

The Larger Linear N-Heteroacenes

Uwe H. F. Bunz*

Organisch-Chemisches Institut and Centre of Advanced Materials, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 225 and 270, 69120 Heidelberg, FRG

CONSPECTUS: The close structural and chemical relationship of N-heteroacenes to pentacene suggests their broad applicability in organic electronic devices, such as thin-film transistors. The superb materials science properties of azaacenes result from their improved resistance toward oxidation and their potential for electron transport, both of which have been demonstrated recently. The introduction of nitrogen atoms into the aromatic perimeter of acenes stabilizes their frontier molecular orbitals and increases their electron affinity. The HOMO–LUMO gaps in azaacenes in which the nitrogen atoms are symmetrically placed are similar to those of the acenes. The judiciously placed nitrogen atoms induce an “umpolung” of the electronic behavior of these pentacene-like molecules, i.e., instead of hole mobility in thin-film transistors, azaacenes are electron-transporting materials. The fundamental synthetic approaches toward larger azaacenes are described and discussed. Several synthetic methodologies have been exploited, and some have been newly developed to assemble substituted azaacenes. The oldest methods are condensation-based. Aromatic *o*-diamines are coupled with *o*-dihydroxyarenes in the melt without solvent. This method works well for unsubstituted azaacenes only. The attachment of substituents to the starting materials renders these “fire and sword” methods less useful. The starting materials decompose under these conditions. The direct condensation of substituted *o*-diamines with *o*-quinones proceeds well in some cases. Fluorinated benzene rings next to a pyrazine unit are introduced by nucleophilic aromatic substitution employing hexafluorobenzene. However, with these well-established synthetic methodologies, a number of azaacene topologies cannot be synthesized. The Pd-catalyzed coupling of aromatic halides and aromatic diamines has therefore emerged as versatile tool for azaacene synthesis. Now substituted diaza- and tetraazaacenes, azapentacenes, azahexacenes, and azaheptacenes are accessible. Pd-catalysis-based coupling methods for both activated and nonactivated *o*-dihalides have been developed. The larger azaacene representatives were unknown before but are of conceptual and theoretical interest. Azaacenes, particularly the symmetrical bis(triisopropylsilylethynyl)-substituted tetraazapentacene, are primarily used in organic field-effect transistors, but smaller azaacenes shine in the field as organic light-emitting diode (OLED) emitters. Diazatetracenes and substituted benzoquinoxalines are successful, improving electron injection and increasing OLED brightness, as compared to that of pure tetracenes. On the basis of the acene framework, nitrogen atoms in the acene perimeter and aggregation-precluding molecular appendages create solid-state fluorescent species. Azaacenes are expanding the range and complementing the purview of acenes in organic electronic applications. They enlarge the profiles of acenes with respect to synthetic strategies, structures, properties, and applications.



■ INTRODUCTION

Large linearly annulated acenes (tetracene, pentacene, hexacene, etc.) are fascinating molecules with respect to structure and electronics but also exciting in their applications for organic electronics.¹ Pentacene is a reference system for hole transport in organic field-effect transistors (OFETs); it was prepared by Clar in 1929, but its potential as an organic semiconductor has only been discovered much later.² Higher acenes suffer from insolubility and high reactivity, making their processing difficult. Nevertheless, the chemistry of the larger acenes has recently been aggressively developed. In particular, Anthony et al.³ and Tönshoff and Bettinger⁴ were successful in establishing hexacenes through nonacenes, stabilizing these species through bulky substituents or in cryogenic matrices. The N-heteroacenes are a different story. While the first large azaacenes have been known since the end of the 19th century, azapentacenes and their larger siblings form almost exclusively

as the *N,N'*-dihydro compounds (Figure 1, **A**) through simple condensation reactions of aromatic *o*-diamines with aromatic *o*-dihydroxyarenes, *o*-quinones, or activated *o*-dihalides.⁵ The oxidized azapentacenes (**B**) were only prepared in 1967 by the groups of Leete and Zimmermann⁶ through dehydrogenation of their *N,N'*-dihydro compounds using quinones or lead(IV) salts. Azaacenes were forgotten until Nuckolls exploited an *N,N'*-dihydrodiazapentacene as the active species in an OFET—a meaningful pentacene substitute.⁷ In their reduced form, **A**, the azaacenes are electron-rich species, while in their oxidized form, **B**, they are electron-poor and pyrazine-like.

An interesting point is the aromaticity of azaacenes. The *N,N'*-dihydro compounds **A** are formally antiaromatic, electron-rich $4n$ π -electron systems, while the oxidized

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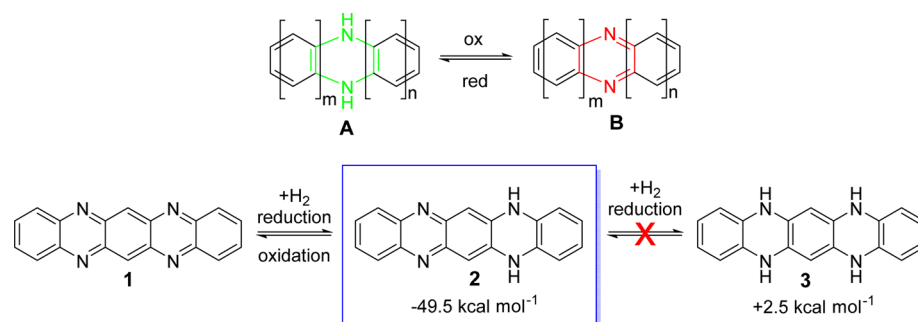


Figure 1. Calculated heats of hydrogenation (B3LYP/6-311+G** without zero-point energy corrections) for the reduction of **1** into **2** and **3**.

Table 1. Reviews Dealing with the Topic of Large Azaacenes

author	citation	title
Bunz, U. H. F.	<i>Chem.—Eur. J.</i> 2009 , <i>15</i> , 6780	N-Heteroacenes
Bunz, U. H. F.	<i>Pure Appl. Chem.</i> 2010 , <i>82</i> , 953	The Larger N-Heteroacenes
Bunz, U. H. F.; et al.	<i>Angew. Chem., Int. Ed.</i> 2013 , <i>52</i> , 3810	Large N-Heteroacenes: New Tricks for Very Old Dogs?
Bryant, J. J.; et al.	<i>Chem.—Asian J.</i> 2013 , <i>8</i> , 1354	Click To Bind: Metal Sensors
Miao, Q.	<i>Synlett</i> 2012 , 326	N-Heteropentacenes and N-Heteropentacenequinones: From Molecules to Semiconductors
Miao, Q.	<i>Adv. Mater.</i> 2014 , <i>26</i> , 5541	Ten Years of N-Heteropentacenes as Semiconductors for Organic Thin-Film Transistors.
Richards, G. J.; et al.	<i>Org. Biomol. Chem</i> 2011 , <i>9</i> , 5005	Putting the “N” in ACENE: Pyrazinacenes and Their Structural Relatives

azaacenes **B** are electron-poor $4n + 2$ π -electron Hückel aromatic systems. The N,N' -dihydro compounds (formally antiaromatic) are stable for azapentacenes and larger representatives; when the π system in **B** is interrupted by an antiaromatic dihydropyrazine ring to give **A**, two smaller aromatic systems result, featuring one Clar sextet each (Figure 1). Nucleus-independent chemical shift calculations reveal that the aromaticity of azaacenes containing **A** is reduced (compared with **B**) but that they are not antiaromatic. Once five rings are linearly connected, MnO_2 or chloranil can be used to reform the azaacenes **B** from **A**, while for N,N' -dihydroazatetracenes, oxidation is spontaneous in air.

