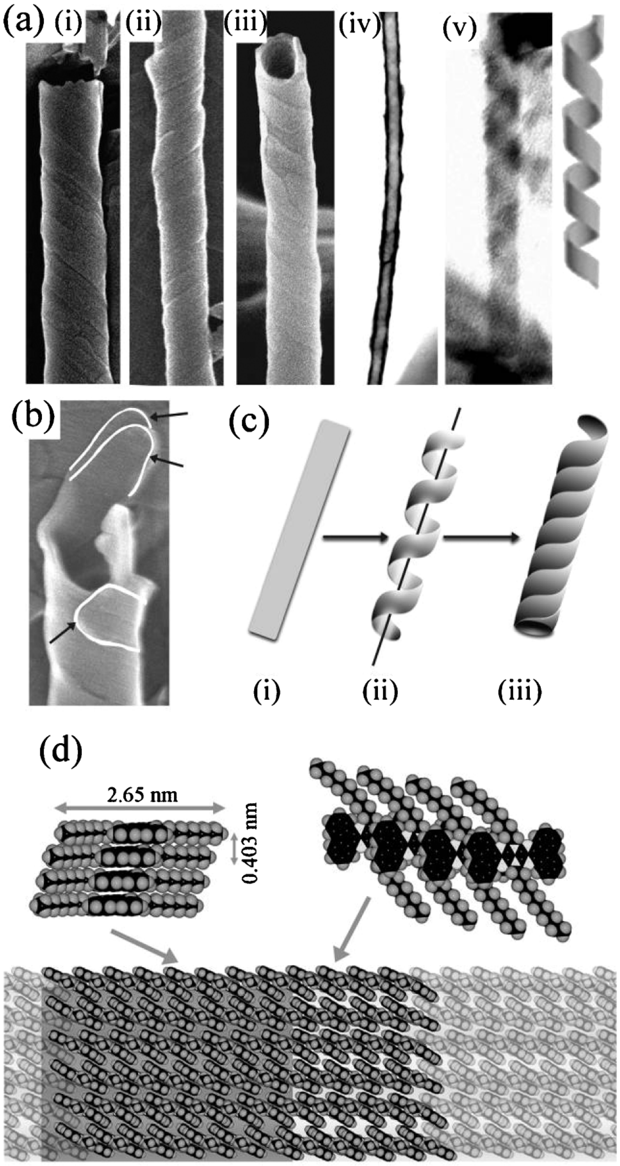


Fig. 3 Helical forms of pyrazinacene nanotubes. (a) (i)–(iii) SEM images of typical helically coiled tapes of **39**. (iv) STEM image showing internal cavity and exterior unevenness of the tubes. (v) An uncoiled helix with a model at right. (b) Evidence for multi-walled nanotubes. White lines indicate the ends of three tapes composing this tube. (c) Mechanism of formation of self-assembled pyrazinacene nanotubes: (i) molecules of **39** aggregate to form a bilayer (or multilayered) tape (~130 nm wide); (ii) the tape twists to form a helical structure; (iii) closing of the helix permits formation of a hollow cylindrical structure microns in length with ~150 nm internal diameter. (d) Proposed model of the molecular level packing of **39**. Single-headed arrows indicate the respective viewing directions for the two structures given. (Reprinted with permission from ref. 52. Copyright Royal Society of Chemistry).

