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Synthesis and Optical Properties of Diaza- and Tetraazatetracenes

Benjamin D. Lindner,[a] Jens U. Engelhart,[a] Michaela Märken,[a] Olena Tverskoy,[a]
Anthony L. Appleton,[b] Frank Rominger,[a] Kenneth I. Hardcastle,[c]
Markus Enders,[d] and Uwe H. F. Bunz*[a]

Abstract: A series of functionalized diaza- and tetraazatetracenes was synthesized, either by condensation of an aromatic diamine with an *ortho*-quinone/diethyloxalate followed by chlorination with $POCl_3$ to give diazatetracenes or by palladium-catalyzed coupling of a phenylenediamine with various 2,3-dichloroquinoxalines to give tetraazatetracenes (after oxidation with MnO_2). Representative examples included halogenated and nitrated derivatives. The optical properties of these azatetracenes were discussed with respect to their molecular structures and substitution patterns. The diazatetracenes and tetraazatetracenes formed two different groups that had significantly different electronic structures and properties. Furthermore, 1,2,3,4-tetrafluoro-6,11-bis((triisopropylsilyl)-ethynyl)benzo[*b*]phenazine was synthesized, which is the first reported fluorinated diazatetracene. Single-crystal X-ray analysis of this compound is reported.

Keywords: alkynes • diamines • heterocycles • palladium • tetracenes

Introduction

Herein, we report different synthetic routes to alkynylated "Anthony-like" diaza- and tetraazaacenes and investigate the influence of their specific molecular structures on their optical properties.[1] Larger azaacenes and *N,N*-dihydrooligoazaacenes have been known since the end of the 19th century.[2] However, there are only a few reports of their synthesis and practically no procedures that allow the systematic access to a range of their functionalized derivatives. With the advent and promise of organic electronics, this class of compounds has experienced a bit of a "gold rush", and several groups are now researching afresh their synthesis.[3–11] Azaacenes promise to be electron-transporting complements of acenes and therefore are of potential importance in organic-electronic applications. A few azaacenes have been successfully utilized as the semiconducting layers in thin-film transistors, as demonstrated by Miao et al. and others.[8–11]

Nevertheless, when compared to other classes of substances, there is a dearth of substituted azaacenes and only few methods for their synthesis. In most cases, the azaacene core was constructed by using the classic condensation of an *ortho*-quinone (or an aromatic *ortho*-dihydroxy compound) with an aromatic *ortho*-diamine. Whilst exploiting this approach, we have developed a palladium-catalyzed Buchwald–Hartwig-type coupling reaction for the synthesis of larger heteroacenes.[12] Herein, we report our synthetic efforts towards preparing substituted azatetracenes and the influence of molecular structure on their optical/electronic properties.

Results and Discussion

Synthesis: We performed the condensation of anthracene diamine **1** with diethyloxalate to give the intermediate naphthoquinoxalinedione, which, upon reaction with $POCl_3$, furnished the target compound (**2**) in 26% overall yield (Scheme 1).[3d] Diaminonaphthalene **4** reacted with *ortho*-quinone and *ortho*-chloranil to afford the corresponding diazatetracenes **3a** and **3b**, respectively.[3a,d] When compound **4** was treated with *ortho*-fluoranil, we isolated two compounds following column chromatography on silica gel: the desired tetrafluorodiazatetracene (**3c**) but also a second compound (Scheme 2).[13] When we performed the condensation reaction in EtOH, the electrophilic compound **3c** reacted with the solvent in an nucleophilic-aromatic-substitution reaction to give compound **5** in 24% yield. This result was not too surprising, as highly fluorinated ring compounds

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[a] Dipl. Chem. B. D. Lindner, Dipl. Chem. J. U. Engelhart, M. Märken,
O. Tverskoy, Dr. F. Rominger, Prof. U. H. F. Bunz
Organisch-Chemisches Institut
Ruprecht-Karls-Universität Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)
E-mail: uwe.bunz@oci.uni-heidelberg.de

[b] Dr. A. L. Appleton
School of Chemistry and Biochemistry
Georgia Institute of Technology
901 Atlantic Drive, Atlanta GA, 30332 (USA)