The hydrogenation of **1** into **2** is surprisingly exothermic ($-49.5 \text{ kcal mol}^{-1}$ calculated). The larger the azaacene under consideration, the more exothermic is its hydrogenation. The reduction of **2** into **3** is experimentally difficult and also, if calculated, thermodynamically unfavorable ($+2.5 \text{ kcal mol}^{-1}$). A large bathochromic shift is observed in the UV–vis spectra in going from **A** to **B**; the dihydropyrazine—despite being planar in the azaacenes—seems to interrupt conjugation.

These are fundamental properties, but recently azaacenes have appeared as useful organic semiconductor materials and as sensor cores.⁸ As the azaacenes have elicited much interest, several reviews have appeared (Table 1) dealing with the synthesis and uses of azaacenes as OFET materials for electron or ambipolar transport. Particularly for **4**, spectacular electron mobilities ($>3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) are claimed (see Table 1, entries 5 and 6). The attachment of triisopropylsilyl (TIPS)-acetylene groups stabilizes and solubilizes azaacenes, identical to how they work for the larger acenes. The TIPS-ethynyl groups increase the solubility of acenes and azaacenes in organic solvents and thus simplify characterization and solvent processing.

This Account will touch on several topics. First, synthetic approaches toward azaacenes are outlined (simple condensation, alkynylation of azaacenequinones, and Pd-catalyzed coupling) and their usefulness is evaluated. Also discussed are the limit of size for linear acene-like azaaromatics and whether there are strategies to circumvent and extend this limit. In the

second part, the spectroscopic and electronic properties of azaacenes are discussed, and a peculiar electronic effect is highlighted. With this base, structural studies in the solid state are discussed. The exploitation of azaacenes as the active species in OFETs for electron or ambipolar transport (when they are in the **B** form, Figure 1) or hole transport (in the **A** form) and for organic light-emitting diodes (OLEDs) is probed. We will conclude with an outlook to see where structural and applicative concepts lead, what the fundamental questions are in the field, and how azaacenes fit into the future of semiconducting organic materials.

■ SYNTHETIC ROUTES

Conventional Approaches

A conventional synthetic route toward N-heteroacenes uses condensation/alkynylation methods developed for the preparation of acenes, with the exception that one of the starting materials contains a heterocyclic unit.⁹ For example, 2,3-pyridinedialdehyde condenses with cyclohexanedione to give quinone **5** (Figure 2), which is alkynylated and deoxygenated to afford **6**, exactly as is done for bis(triisopropylsilylethynyl)pentacene (TIPSpent).³

The heterocyclic quinone **7** is available, and its alkynylation by a modified Anthony protocol gives **8**. Deoxygenation and dehydrogenation then furnishes **4** (Figure 3).¹⁰ Lithium acetylides add to the quinones, transforming **7** into **8**. Ethynyl Grignard reagents are superior in the alkynylation of **7**. The deoxygenation of **8** to give **9** was initially performed using sodium hypophosphite with potassium iodide in acetic acid. Later it was discovered that a simple acidic solution of SnCl_2 also works efficiently for the deoxygenation of **8**. The optimized conditions (magnesium acetylide, SnCl_2 ; see Figure 3a) furnish **9** in 61% yield instead of 4% yield (lithium acetylide, sodium hypophosphite, acetic acid), making **9** now easily available. The oxidation of **9** with MnO_2 is straightforward and gives **4** in 97% yield.

This approach should be feasible for any available heterocyclic p -quinone and was demonstrated for **10** and **12**.

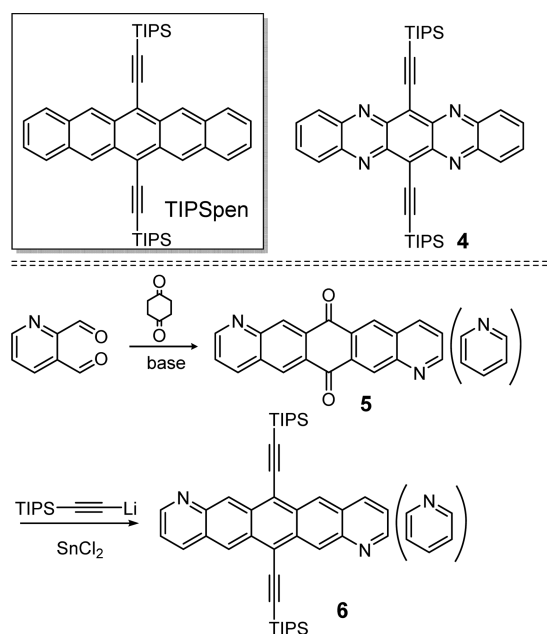


Figure 2. Synthesis of **6** and structure of TIPSpent.

If the quinones are electron-poor, tin chloride has to be used in an acidic medium to achieve successful deoxygenation; for longer known examples,^{10e,f} a mixture of sodium hypophosphite, potassium iodide, and acetic acid works well to remove the two hydroxyl groups (Figure 3b) to give **11** and **13**, respectively.

In the direct synthesis of azaacenes, one compares, in a general scheme, aromatic *o*-diamines with aromatic *o*-dihydroxy compounds; although harsh, these conditions are successful for the production of unsubstituted di- and tetraazaacenes. These long-established methods have been extensively discussed in the reviews shown in Table 1. The melt condensation is also successful when aromatic diamines are cocondensed with dichloroquinoxaline. These “fire and sword” methods are valuable for the synthesis of unsubstituted azaacenes. In the case of TIPS-ethynyl-substituted azaacenes, known examples of this reaction are restricted to the coupling of *o*-quinones to diaminoanthralene **14** and diaminoanthra-

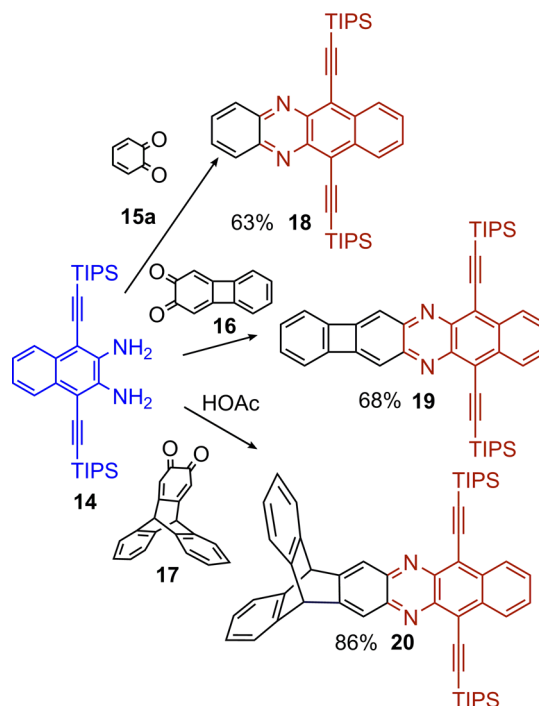


Figure 4. Synthesis of diazatetracenes **18–20** using *o*-quinones.

cene **21a** (Figures 4 and 5). While the formation of diazatetracenes proceeds smoothly, directly, and in good yields (Figure 4), the successful synthesis of diazapentacenes by this method is structure-dependent (Figure 5).

