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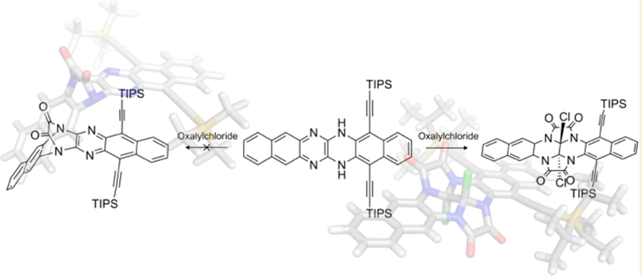
Reactions of Large Tetraaza-*N*,*N*′-dihydroacenes: Formation of Unexpected Adducts and an Unstable Tetraazahexacene

Jens U. Engelhart,[∥] Benjamin D. Lindner,[∥] Olena Tverskoy, Manuel Schaffroth, Frank Rominger, and Uwe H. F. Bunz*

Organisch-Chemisches Institut, Ruprecht-Karls-Universität, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

Supporting Information

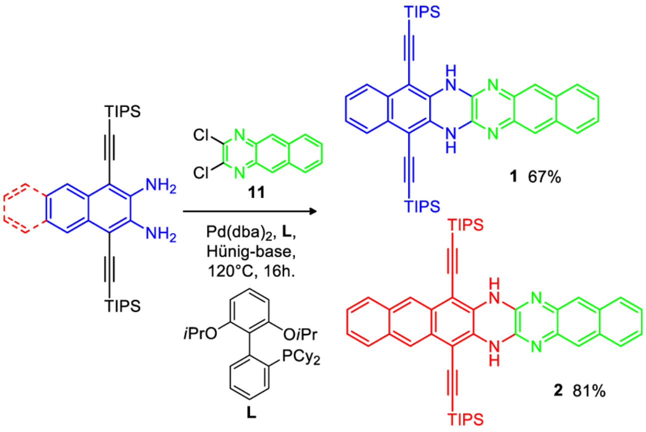
ABSTRACT: We report the reaction of several *N*,*N*′-dihydrotetraazaacenes with oxalylic chloride to give unusual adducts, which were characterized by single-crystal X-ray structures.



Large azaacenes have found significant attention as attractive charge transport complements to pentacene.[1,2] Tetraazacenes are electron-transporting materials and have successfully been used in thin-film transistors with surprisingly high mobilities.[3] Despite this interest there is only very little information about the reaction chemistry of such materials or that of their *N*,*N*′-dihydrodiazaacenes.[4] Here we describe the surprising reaction of *N*,*N*′-dihydrotetraazapenta-, -hexa-, and -heptacenes **1**, **2**, and **4** with oxalylic chloride to give novel bridged arenes with unusual structures.[5] While synthetic access toward novel and attractive large *N*-heteroacenes and their *N*,*N*′-dihydro derivatives has exploded in the past few years, their reaction chemistry is unknown but clearly worth being explored, as the presence, in particular, of the N−H units in the *N*,*N*′-dihydroazaacenes might allow the construction of larger but potentially three-dimensional acene-like stiff structures. Alternatively, expansion of the π-system in the dihydroazaacenes could happen in the second dimension, giving rise to more extended planar or twisted structures. Alas, neither concept has been pursued hitherto. We think that the *N*,*N*′-dihydrooligoazaacenes present an exciting opportunity to prepare new, structurally unusual materials and to develop novel reactions for the functionalization of these long known yet intriguing acene-like materials.

The starting point of our investigation was the Pd-catalyzed reaction of diaminoanthracenes and -naphthalenes with 2,3-dichlorobenzo[*g*]quinoxaline (**11**)[6] to give the coupling products **1** and **2** (Scheme 1) in good to excellent yields after chromatography and crystallization. Attempts to oxidize **1** into **3** using MnO_2 under our recently established conditions did furnish the material, but **3** decomposes quickly in solution, even though we were able to obtain a ^{1}H NMR spectrum of **3** as well as its UV−vis spectrum. To circumvent this problem we envisioned to make a precursor such as **A** just by reacting **1** with oxalylic chloride (Scheme 2) in the presence of an auxiliary base. Pyrolysis or photolysis in a thin film should lead to the removal of two equivalents of CO and formation of the tetraazahexacene **3** (Scheme 2).