[c] Dr. K. I. Hardcastle
Department of Chemistry, Emory University
1515 Dickey Drive, Atlanta, GA 30322-1003 (USA)

[d] Prof. M. Enders
Anorganisch-Chemisches Institut
Ruprecht-Karls-Universität Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)

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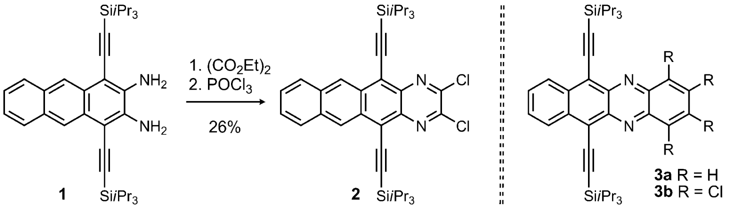
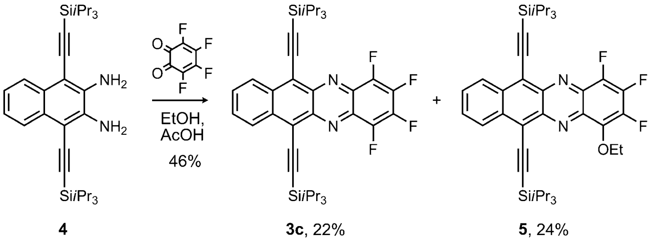


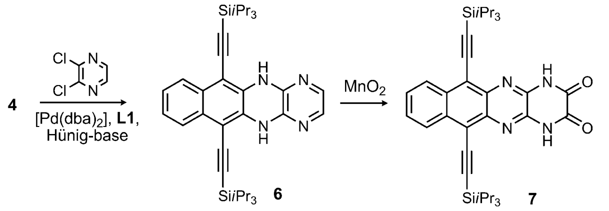
Scheme 1. Synthesis of diazaacene **2** and a structural comparison with known diazaacenes **3a** and **3b**.[3a,d]



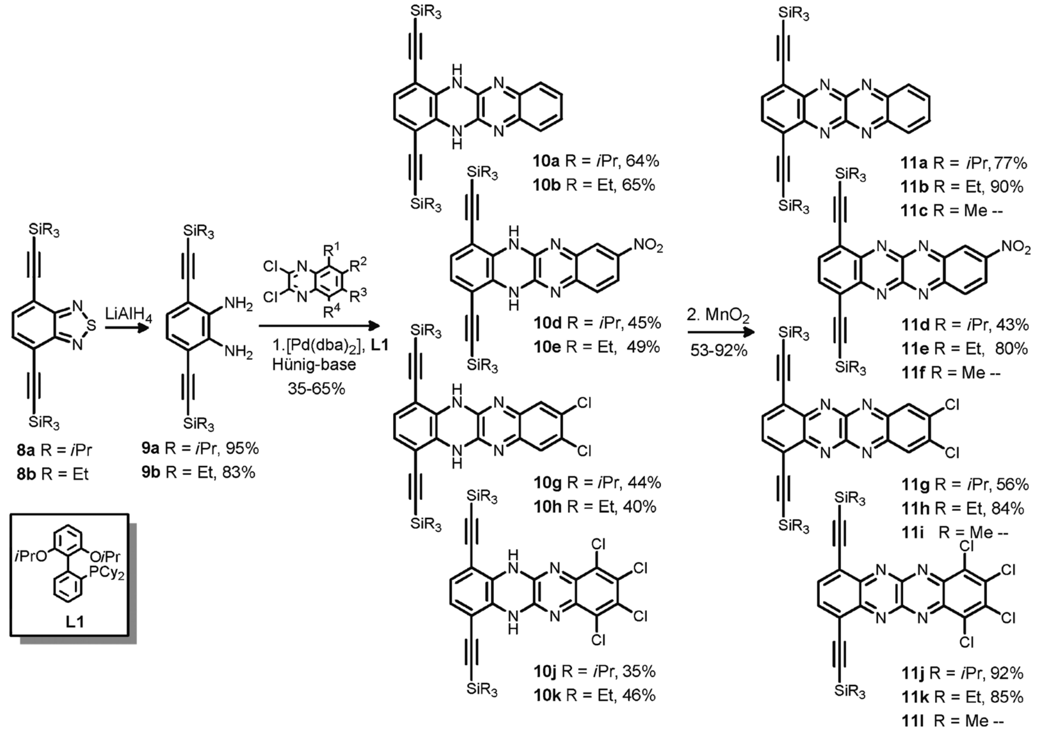
Scheme 2. Synthesis of partially fluorinated diazatetracenes **3c** and **5**.