Coupling of **21a** with **15a,b** furnishes **22a,b**, and oxidation with MnO_2 transforms them into **23a,b** in yields exceeding 90%. The reaction of **21a** with **16** proceeds smoothly and directly to give **24** without the need of an oxidant.¹¹ While the condensation of **21a** with **17** works well, the formed intermediate (the *N,N'*-dihydro form of **25**) still must be oxidized into **25**.¹² The difference in reactivity and the direct formation of azaacene **24** are puzzling. Heuristically, large azaacenes preferentially form when *one* formally antiaromatic Hückel ring, as in **A**, is incorporated into the system. The presence of two formally antiaromatic Hückel rings¹³ apparently destabilizes the system and makes it less accessible.

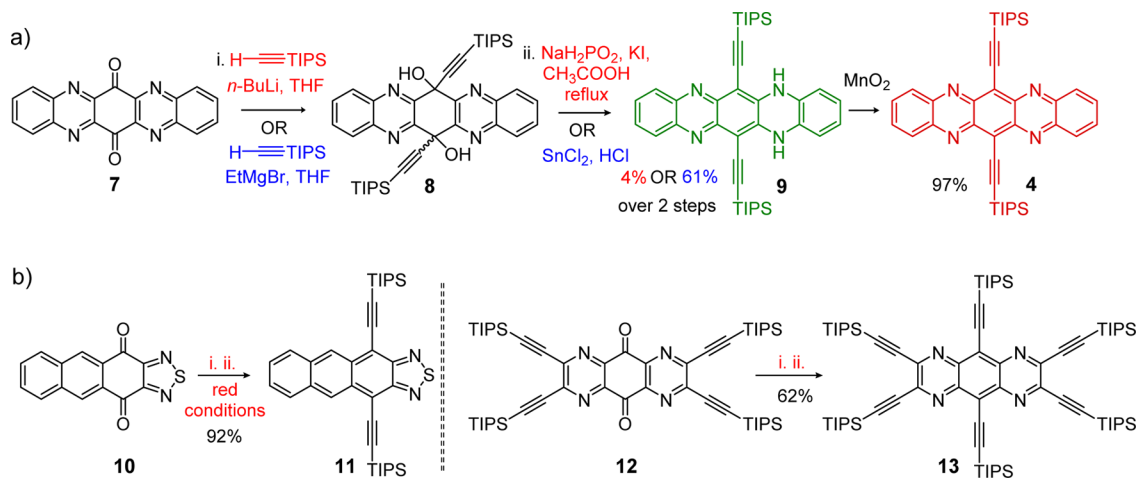


Figure 3. (a) Synthesis of **4** using either Grignard reagents or lithium alkynylides. (b) Alkynylation of other heterocyclic electron-poor *p*-quinones **10** and **12**.

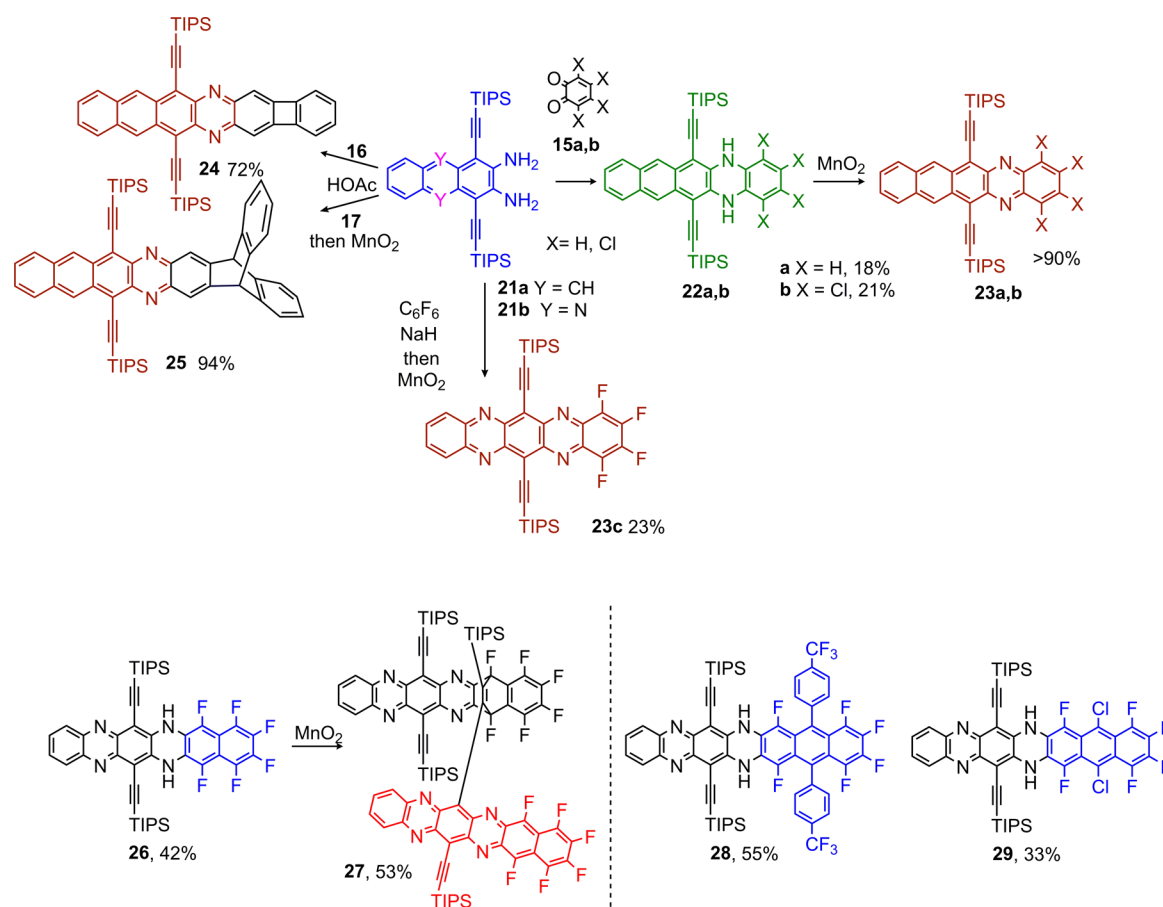


Figure 5. (top) Synthesis of diazapentacenes 23–29 by coupling of diamines 21 and *o*-quinones or hexafluorobenzene. (bottom) Structures of larger *N,N'*-dihydroazaacenes and the oxidation of the *N,N'*-dihydrohexafluorotetraazaacene 26 into a dimer adduct.

The *N,N'*-dihydro compound formed from 24 would display two antiaromatic units, a dihydropyrazine and a cyclobutadiene; it is therefore not formed.