Scheme 1. Synthesis of the *N*,*N*′-Dihydrotetraazaacenes Using Pd-Catalyzed Coupling Reactions



Upon reaction of **4** with oxalylic chloride (Scheme 3), we did *not* obtain material that could be reconciled with a structure such as **A**, as we observe two C═O-type signals in the ^{13}C NMR spectrum, instead of one, as would be expected for **A**. We reacted the compounds **1** and **2** with oxalylic chloride in the presence of triethylamine to obtain the coupling products **6** and **7** as light brown and yellow solids with yellow fluorescence. Only after growing crystalline specimen from **5** and **6** (Figure 1) and solving their X-ray crystal structures did we identify the adducts to possess the structures **5**−**7**, the latter one concluded

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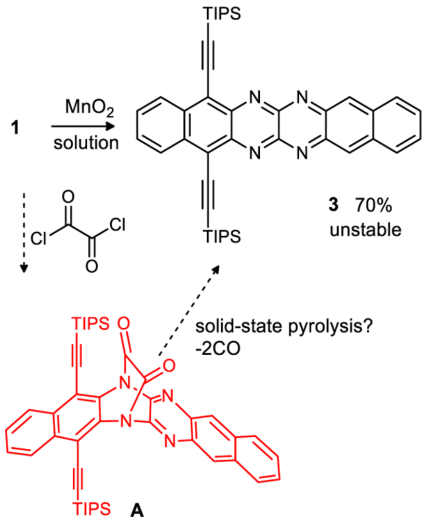
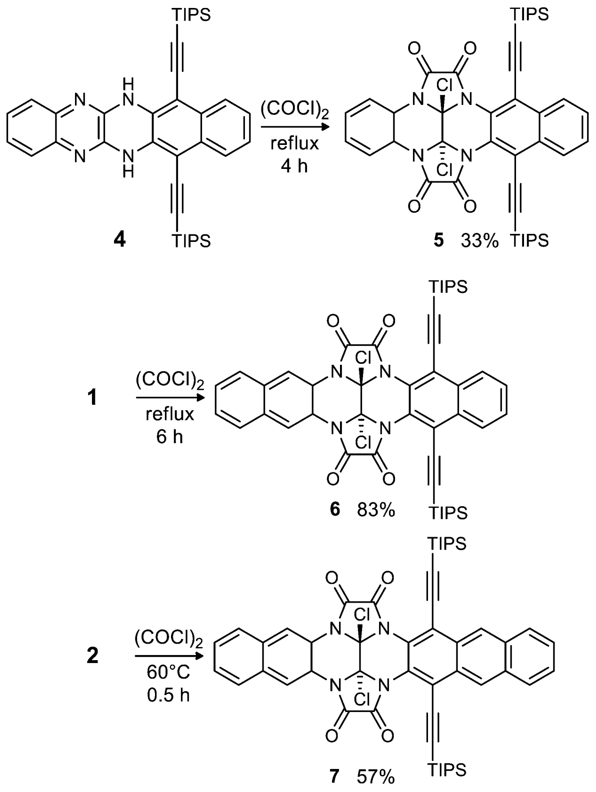
Scheme 2. Two Possible Routes to Azaacene 3