easily undergo nucleophilic substitution, particularly with alcohols.[14] The position of the ethoxy substituent was deduced from the doublet splitting of the OCH_2 moiety in the ^1H NMR spectrum of compound **5**, which was due to the coupling with the single F atom at the *ortho* position.[15] To the best of our knowledge, compounds **3c** and **5** are among the first reported fluorinated azaacenes.[11b,16]

The coupling of a dichloropyrazine with an *ortho*-diamine in the presence of pyridine as a base to obtain fluoflavine derivatives, as reported by Guirado et al., was unsuccessful in our case.[17] In contrast, our recently developed palladium-catalyzed coupling conditions for heteroacenes gave satisfactory-to-good yields.[3f,h] During the course of this work, we re-tried the synthesis of compound **6**. However, the attempted coupling of compound **4** to 2,3-dichloropyrazine only resulted in trace amounts of compound **6**, which was oxidized by MnO_2, but not into a tetraazatetracene; rather, it was oxidized into the yellow bis-amide **7** (Scheme 3). Surprisingly, the Pd-catalyzed coupling approach worked significantly better for the synthesis of isomeric tetraazacenes **10** (Scheme 4). This class of compounds has been known since 1968, when Kuhn, Skrabal, and Fischer first synthesized the unsubstituted tetraazatetracene and discussed its electronic properties.[18] Starting from known benzothiadiazoles **8a** and



Scheme 3. Trace synthesis of compounds **6** and **7**. dba = dibenzylideneacetone.



Scheme 4. Synthesis of the tetrazaacenes **11**.

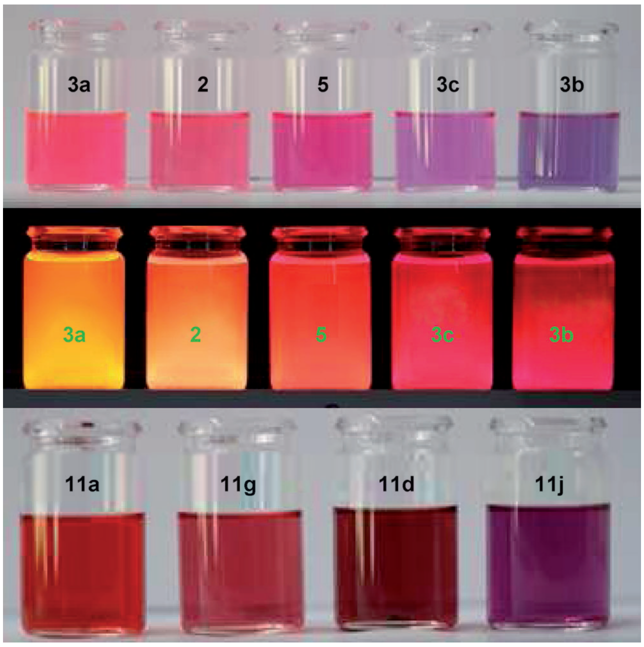


Figure 1. Photographs of solutions of compounds **2**, **3a**–**3c**, and **5** in CH_2Cl_2 in daylight (top row) and under a hand-held black light with illumination at 365 nm (middle row); bottom row: photographs of solutions of compounds **11a**, **11d**, **11g**, and **11j** in daylight.