These trends are computationally supported according to the heats of hydrogenation. The hydrogenation of 1 into 2 is exothermic, while that of 2 into 3 is not (see Figure 1). In 24 the cyclobutadiene ring takes over the role of the first *N,N'*-dihydropyrazine ring, turning the system into a formally antiaromatic $4n$ π -electron system, and therefore, the hydrogenation of 24 should be energetically unfavorable; consequently, the pyrazine ring in 24 forms directly. An extension of this method uses 21b, the phenazine version of 21a, in the base-promoted reaction with hexafluorobenzene.^{10d} Upon addition of NaH to a solution of 21b and C_6F_6 in dimethylformamide, a nucleophilic aromatic substitution occurs, providing tetrafluoride 23c in 23% yield after oxidation of the formed *N,N'*-dihydrotetraazapentacene. While the yield is not high, the reaction is convenient to build up partially fluorinated azaacenes. It is a fairly atom-economical process, using hexafluorobenzene as a commercially available coupling partner and losing only 2 equiv of NaF. This reaction was extended toward larger perfluorinated aromatics and gives the coupling products 26, 28, and 29 reliably in yields ranging from 33 to 55% (Figure 5, bottom). These addition products are isolated as their *N,N'*-dihydro forms, and the ones formed from the reaction of 21b with highly fluorinated anthracenes (28, 29) are so electron-poor that they cannot be oxidized into the respective tetraazaheptacenes. The perfluoronaphthalene adduct 26 was oxidized by MnO_2 , but the formed azahexacene is

not observed; instead dimerization to give 27 occurs. The direct condensation has value for the preparation of diazatetracenes and some diazapentacenes but is not universally applicable and leaves much to be desired.

Palladium-Catalyzed Couplings: A Way to Larger Azaacenes

Diamines 14 and 21a do not react with 2,3-dichloroquinoxaline (30a) at elevated temperatures. Microwave, ultrasound, or addition of bases does not help either. We conquered the condensation of 14 with 30a by employing Pd catalysis. A Pd(0) precatalyst in the presence of 31 (or a similar biarylphosphine ligand) couples 14 to 30; with Hünig's base as the solvent,¹⁴ dihydrotetraazapentacene 32a forms in 85% yield. Oxidation using MnO_2 gives the target 33a in 68% yield.¹⁵ A variety of different tetraazaacenes,¹⁶ -pentacenes, and also -hexacenes¹⁷ were prepared thusly. 30a is an excellent coupling partner in Pd-catalyzed reactions. It is a highly activated electron-poor arene and was the first choice of reagent. As the chloride substituents at the 2 and 3 positions of 30a are the most reactive ones in quinoxaline, halide substituents at the 6 and 7 positions in the second ring of the quinoxaline can be present but do not react with 14 or 21a. Also, while nitrotetraazapentacene 33f was obtained, the nitro compound 32g could not be oxidized any further in our hands. Halogenated *N,N'*-dihydrotetraazapentacenes, -pentacenes, and -hexacenes are generally obtained in good to excellent yields. The oxidation of 32a gave 33a, and oxidation of the other

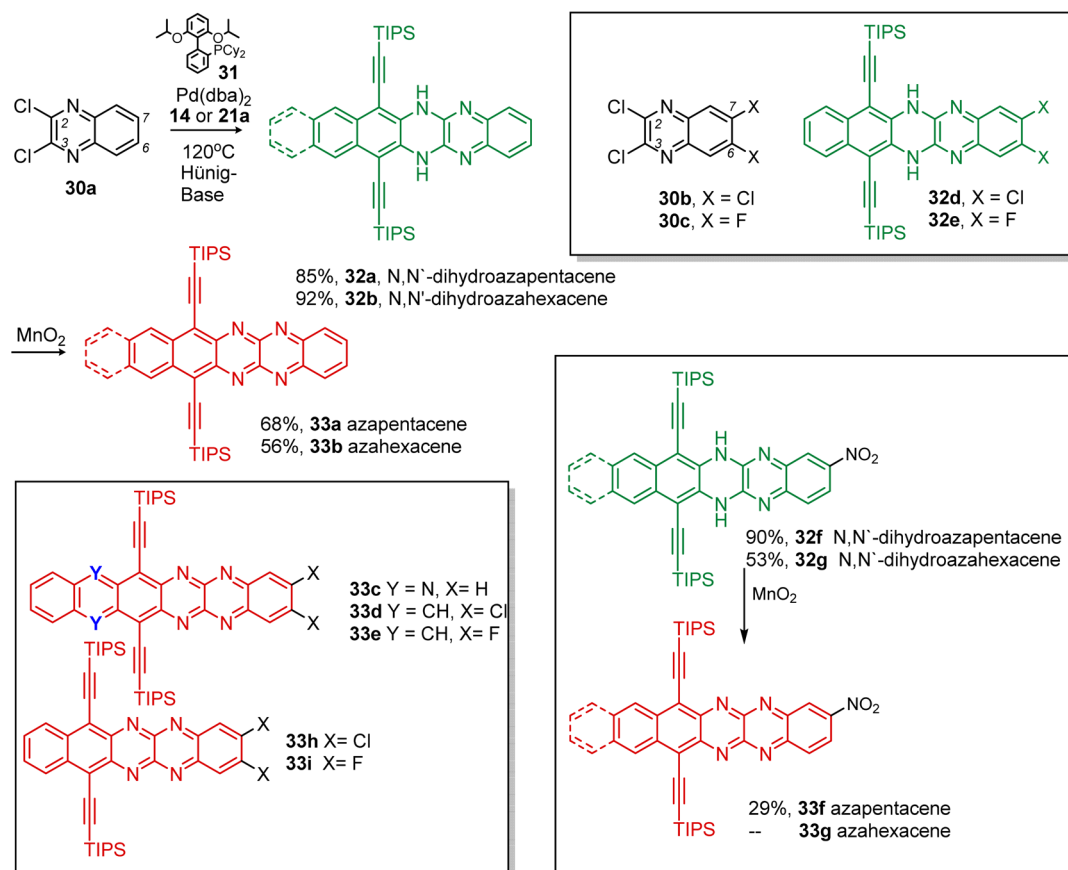


Figure 6. Pd catalysis for the synthesis of **32** and **33**.

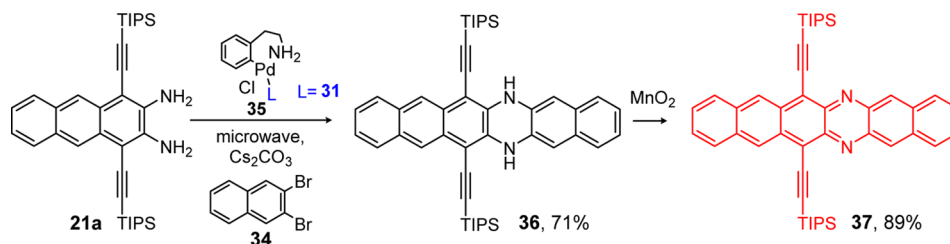


Figure 7. Synthesis of diazahexacene **37**.

N,N' -oligoazaacenes also furnished the respective azaacenes in fair to excellent yields by this method (Figure 6).