Scheme 3. Reaction of Oxalylic Chloride with *N,N′*-Dihydrotetraazaacenes



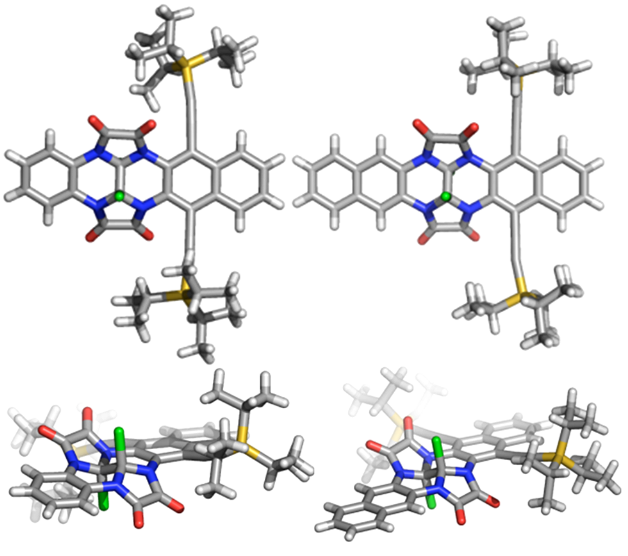
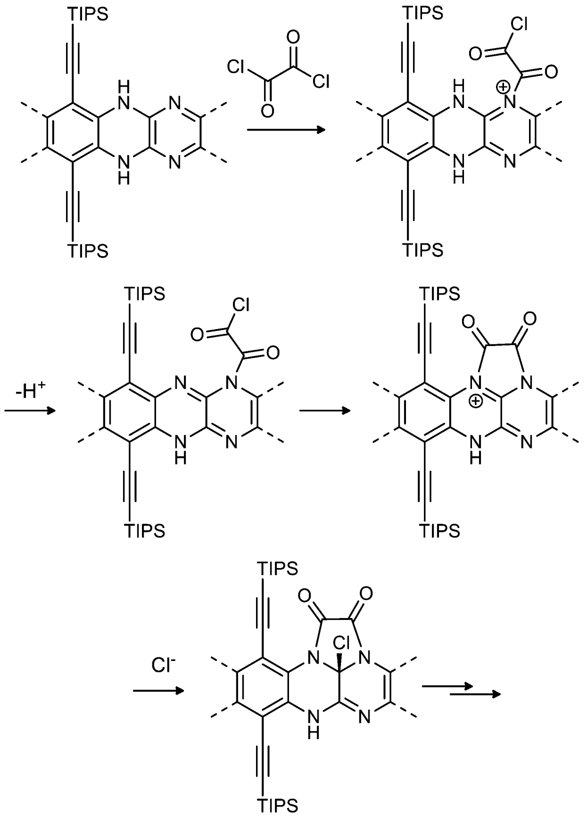


Figure 1. Single-crystal X-ray structures of **6** (left) and **5** (right).

Scheme 4. Reaction of Oxalylic Chloride with *N,N′*-Dihydrotetraazaacenes: Mechanistic Rationalization



from the analogous spectroscopic data. The structures are unexpected at first glance but can be explained easily if one suggests the following reaction sequence (Scheme 4): attack of the nucleophilic pyrazine-nitrogen, loss of a proton from the NH unit, and second attack of the remaining C═OCl part of the former oxalylic chloride. The first half of the sequence is then finished by the addition of a chloride ion to the iminium salt. Repetition of this sequence would lead to the observed embedded tetracyclic core. Attempts to dehalogenate **5** with *n*-BuLi or even only with KI furnished back the starting material **4** and not the just dehalogenated species.

The single crystal structures of **5** and **6** are shown in Figure 1. The bond lengths and bond angles are inconspicuous and corroborated by independent SPARTAN calculations (B3LYP 6-31G**). The tetracyclic center is nonplanar and therefore avoids the interaction with the bulky TIPS-ethynyl group. Upon removal of the two chlorine substituents in silico, a structural element as shown in Figure 2 would develop, but it is highly strained, as the TIPS groups and the C═O units put the aromatic board into a significant twist. Attempts to dehalogenate the adducts with KCN in a halophilic reaction[7]

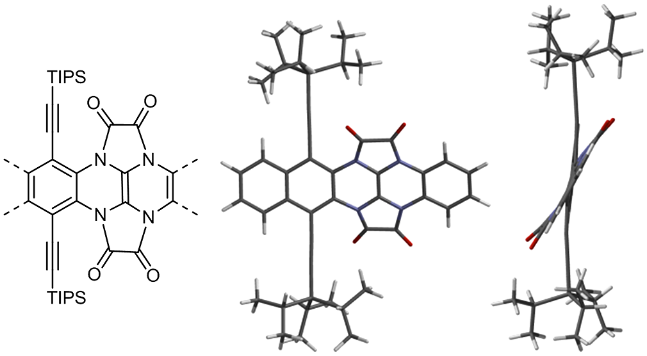


Figure 2. Structural element of the formally dechlorinated coupling products (right) and B3LYP 6-31G** calculations of the dechlorinated derivative of **5**. The twist of the arene is 35°.

only led to the reformation of **1**, **2**, or **4**, perhaps due to the significant strain that would be built up when the tetracyclic core is close to the bulky TIPS groups.