8b, reduction with lithium aluminum hydride afforded compounds **9a** and **9b** in almost quantitative yield; both were competent coupling partners when reacted in the presence of $[Pd(dba)_2]$ and ligand **L1** to give substituted 2,3-dichloroquinoxalines.[3f–h,12] *N,N*-Dihydrotetraazatetracenes **10a**–**10h** were obtained in 35–65% yield; oxidation of these somewhat-air-sensitive intermediates by MnO_2 furnished tetraazatetracenes **11a**–**11h** in 43–92% yield as analytically pure samples after column chromatography on silica gel and crystallization. The coupling yields of TIPS-substituted **11** were very similar to those of the TES-substituted azaacenes, even though the oxidation of the TIPS-ethynyl-substituted derivatives of compound **10** was, on average, less efficient. These improved coupling results, when compared to the synthesis of **6**, were perhaps owing to the enhanced oxidative stability of the formed *N,N*-dihydrotetraazacenes (**10a**–**10h**), which apparently did not poison the coupling catalyst in its Pd^{2+} form as they were probably not able to reduce it into Pd^0.[3f]

Optical properties and quantum chemical calculations: Figure 1 shows a photograph of solutions of the diazaacenes (top and middle rows) and of the tetraazaacenes (bottom row). All of the solutions were deeply colored and the diazaacene solutions were also quite fluorescent. Both the absorption and emission colors were dependent upon the specific structure of the azatetracene. The tetraazaacenes were non-fluorescent, but also formed red-to-purple-colored solutions. The absorption and emission spectra of the diazaacenes are shown in Figure 2. As expected, small Stokes shifts were observed, which were testament to the rigid molecular frameworks and typical of acene-type structures. We also observed the vibronic fine-structure of the long-wavelength α-band.

The absorption maxima of the diazaacenes were in the range 572–620 nm, in accordance with our recent results.[3d]

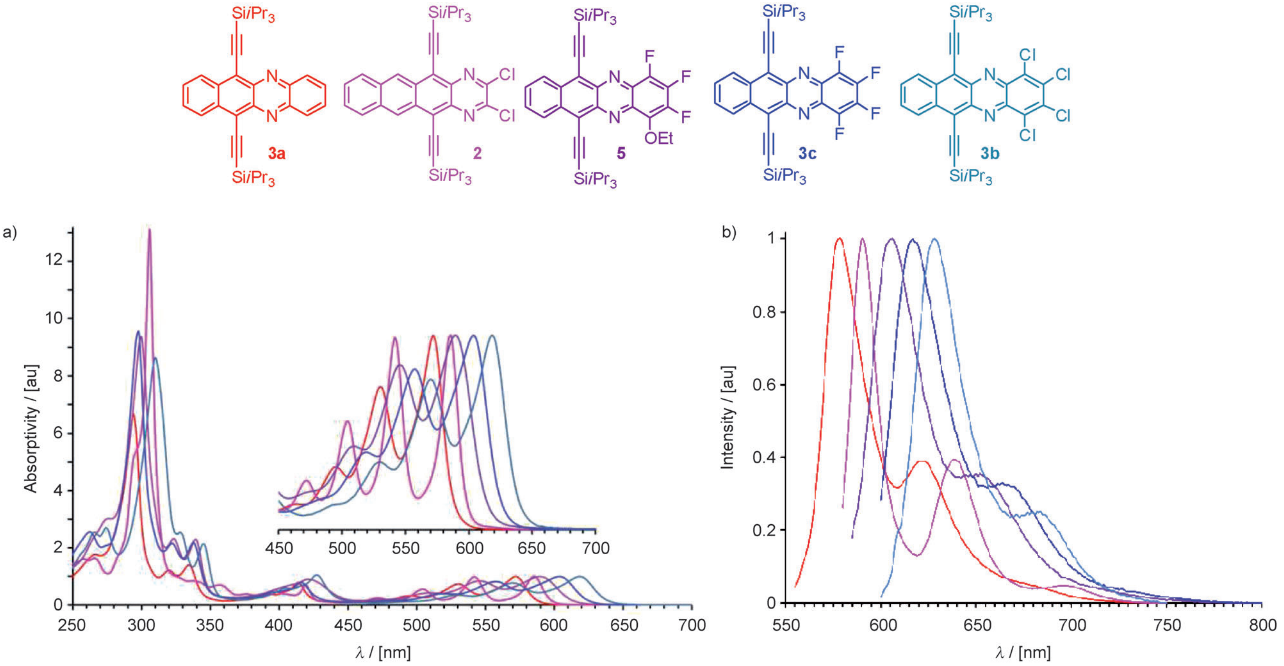


Figure 2. a) Normalized absorption spectra of compounds **2**, **3a**–**3c**, and **5** in *n*-hexane. b) normalized emission spectra of compounds **2**, **3a**–**3c**, and **5** in *n*-hexane. **3a**: λ_{max} absorption 572 nm (2.17 eV), λ_{max} emission 577 nm; **2**: 586 nm (2.12 eV), 590 nm; **5**: 588 nm (2.11 eV), 605 nm; **3c**: 602 nm (2.06 eV), 616 nm; **3b**: 620 nm (2.00 eV), 627 nm.