2,3-Dichloro-6,7-dihaloquinoxalines **30b,c** couple smoothly with **14** and **21a** to give N,N' -dihydrodihaloazaacenes **32** with four or six ring nitrogen ring atoms and five or six linearly connected rings. Oxidation of **32** by MnO_2 provides access to azaacenes **33c–e**. The simple protocol does not work for the reaction of **21a** with the unactivated dibromide **34**. Careful optimization of the reaction conditions and choice of the catalyst (**35**) gives the coupling product **36**. Microwave irradiation and Cs_2CO_3 as a base are critical. **36** is oxidized in good yield into **37** (Figure 7), which is stable for short periods of time even in the solid state.¹⁸

Attempts to obtain a single crystal of **37** for structural analysis failed. Instead, upon removal of the solvent and crystallization, dimer **38** was observed. We notice that diazahexacenes dimerize, similar to the analogous hexacenes.¹⁹ The tendency to dimerize is amplified when one attempts to oxidize the coupling product of **21a** to 2,3-dibromoanthracene.

Here a diazaheptacene cannot even be observed spectroscopically. Instead, only the butterfly dimer **39** is isolated (Figure 8).

This result set back our attempts to create persistent azaheptacenes and might hint at the fundamental size restrictions for “classic” linear azaacenes; strategic placement of bulky trialkylsilyl groups seemed valid.²⁰ The necessary building blocks **40a,b** and **40c,d** were coupled to give **41a,b** (Figure 9). The increased steric demand of the trialkylsilyl groups suppressed effective coupling, so **41b** was obtained in only 18% yield, while **41a** was formed in 83% yield. This effect is subtle, as small increases in the steric demand of the coupling partners dramatically reduced the yield of the reaction. When both coupling partners **40** in Figure 9 carried [tri(cyclohexyl)silyl]alkynyl substituents, the coupling yield was further diminished, and only traces of the product **41** were obtained.

The oxidation of **41a,b** with MnO_2 was finished in 40 s, but product **42a** dimerized spontaneously despite the presence of four TIPS-ethynyl groups. **42b** was more robust and could be held in solution for more than 1 h (Figure 10). We were surprised that diazaheptacene **42b** did not experience

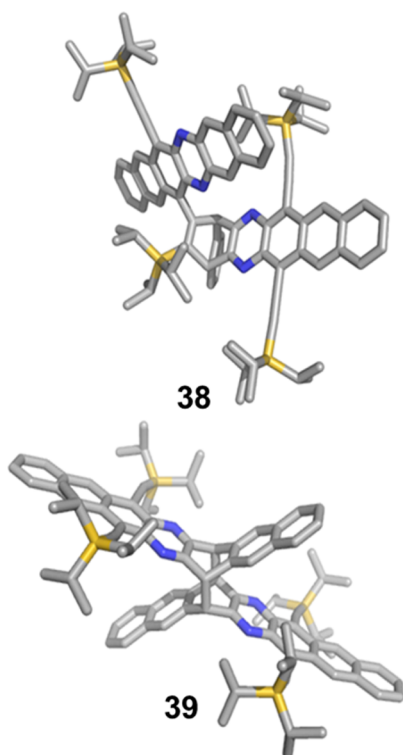


Figure 8. Dimerization products **38** (from diazahexacene **37**) and **39** (from a diazaheptacene).

spontaneous back-reduction into **41b**. Despite the relatively large trialkylsilyl groups, **42b** dimerized slowly to give **43** and **44** (Figure 10), but after 1 h only traces of the two dimerization products **43** and **44** had formed. For the less highly substituted derivatives of **42**, this apparently not very selective dimerization is much faster (see the top panel of Figure 1 in ref 20 for more details).²⁰ Reduction (-0.79 V vs Fc/Fc⁺) and oxidation potentials of **42b** (0.56 V vs Fc/Fc⁺) were determined by cyclic voltammetry; **42b** is both easily reduced and easily oxidized. The absorption maximum of **42b** was located at around 900 nm. Larger trialkylsilyl groups would be better for stabilization, but the coupling to give **41** would be more difficult unless more active catalysts can be found; the quest for the larger azaacenes remains an active challenge, and it is not clear whether azaoctacenes or azanonacenes can be prepared and would persist.

SPECTROSCOPY

The UV–vis spectrum of **4** is similar to that of TIPSpEn. Hückel theory predicts that the substitution of a ring CH group

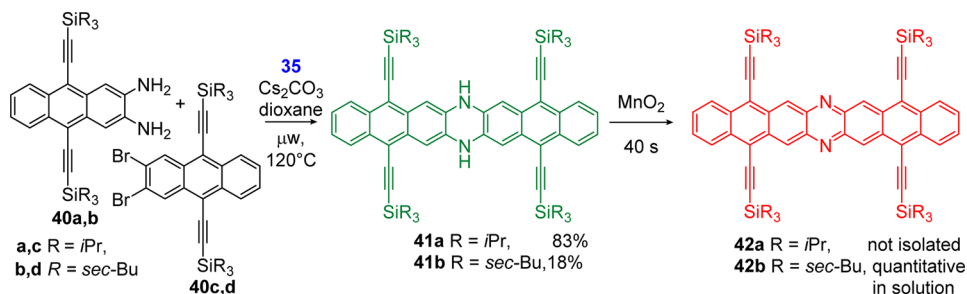


Figure 9. Synthesis of diazaheptacenes **42**.

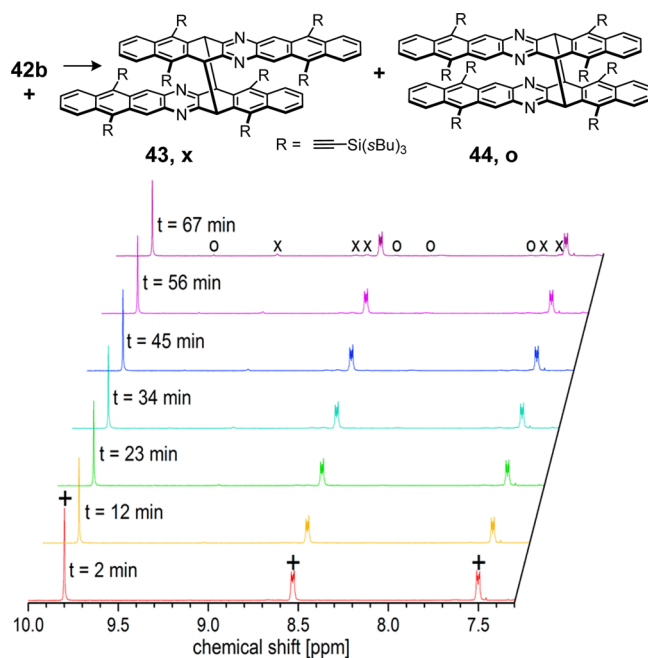


Figure 10. Stability of **42b** in solution (CDCl₃) as determined by ¹H NMR spectroscopy over 1 h. Reproduced from ref 20. Copyright 2014 American Chemical Society.