Tautomerism in reduced pyrazinacenes

An aspect of the pyrazinacenes which has no parallel in the normal hydrocarbon acenes is that of potential NH tautomeric processes in reduced (or protonated) species. Study of this phenomenon is made possible by the relative stability of the dihydropyrazine-containing compounds. The potential importance of this feature has also been emphasised by Bunz.[1b] Our work on pyrazinacenes has focused on the preparation and characterization of compounds containing several adjacently fused pyrazine rings, which we term "pyrazinacenes". Previously, compounds containing up to six adjacently fused pyrazine rings had been synthesized.[18] However, due to the synthetic methods used, the reduced ring position is fixed by the presence of large substituents on the dihydropyrazine moieties. We have used a new methodology to synthesize pyrazinacenes containing up to five adjacently fused pyrazine rings containing unsubstituted (*i.e.* with no large alkyl or aryl substituents) reduced pyrazine rings. During the development of these synthetic methods, we were intrigued by the possibility of protic tautomerism in pyrazinacenes, which does not have an analogue in the CH acenes. Prototropic rearrangements in reduced pyrazinacenes have been suggested previously in for example the structure of 5,14-dihydro-5,7,12,14-tetraazapentacene (see Scheme 1, **3**), which was erroneously reported for over a century. In 1987, its true structure was determined by NMR to be the 5,14-dihydro form, one of two possible tautomers.[58,59] This system was also studied by Tang[35] who performed *N*-alkylations and could isolate two tautomers of **3** as their *N*-methyl derivatives. In that case it was important to note the effect of the HOMO–LUMO band gap since this might provide a means for tuning the electronic properties by varying the tautomer structure. Siri and co-workers noted a prototropic rearrangement during synthesis of substituted dihydrotetraazapentacenes, which was dependent on the electronic influence of the substituent.[14] We observed a similar re-arrangement during single-crystal X-ray crystallographic analysis of the compound that was expected to be 2,3-dicyano-5,12-dihydro-8,9-diphenyl-1,4,5,6,7,10,11,12-octaazatetracene, **42**.[20] Actually, its tautomeric analogue **43** containing the 6-11-dihydro moiety was obtained. A preliminary variable temperature (VT) ^{1}H NMR study on the monosodium salt of **43** (**43·Na**; used to avoid the appearance of too many tautomers; Fig. 4) revealed splitting of the resonance due to exchangeable amine protons at a depressed temperature consistent with the existence of two isomers of **43**. *N*-Alkylation of a similar octaazatetracene compound gave multiple products due to alkylation of different tautomers (Fig. 4d)

We have used molecular dynamics simulations to study the deprotonation/reprotonation processes necessary for tautomerism in a series of pyrazinacenes containing three, four, five and six linearly fused pyrazine rings.[60] For monoprotic tautomerism, the free energy barrier varies from around 20–50 kcal mol^{-1} depending on the number of rings and the positions of the protons. Our calculations also revealed that both mono and diprotic tautomerism affect the HOMO and LUMO energy levels and band gap. In the case of diprotic tautomerism when there are at least three fused pyrazine rings, a delocalization of the HOMO occurs along these rings with no (or just minor) contributions due to the remaining portion of the molecule (**44–47**, Fig. 5). The shift of protons along the molecule in a certain direction causes a reduction of delocalization in the same direction or a transfer of electronic density in the opposite direction.

As an extension to this work, we used DFT methods to model the structural, electronic and energetic properties of a series of multiply reduced extended pyrazinacenes **48a–g** (Scheme 7).[61] We expect that if such extended pyrazinacenes or fused polypyrazines can be synthesized, they will most likely exist in their most