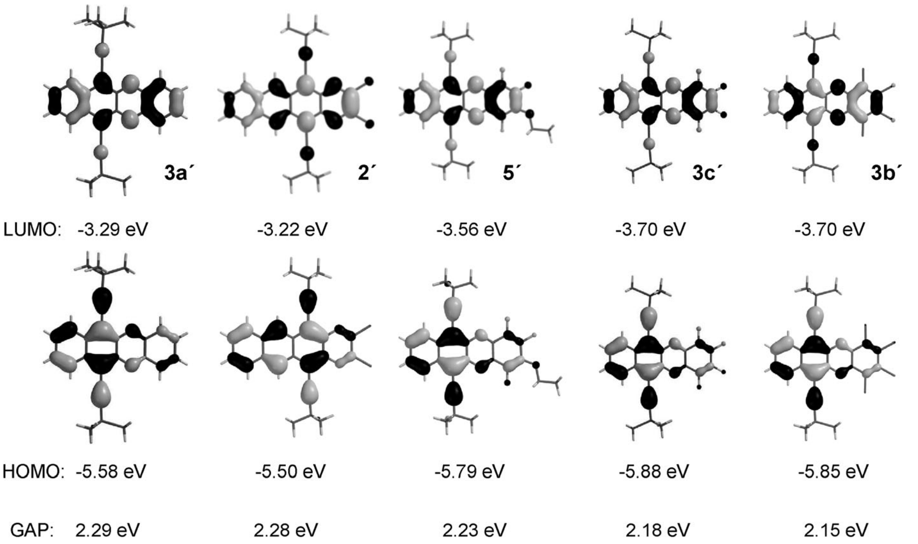


Figure 3. Quantum-chemical calculations (B3LYP 6-311+G**, Spartan ′10) for compounds **3a′**, **2′**, **5′**, **3c′**, and **3b′**. The gaps were overestimated by about 0.1–0.15 eV.

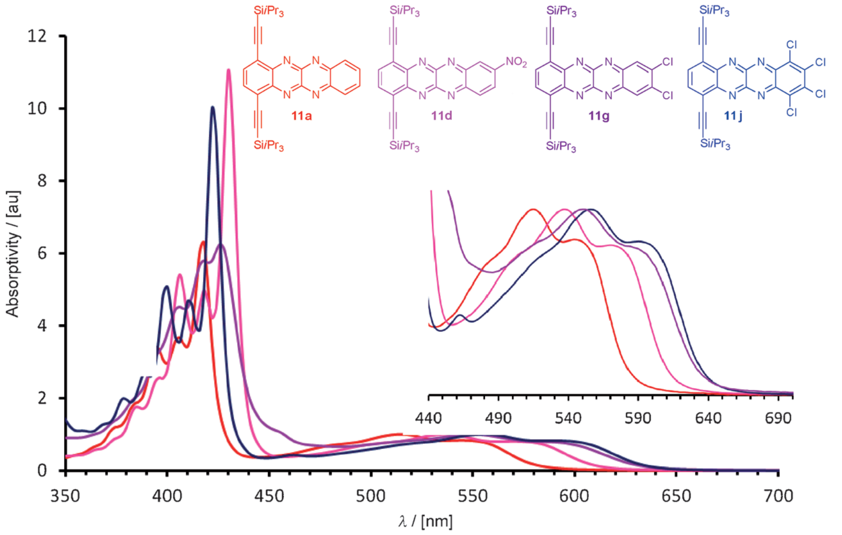


Figure 4. Absorption spectra of compounds **11a**, **11g**, **11d**, and **11j** in *n*-hexane. **11a**: 548 nm (2.27 eV); **11g**: 574 nm (2.16 eV); **11d**: 590 nm (2.10 eV); **11j**: 598 nm (2.08 eV).