Quantum chemical calculations (Figure 2) confirmed this assessment, and the corresponding dechlorinated compounds would be twisted, due to the interaction of the TIPS-alkyne units with the cyclic 1,2-dione, making their formation improbable. More surprising though is that the corresponding formal diazabicyclo[2.2.2]octane **8** (Figure 3) is not observed either.

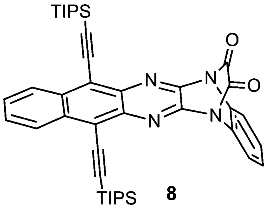


Figure 3. Expected adduct **8** of oxalylic chloride to **1**.

To further investigate the reactivity of the NH compounds, we treated **2** and **4** with acetyl chloride in the presence of triethylamine to yield **9** and **10**, stable solids under ambient conditions. Here we find transposition of the NH groups according to the UV–vis spectra (Figure 4). The UV–vis spectra show the presence of an anthracene unit for **9** (as the acetylated derivative of **4**) and the presence of a tetracene unit in the case of **10**. If the original N–H positions would have been acetylated, the largest π-system would have been a naphthalene (for **9**) and an anthracene (for **10**). However, as we find anthracene and tetracene chromophores we conclude that the acetylation is accompanied by transposition of the N-R units. Neither ^{13}C nor ^{1}H NMR spectroscopy can prove the transposition, as the expected spectra are too similar, so UV–vis is a convenient way to assess the correct position of the acetyl group on the two different rings. Also when positioning the acetyl groups in the outer positions of the molecule, the steric pressure is significantly reduced (Figure 5).

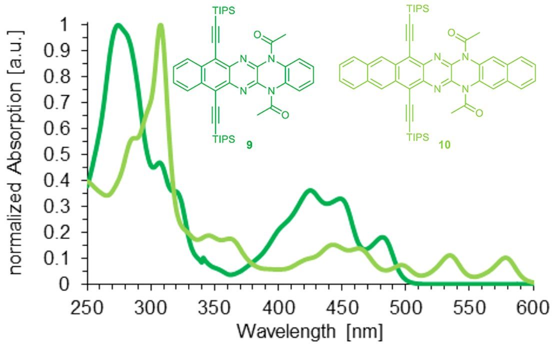


Figure 4. Normalized absorption spectra of **9** and **10**.

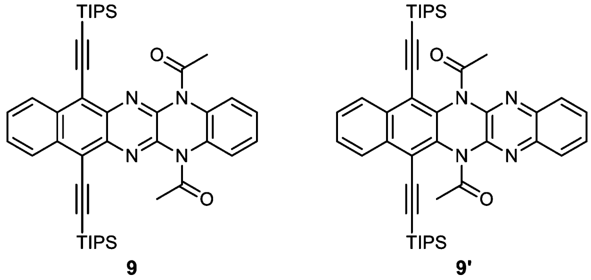
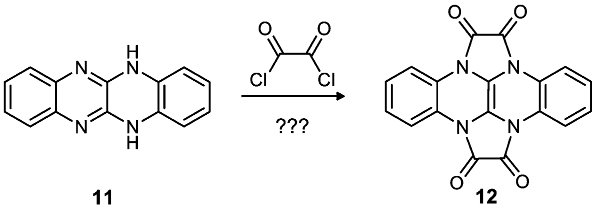


Figure 5. Structural element of the formally dechlorinated coupling products.

Quantum chemical calculations corroborate that the two acetyl isomers have different strain energies. The difference between the two isomers is 9.8 kcal/mol favoring **9** thermodynamically.[8] The aromatic core of **9′** displays a stronger kink (Supporting Information).