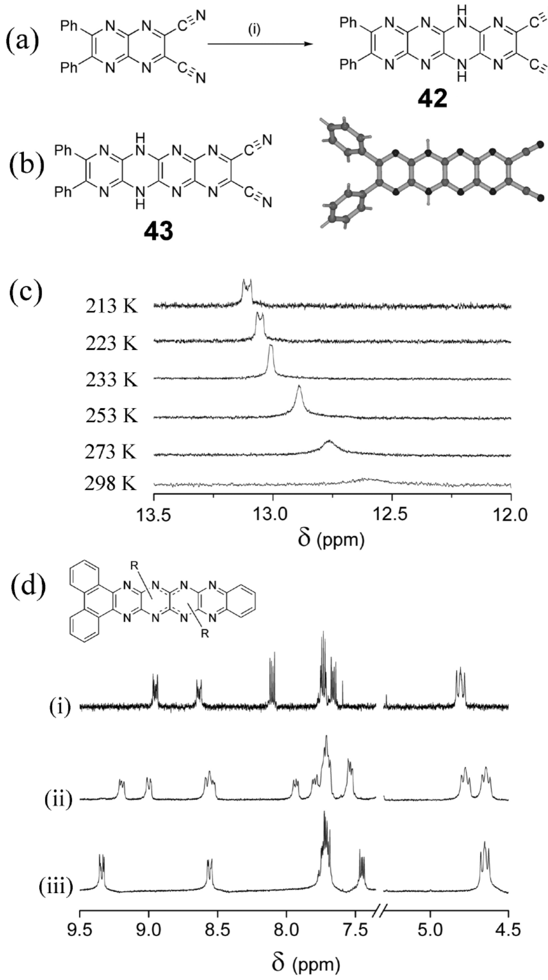


Fig. 4 (a) Synthesis of **42**. (i) 2,3-dicyano-5,6-diaminopyrazine, dimethylsulfoxide, Na_2CO_3, 100 °C. (b) Chemical structure of **43** and its molecular structure obtained by single crystal X-ray crystallographic analysis. (c) VT-^{1}H NMR spectra of **43·Na$^+$** showing the splitting of the NH resonance at low temperature. (d) Proposed chemical structure and ^{1}H NMR spectra (i)–(iii) of compounds obtained by *N*-alkylation of dihydro-5,6,7,8,13,14,15,16-octaaza-[*n*,*p*]-dibenzohexacene. (Reprinted with permission from ref. 60. Copyright American Chemical Society).

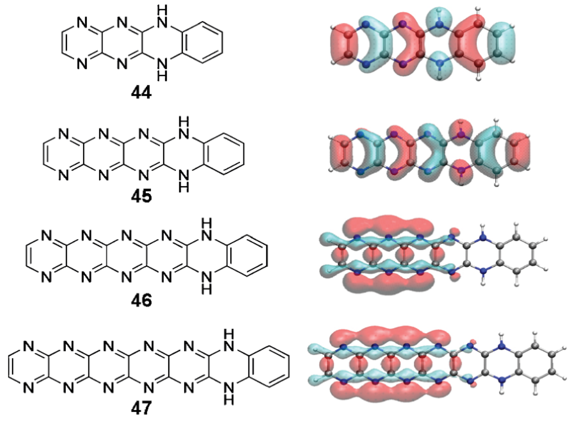
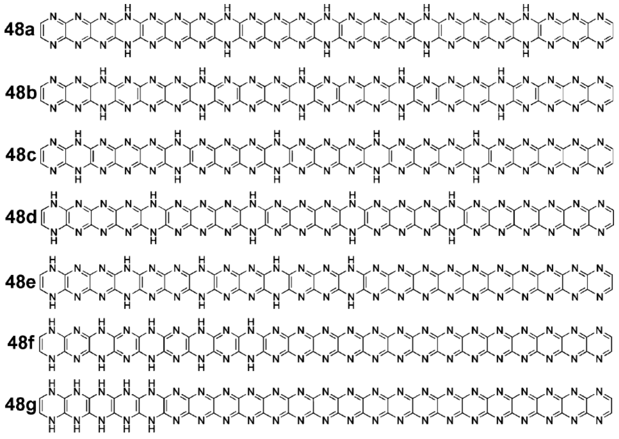


Fig. 5 Pyrazinacenes **44–47** and their calculated HOMO structures. In the case of **46** and **47**, the HOMO is delocalised across the fused pyrazine rings with little contribution from the remaining portion of the molecules. (Reprinted with permission from ref. 60. Copyright American Chemical Society).