These compounds (**2**, **3c**, and **5**) bridged the color gap between compounds **3a** and **3b**. Quantum-chemical computational studies (Figure 3) on model compounds (primed numbers, TMS instead of TIPS) corroborate this trend. Diazaacenes **3c′** and **3b′** had almost identically lying frontier molecular orbitals. Surprisingly, the net effect of fluorine substitution in compound **3c′** was quite similar to that of chlorination in compound **3b′**. The combination of the −I and the +M effects of the fluorine atoms in compound **3c′** was similar to the electronic effect that chlorine substitution exerted upon the diazatetracene core in compound **3b′**.

However, the quantum-chemical calculations at this level of theory (B3LYP 6-311+G**) did not include configuration interactions, and therefore overestimated the optical gap by approximately 0.1–0.15 eV, which was acceptable. Contrary to the diazaacenes, tetraazaacenes **11** were all non-fluorescent. Figure 4 shows the absorption spectra of TIPS-substituted tetraazacenes **11**. Noticeably, the vibronic fine structures of compounds **11a**, **11d**, **11g**, and **11j** were considerably less distinct than those observed in the diazatetracenes. In addition, the middle peak in the UV/Vis spectra of compounds **11** was the most-intense, which was also contrary to the features observed for the diazatetracenes. When comparing the diaza- and tetraazatetracenes (see below), the structure of the frontier molecular orbitals suggested that the latter compounds had more of an internal-charge-transfer (ICT) character. It was unclear whether this property was due to the position of the alkyne groups (central versus on the terminal benzene). The ICT character also led to the ground- and excited-state structures being somewhat different, and a decreased Franck–Condon-overlap of the two states. Therefore, the broadened absorption bands and the loss of fluorescence were two sides of the same coin. We will test this hypothesis in the future by making diazaacenes in which the terminal rings contain alkyne substituents. Quantum-chemical calculations on the TMS-substituted model systems (**11c**, **11f**, **11i**, **11l**) showed that the LUMOs of compound **11** were typically lower lying than those of the diazaacenes.

The introduction of two additional nitrogen atoms had an effect similar to that of the tetrafluorination or the tetrachlorination of one of the outer rings in terms of the electronic effect on the position of the LUMOs in azaacenes. Interestingly, the quantum-chemical calculations on compounds **11** reproduced the optical gaps better than those performed on the diazaacenes. The reason for this result is unclear.

The diazatetracenes and the tetraazatetracenes were structurally most similar; however, their optical properties were quite different. In particular, the lack of fluorescence in compounds **11** was surprising. The reason for this behavior could be due to the orbital structure of the diazaacenes versus that of the tetraazaacenes. In the latter case, that is, in compounds **11**, the HOMOs and the LUMOs were spatially quite disjointed for all of the investigated derivatives.[19] Therefore, the frontier molecular orbitals occupied different parts of the molecule (Figure 3, Figure 5). In the excited states of tetraazaacenes **11**, there was presumably some ICT, so the initially formed excited states relaxed and changed their geometry. Apparently, this relaxation happened to such an extent that nonradiative decay was effective in all of the derivatives of compound **11**. The unusually poorly resolved optical bands underscored this point.