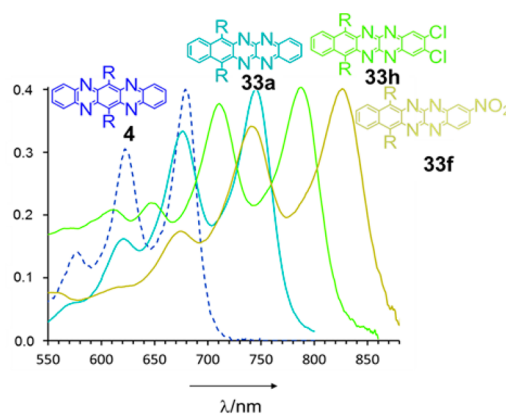


Figure 11. UV–vis spectra of azapentacenes **4**, **33a**, **33h**, and **33f** in hexanes. R = TIPS–C≡C–.

by nitrogen should only change the Coulomb integral α , while the resonance integral β is left unchanged; β influences the spacing of the HOMO and LUMO, while α determines their absolute positions. Nitrogen substitution in the ring and electronegative substituents should stabilize the HOMO and LUMO equally. That is the case for halogenated TIPSpEn, the

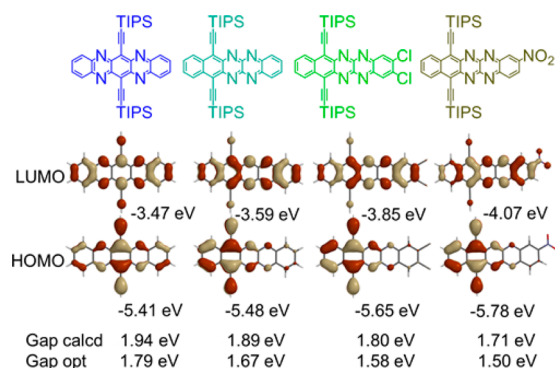


Figure 12. Quantum-chemical calculations (B3LYP/6-31G**//B3LYP/6-31G**) on compounds **4**, **33a**, **33h**, and **33f** (left to right).

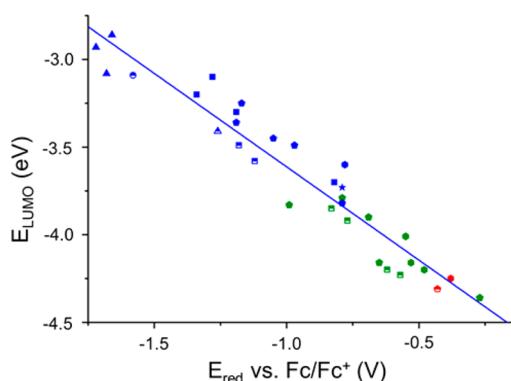


Figure 13. Calculated LUMO position vs reduction potentials measured by cyclic voltammetry for a series of azaacenes and acenochalcodiazoles of different sizes. Reproduced with permission from ref 17b. Copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA.

UV spectra of which resemble that of TIPSPen²¹ to a surprising degree.²² The UV–vis spectra of azaacenes are red-shifted upon rearrangement of the ring nitrogens and/or the attachment of electronegative substituents in their “eastern” part (Figure 11).

This behavior can be understood by inspection of the frontier molecular orbitals calculated using density functional theory (DFT) (Figure 12).²³ The LUMO coefficients of **4**, **33a**, **33h**, and **33f** are evenly distributed over the whole molecular skeleton, i.e., the electronegative substituents stabilize the LUMO efficiently. With the exception of **4**, the azaacenes’ HOMOs do not have large coefficients at the positions where the electronegative substituents and the (now regrouped) ring nitrogens reside. Therefore, their HOMOs are less stabilized than their LUMOs (Figure 12). The effect of their disjoint orbital distribution²⁴ results in red-shifted optical spectra. Qualitatively, the stabilization of the HOMO inversely scales

with the substituents’ electron-withdrawing character. The uniform distribution of the LUMO, however, suggests that azaacenes could be useful as electron-transporting materials if other prerequisites (i.e., optimal π – π orbital overlap and correct morphology) are also achieved. Electronegative substituents are powerful tools to manipulate not only the LUMO position of N-heteroacenes but also their HOMO–LUMO gap and, thereby, their optical properties.

A second outcome of the quantum-chemical calculations was a successful correlation of the calculated LUMO position with the first reduction potential as obtained by cyclic voltammetry using the ferrocene/ferrocenium (Fc/Fc⁺) couple as the standard (Figure 13). For tetraazaacenes and hexaazaacenes, the correlation plot works well. For diazaacenes, the calculated LUMO position predicts the reduction potentials to be too high. The slope of the regression line is close to unity, indicating that for the larger azaacenes’ reduction potentials, the DFT (B3LYP/6-311+G**//B3LYP/6-311+G**)–calculated LUMO positions and electron affinities are closely connected. Increasing the number of nitrogens, attaching electronegative substituents, and enlarging the π perimeter all lower the reduction potential and increase the electron affinity of azaacenes. The linear correlation works best for easily reduced tetraazaacenes and to a lesser extent for the diazaacenes, but it shows the power of these fairly simple DFT calculations: one gets out reasonable numbers even though, strictly speaking, the LUMO position has no physical meaning in DFT calculations.

SOLID-STATE STRUCTURES AND USES OF AZAACENES IN ORGANIC ELECTRONICS

The application of azaacenes in organic electronics devices necessitates the knowledge of their structures in the solid state. Compound **4**, first synthesized by us,¹⁰ was investigated by Miao and co-workers²⁵ as an electron-transporting material in OFETs. The single-crystal structure of **4** (Figure 14) is almost identical to that of TIPSPen; that is not the case for the closely related compound **45**, which crystallizes in a herringbone-type packing pattern. The position of the nitrogen atoms in the perimeter matters a good deal, as the electron mobility of **45** is lower than that of **4** by 4 orders of magnitude (Figure 15).²⁶ The packing of **4** apparently is ideal for charge (electron) transport. The measured electron mobilities of **4** in thin-film transistors reached $\mu^- = 3.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This is much higher than the value published by Zhang for **6**⁹ and that for tetrachloride **46**²⁷ (Figure 15). It seems that **4** is by far the best electron-transporting material in this series.

The *N,N*-dihydrotetraazapentacene **32d**, which is electron-rich because of the presence of form **A**, develops an almost processing-independent morphology (Figure 16) with a hole

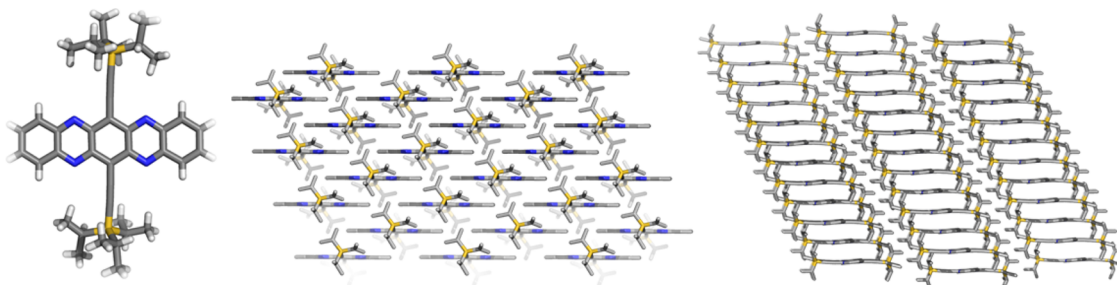


Figure 14. Single-crystal structure of the symmetrical tetraazapentacene **4**.