Scheme 7 Chemical structures of pyrazinacene tautomers **48a–g**.

stable multiply reduced form. Our computational study involved the gradual accumulation of reduced moieties towards one end of the molecule and towards the center of the molecule. The purpose was to observe the effect of tautomeric processes on the relative stabilities and associated electronic structures of the resulting isomers (tautomers). The calculated structures of the HOMOs and LUMOs of compounds **48a–g** (Fig. 6) illustrate the effect of accumulating the dihydropyrazine moieties towards one end of the molecule. It is evident that the relative positions of the reduced pyrazine groups are strongly coupled with the structures of both HOMO and LUMO supporting our previous proposal of the coupling of electronic and proton transport if the dihydropyrazine groups could be dynamically shifted under an applied potential (electronic or protic). As the reduced moieties accumulate at the end of the molecule, a decrease in stability is predicted. The number of Clar sextet rings decreases as the reduced moieties accumulate and this is known to reduce aromatic stabilization. Also, as discussed previously, it is known that the antiaromaticity of the dihydropyrazine moiety can be 'delocalized' if fused with other aromatic benzenoid systems. In passing from tautomers **48a–g**, dihydropyrazine groups approach each other so that the proposed dispersion of their antiaromaticity (and the probable associated instability) by delocalization becomes increasingly unfavorable and the total energy of the system increases sharply. Thus we predict that protic transport should occur through a concerted proton transfer without intramolecular aggregation of the dihydropyrazine groups. Our calculations also predict a narrowing of the band gap as the dihydropyrazine rings accumulate, and compounds **48e–g** are predicted to have a band gap approaching zero which may equate to metallic characteristics in their electrical conductivity (Fig. 7).

Conclusions and outlook

Pyrazinacenes have attracted significant interest for several reasons. Several groups of researchers have shown that pyrazinacenes not only exhibit performances on a par with their non-aza substituted equivalents in molecular electronic applications but also offer advantages such as ease of preparation, stability and opportunities to modify electronic or physical properties through elaboration at nitrogen atoms. In addition to applications related