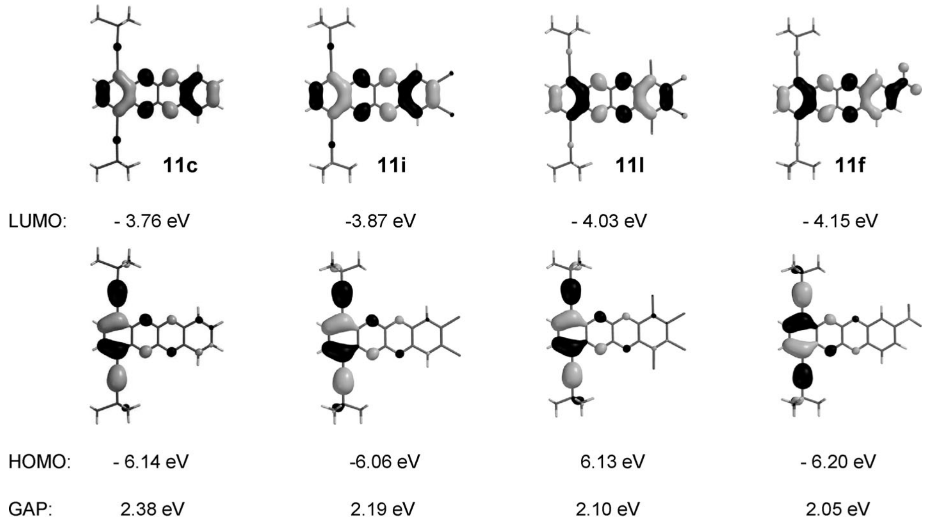


Figure 5. Quantum-chemical calculations (B3LYP 6-311+G**, Spartan ′10) for compounds **11c**, **11f**, **11i**, and **11l**.

Single crystal analysis: Unfortunately, we were not able to obtain single crystals of compounds **11**, but we were able to obtain suitable crystals of compounds **3b** and **3c**, and therefore we were able to investigate the difference in the packing of these consanguine structures. For a comparison of their crystal lattices and cell parameters with that of unsubstituted compound **3a**, see Table 1.[3a]

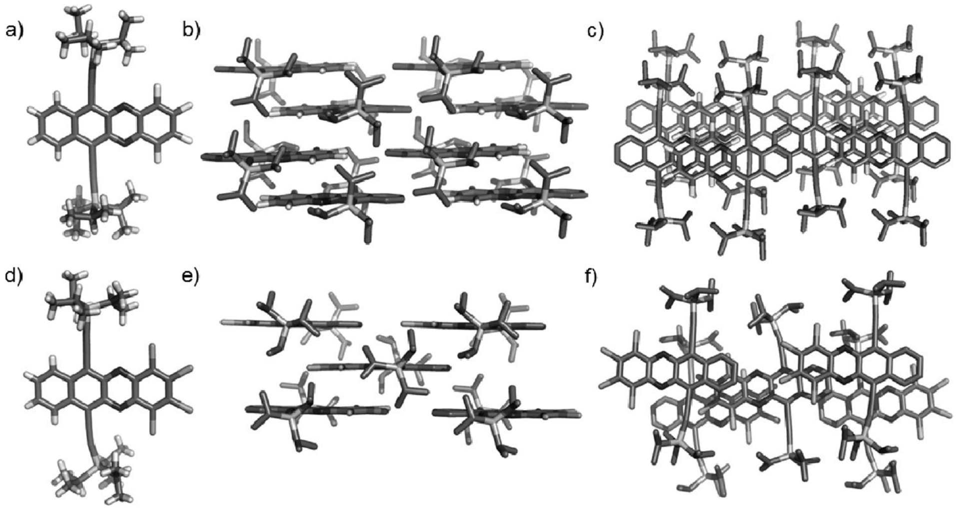


Figure 6. a–c) Packing of compound **3c** and d–f) of compound **3b**.

Both **3b** and **3c** formed brick-wall-type packing motifs that appeared to be superficially similar. However, compound **3b** crystallized in a monoclinic cell, whilst compound **3c** was triclinic, with different axis lengths and angles. Also, their molecular packing motifs differed. In compound **3c** (Figure 6), the molecules formed 1D, offset stacks, in which the fluorinated parts of two successive molecules were stacked on top of the pyrazine unit of the other molecule, with a small plane-to-plane-distance of 3.25 Å. This structure was surprising, because when benzene and hexafluorobenzene were co-crystallized, there was a strong interaction between the perfluorinated and benzene rings. This expected packing of the fluorinated above the benzene-like ring of an adjacent molecule did not happen for compound **3c**. Instead, centrosymmetric sandwiches formed and packed into the stacks described above. These stacks were partially interdigitated through the terminal benzene rings with the neighboring ones (nonbonding distance: 3.37 Å), so that an inter-

Table 1. Crystal-structure data of compounds **3a**–**3c**.

Compound	Space group	*a* [Å]	*b* [Å]	*c* [Å]	*α* [°]	*β* [°]	*γ* [°]	*V* [Å]	*Z*
3a	$P\bar{1}$	7.3968(7)	13.893(2)	18.428(2)	112.065(7)	95.624(7)	90.530(8)	1744.31	2[a]
3b	$C2/c$	34.94(1)	15.039(6)	14.898(6)	90.00	104.591(7)	90.00	7576.52	8
3c	$P\bar{1}$	7.6248(4)	14.128(2)	17.729(1)	70.291(3)	81.942(1)	82.755(2)	1773.77	2

[a] See reference [3a].