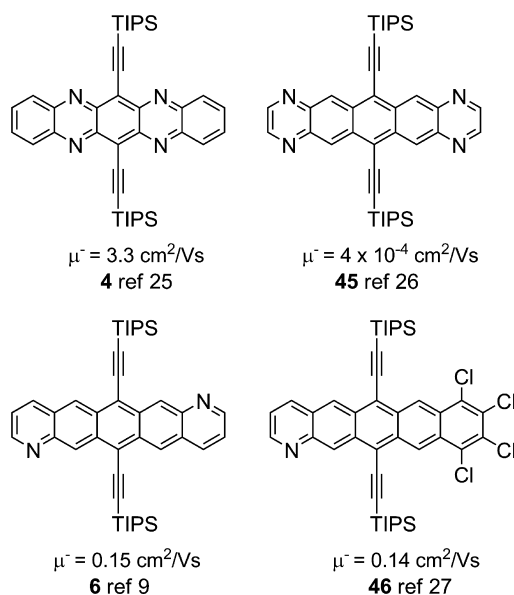


Figure 15. Electron mobilities of bis(TIPS-ethynyl)-substituted azaacenes.

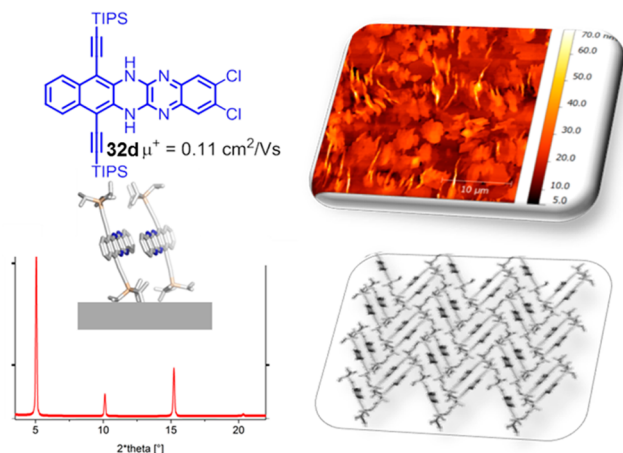


Figure 16. Molecular structure and single-crystal X-ray structure of **32d**, diffraction pattern of a film of **32d** spin-cast from xylene solution with the schematic orientation of the molecules, and the typical morphology of **32d** observed by atomic force microscopy independent of the processing and annealing.^{28a}

mobility of up to $0.11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. However, its packing in the crystalline state is different from its packing in thin films on surfaces, as deduced by a comparison of the thin-film diffraction data with the diffraction pattern in the single-crystalline state. In the thin films, the observed edge-on packing of the molecules is advantageous for efficient charge transport.^{28a}

The molecular structure of **33b** has been determined; the conspicuous bond length alternation observed in the single-crystal structure is reproduced in quantum-chemical calculations. Resonance theory predicts bond length alternation in acenes on the basis of the simple observation that the 2,3-bond participates in more resonance structures with double-bond character. In **33b** the same effect persists and is just more pronounced (Figure 17). The calculated and X-ray crystallographic bond lengths are in good accord. Azaacenes have not yet been employed in thin-film transistors, but the packing of **33b** is attractively similar to that of TIPSPen; **33b** should be useful as an electron-transporting material in OFETs if it becomes possible to obtain thin-film samples with suitable morphologies, which is not a trivial task (Figure 18).

While the larger azaacenes are predestined to be charge carrier materials in OFETs, smaller azaacenes are attractive solid-state emitters. **47** (Figure 19) can be either vacuum- or solution-phase-deposited as the emitting layer in a simple OLED and gives brightnesses of above 1000 cd m^{-2} at operating voltages around 7 V, with solution-processed OLEDs being more efficient. **47** packs in the solid state in such a way that intermolecular contacts of the benzoquinoxaline perimeter are avoided and quenching pathways are efficiently blocked.^{28b}

Is it possible to boost the emissive properties of tetracenes? Tetracene is an orange nonfluorescent solid, but bis(TIPS-ethynyl)tetracene²⁹ is orange-red fluorescent in the solid state. OLEDs with a maximum brightness of 1 cd m^{-2} were fabricated. Upon substitution of the tetracene core with phenyl rings (**48**; Figure 20), the brightness of the OLEDs increased to 5 cd m^{-2} . The tetracenes' performance in OLEDs could be boosted by improving the charge injection and shutting down the solid-state interactions of the acene networks. When **20** (Figure 20) was incorporated as an emitter into a simple OLED stack at an operating voltage of 7 V, a brightness of $>200 \text{ cd m}^{-2}$ was achieved.¹² Directed molecular evolution (i.e., suppression of aggregation and enhancement of charge injection through the pyrazine motif) increases the OLED brightness by a factor of 200 compared with bis(TIPS-

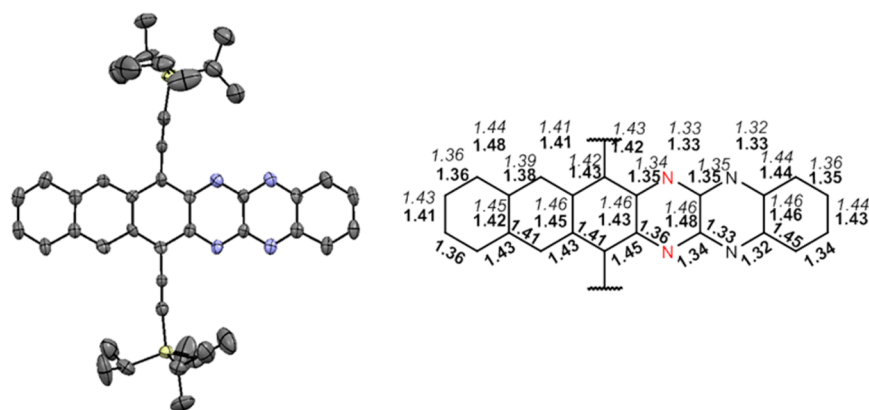


Figure 17. Molecular structure of **33b**. The bond length alternation observed in the crystal structure is expected and predicted by quantum-chemical calculations (B3LYP/6-311+G**//B3LYP/6-311+G**); values shown in italics). Reproduced with permission from ref 17b. Copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA.

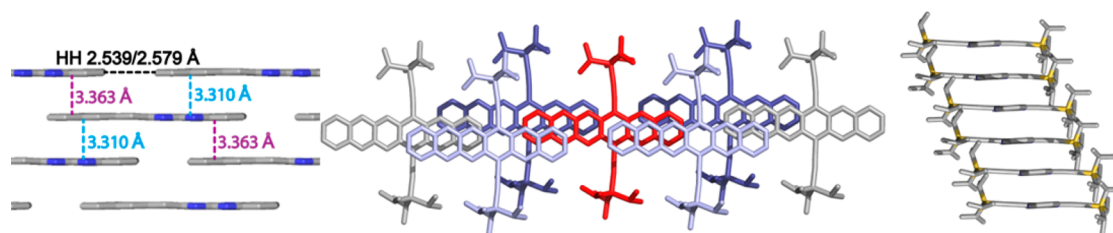


Figure 18. Packing of 33b. The distances shown are less than the sum of the van der Waals radii of two carbon atoms (3.4–3.6 Å), suggesting that in this brick-wall-motif packing there is a promising electronic interaction of the molecules in the solid state. Reproduced with permission from ref 17b. Copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA.