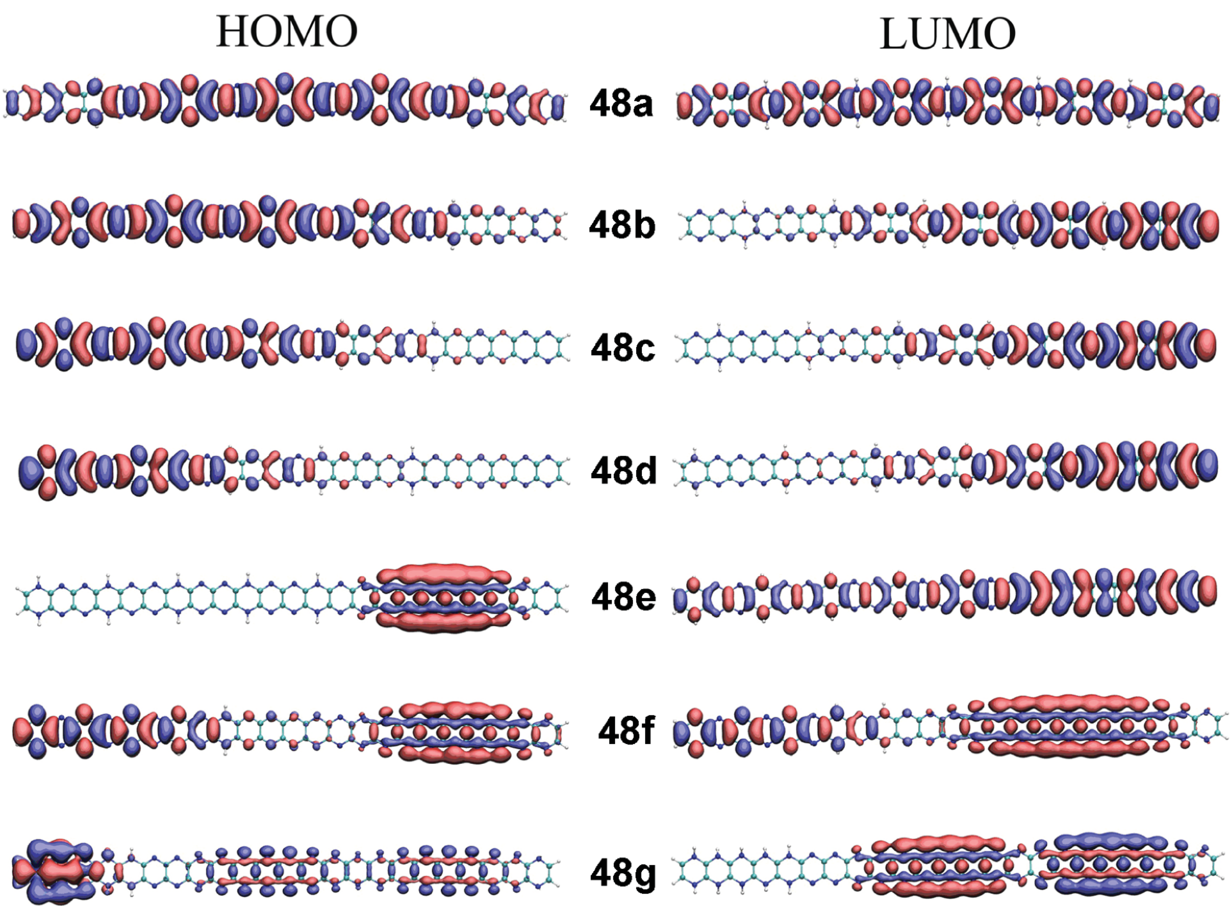


Fig. 6 Calculated structures of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of **48a–g**. (Reprinted with permission from ref. 61. Copyright Royal Society of Chemistry).

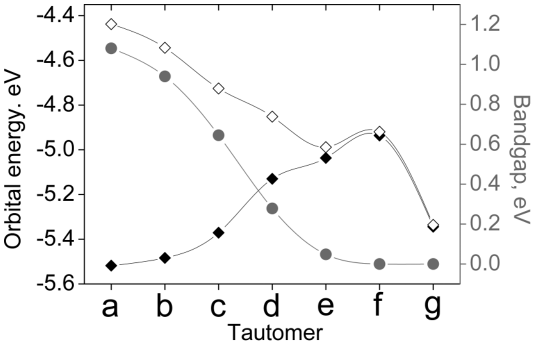


Fig. 7 Graph of calculated molecular orbital energy levels and the consequent band gap for tauotmers of **48**. (Black diamond) HOMO level. (Empty diamond) LUMO level. (Gray circle) bandgap. (Reprinted with permission from ref. 61. Copyright Royal Society of Chemistry).

to p-type semiconducting properties, azaacenes can exhibit n-type semiconducting behaviour and also show promise in applications utilizing liquid crystals, photoluminescent or electroluminescent materials and self-assembled structures. Tautomerism in reduced pyrazinacenes is an unexploited phenomenon which could find application in a number of technologies. One can imagine isolated lengthy reduced pyrazinacenes acting as discrete proton transporters in protonic devices or polymeric derivatives being used in proton-conducting membranes inside fuel cells. Also, the tautomeric process in pyrazinacenes can result in a change in HOMO–LUMO energy levels and band gap which opens up new possibilities related to optoelectronics and photoluminescent probes. It is likely that the pyrazinacenes will continue to attract scientific interest as a result of their various properties and some of the advantages over their non aza-substituted congeners. We predict the significant growth of this class of compound hopefully ultimately leading to genuine applications as molecular electronic materials, dyestuffs and fluorescent biolabels.

Acknowledgements

This work was financially supported by the World Premier International Research Center Initiative, from MEXT, Japan and the Core Research for Evolutional Science and Technology (CREST) program of Japan Science and Technology Agency (JST).

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