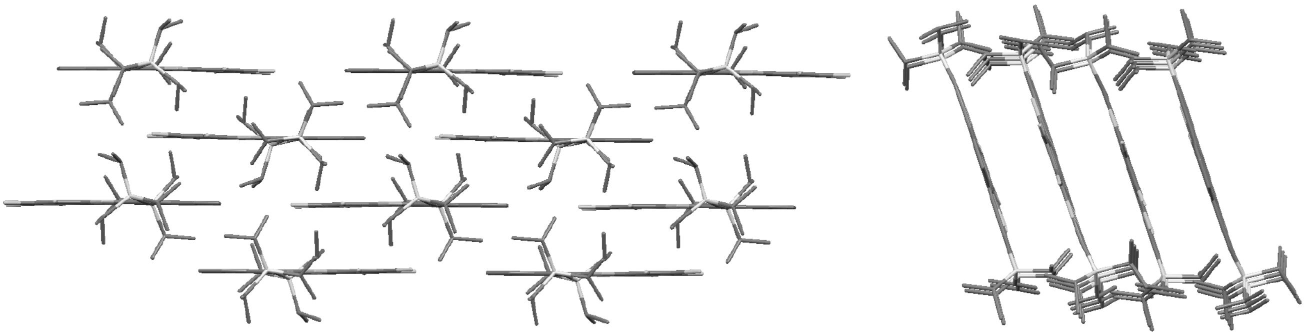


Figure 7. Close contacts in the packing of compound **3b**. The ABCD layer structure is shown in two views.

esting tightly packed 2D brick wall resulted for compound **3c**. In the single-crystal structure of compound **3b**, the formation of centrosymmetric dimers was also observed, in which the chlorinated rings stacked on top of the pyrazine rings of the successive molecules. Contrary to fluorinated compound **3c**, this motif did not repeat itself in the formation of ABABAB stacks, but rather an additional double layer (C,D) of centrosymmetric dimers was observed, so that a repeating ABCDABCD layer sequence resulted (Figure 7). The average overall perpendicular distance between the layers of acene **3b** was 3.50 Å. In the related compounds (**3a** and **3c**), the analogous layer-to-layer distances were 3.36 and 3.27 Å respectively.

Overall, the structures of compounds **3a** (H) and **3c** (F) were almost identical, whilst the packing of compound **3b** (Cl) was different from both of them. Therefore, we note that halogenated quinoxaline subunits exerted a commanding influence on the overall packing motifs of the azaacenes.

Conclusion

By using several different procedures (condensation to *ortho*-quinones, condensation with diethyloxalate/$POCl_3$, and Pd-catalyzed cyclo-Buchwald–Hartwig coupling reactions followed by oxidation with MnO_2) we furnished a range of diaza- and tetraazaacenes with a wide variety of substitution patterns in moderate to good yields.[12] Notably, a partially fluorinated diazaacene (**3c**) was synthesized and characterized by X-ray crystallography. The Pd-catalyzed reactions cleanly furnished tetraazatetracenes **11**. Interestingly, the Pd-catalyzed coupling of compound **4** to dichloropyrazine (to give compound **6**) worked poorly and its oxidation surprisingly afforded compound **7** rather than the desired tetraazatetracene.

The absorption maxima in these azaacenes was fine-tuned in the range 548–620 nm by changing the number of nitrogen atoms and substituents. The tetraazaacenes typically showed higher absorption energies. Electronegative substituents generally lowered the energy of the absorption bands, owing to the different stabilization effects experienced by the HOMOs and LUMOs. Whilst the LUMOs were typically well-stabilized by electronegative substituents, the HOMOs of the azaacenes profited less from the electronegative stabilization, primarily because the orbital coefficients of the HOMOs were small or disappeared at the locus of the substituent. Overall, our approach has fundamentally broadened the number and scope of substituted azatetracenes available. Powerful methods beyond the classic condensation procedures are now available to quickly and efficiently grow this class of compounds.[3f,h]

Acknowledgements

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