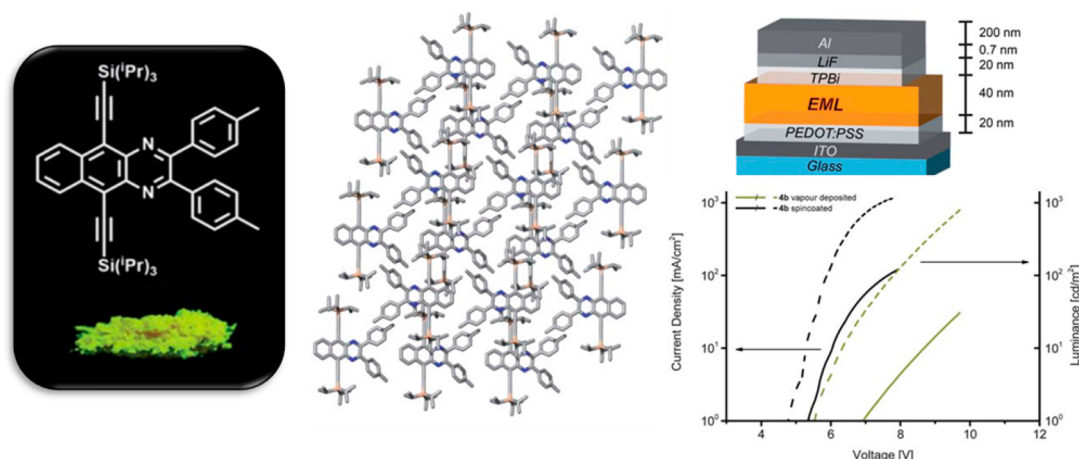


Figure 19. Structure, packing, device buildup (solution-phase), and device performance of 47. Reproduced with permission from ref 28. Copyright 2013 Royal Society of Chemistry.

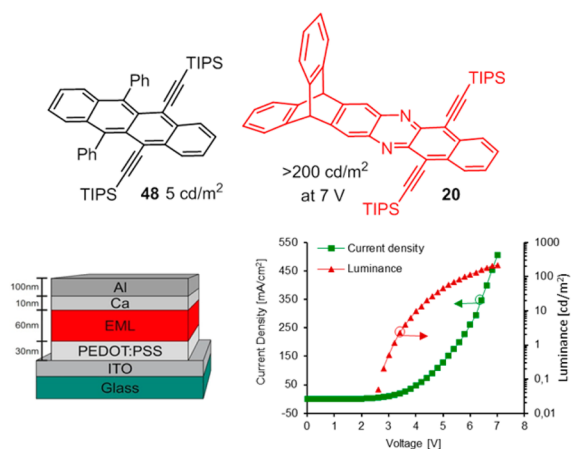


Figure 20. OLED performance of solution-processed diazotetracene 20. Reproduced from ref 12. Copyright 2014 American Chemical Society.

ethynyl)tetracene and a factor of 40 compared with 48. This is an attractive concept that should be further exploited.³⁰

TIPSpEn is a successful molecule in singlet fission; it was of interest whether the nitrogen substitution in azaacenes would influence this behavior, and if so, how.³¹ We therefore investigated the photoinduced excited-state dynamics of 23a using ultrafast transient absorption measurements (Figure 21). The introduction of the nitrogen atoms has a significant impact on triplet formation. The dynamics of the excited-state processes speed up significantly. Singlet fission is now efficient and very fast. This increased relaxation rate (from the singlet into the triplet manifold) implies a higher singlet fission

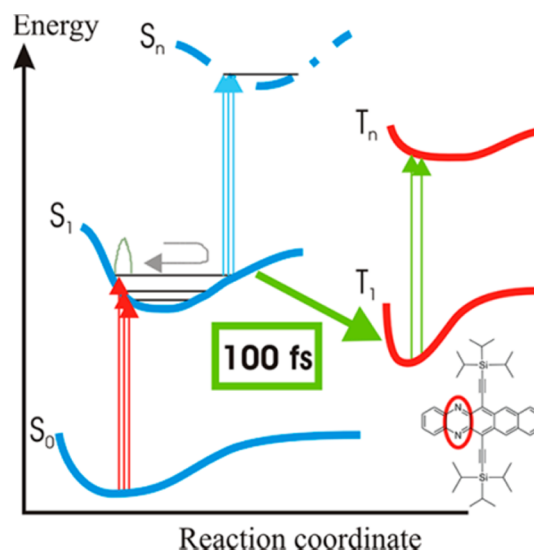


Figure 21. Singlet fission of diazapentacene 23a. Reproduced from ref 31. Copyright 2014 American Chemical Society.

efficiency. Relaxation channels are avoided. The increased (air) stability of diazapentacene 23a compared with TIPSpEn and its increased relaxation rate means that molecules such as 23a have the potential to be better singlet fission materials than pentacene and its derivatives.

CONCLUSIONS

The larger azaacenes have graduated from exotic laboratory curiosities into useful organic electronics materials. The driving

force was the development of synthetic accesses to substituted azaacenes. Substituents confer stability, solubility, and processability on the larger N-heteroacenes. During this adventure, we have refined a series of known synthetic approaches and developed novel ones; today, N-heteroacenes with two, four, and six nitrogen atoms and four to seven annulated rings are accessible. The Pd-catalyzed coupling of aromatic *o*-diamines to aromatic *o*-dihalides (followed by MnO₂-mediated oxidation of the formed *N,N'*-dihydroazaacenes) is a versatile tool to construct N-heteroacenes. Modular approaches furnish the targets in always acceptable and often excellent yields starting from only a handful of central modules that can be prepared in gram quantities.

The science of N-heteroacenes—for decades a backwater of organic chemistry—has finally taken off, and their use as potent electron-transporting materials in thin-film transistors has given this field a powerfully applicative purpose activated by synthetic progress. However, to distribute the ring nitrogens at will in the acene framework still is a great challenge. Pyrazine units are easily introduced, but other topologies are less common and less easily accommodated into large azaacenes. Where is the field going? Azaacenes will have to be available in large quantities and with different topologies and must demonstrate their further usefulness. While large electron mobilities have been reported for **4** (up to 3.3 cm² V⁻¹ s⁻¹), these numbers have not been repeated by other groups, which would be necessary to further popularize azaacenes. The similarity of azaacenes to pentacene looms as a large promise, and the complementary properties of the azaacenes strongly suggest a rich harvest of unique materials with superb properties. Are the larger azaacenes the coming rock stars of organic electronics and materials science? We will see.

AUTHOR INFORMATION

Corresponding Author

*E-mail: uwe.bunz@oci.uni-heidelberg.de.

Notes

The authors declare no competing financial interest.

Biography

Since 2010, **Uwe H. F. Bunz** has been a chaired Professor (Lehrstuhl I) at the Organisch-Chemisches Institut and Director at the Centre of Advanced Materials (CAM) at Ruprecht-Karls-Universität Heidelberg. From 1997 to 2010 he was faculty member first at the University of South Carolina and then at Georgia Institute of Technology. He performed his habilitation in the group of Prof. Klaus Müllen (1992–1997), was a postdoc with Prof. K. Peter C. Vollhardt (1991–1992) and earned his Ph.D. at the Ludwig-Maximilians-Universität Munich with Prof. G. Szeimies (1988–1990), where he studied chemistry (1982–1987). He is interested in alkyne and arene chemistry and the application of conjugated materials (small molecules and polymeric) in organic electronics but also for sensory and biosensory applications. His hobbies are swimming, surfing, cooking, and traveling.

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