In conclusion, *N*,*N′*-dihydroteraazaacenes react with oxalylic chloride to unusual adducts that carry chlorine substituents and aminal units on their central carbon atoms. The strain-induced pyramidalization apparently makes it impossible for the chlorine substituents to leave the scaffold; the formed adducts are therefore stable for hours under air and can be handled indefinitely under atmospheric conditions. This is the first example of reaction chemistry (other than alkylation and acetylation) reported for azaacenes. There are several conclusions gleaned from these experiments. (a) We should be able to perform sterically induced NH-transposition in any *N*,*N′*-dihydrotetraazaacene if desired, when using acetylation/deacetylation sequences. (b) We will investigate the chemistry of **5**–**7** and see if we can use them as building blocks or if every reagent leads back to **1**, **2**, or **4**, respectively. (c) We will perform similar experiments on **11** and see if we obtain structures such as planar **12** (Scheme 5). We expect formation of **12**, as here the sterically cumbersome effect of the TIPS-alkyne groups is absent. Compounds such as **12** would be attractive partners in 1,3-dipolar cycloadditions, carbene additions or Diels–Alder reactions. (d) We have also learned that simple bridging into structures such as **A** does not happen. We do think however, that **5**–**7** are a potentially attractive class of novel compounds.

Scheme 5. Future Reactions?



EXPERIMENTAL SECTION

All reagents and solvents were obtained from commercial suppliers and were used without further purification unless otherwise noted. Dichloromethane was dried using drying columns. Preparation of air- and moisture-sensitive materials was carried out in oven-dried flasks under an atmosphere of nitrogen using Schlenk-techniques. Compound **4**,[1d] diaminoanthracene,[9] and -naphthalene[9] were prepared as reported. 2,3-Dichlorobenzo[*g*]quinoxaline was prepared by the two-step procedure according to literature.[10] Melting points were determined with a melting point apparatus and are uncorrected. ^{1}H NMR were recorded on a 300, 500, or 600 MHz spectrometer, and ^{13}C NMR spectra were recorded on a 75, 125, or 150 MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to traces of $CHCl_3$ or accordingly CD_2Cl_2 in the corresponding deuterated solvent.[11] MS spectra were recorded using electron-impact ionization, fast-atom bombardment ionization, or electrospray ionization methods detected by magnetic sector and FT-ICR techniques, respectively. Crystal structure analysis was accomplished using diffractometers with Mo Kα radiation. Infrared (IR) spectra are reported in wavenumbers (cm^{-1}) and were recorded in the solid state. Absorption spectra and emission spectra were recorded in hexane.

5,16-Bis[[tri(propan-2-yl)silyl]ethynyl]-6,15-dihydrobenzo-[*g*]benzo[6,7]quinoxalino[2,3-*b*]quinoxaline (1). Hünig base (7 mL) was placed under an argon atmosphere in a dried Schlenk tube that contained the diaminonaphthalene (1.00 g, 1.93 mmol), dichlorbenzoquinoxaline (500 mg, 1.95 mmol), $Pd(dba)_2$ (40.0 mg, 69.6 μmol), and ligand **L** (50.0 mg, 107 μmol). The tube was sealed, and the reaction mixture was stirred for 20 h at 120 °C. Without any workup the mixture was purified by flash column chromatography (silica gel, petroleum ether/EtOAc, 98:2, 902 mg, 67%) to obtain the *N,N'*-dihydro compound **1** as an orange solid (dec >250 °C): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.28−1.36 (m, 42H), 7.15−7.22 (m, 2H), 7.34−7.44 (m, 2H), 7.70−7.77 (m, 2H), 7.76 (brs, 2H), 7.86 (s, 2H), 7.97−8.04 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) 11.6, 19.1, 99.3, 102.7, 106.0, 122.9, 125.2, 125.4, 126.2, 127.8, 129.6, 130.8, 132.5, 137.6, 140.7; IR ν = 3375, 2942, 2861, 2129, 1595, 1571, 1453; UV−vis λ_{max} (hexane) 465 nm; ε (465 nm) = 77994 L·mol^{-1}·cm^{-1}; fluorescence λ_{max} (hexane) 467 nm; HR-EI (magnetic sector) *m*/*z* calcd for $C_{44}H_{54}N_4Si_2$ 694.3887, found 694.3886 (100). Anal. Calcd for $C_{44}H_{54}N_4Si_2$: C, 76.03; H, 7.83; N, 8.06. Found: C, 75.76; H, 7.93; N, 7.76. Crystallographic data: space group $P\overline{1}$, $Z = 8$, $a = 7.706(5)$ Å, $b = 23.131(14)$ Å, $c = 45.24(3)$ Å, $\alpha = 90.756(12)°$, $\beta = 90.191(12)°$, $\gamma = 94.472(12)°$, $V = 8039(8)$ Å^3.

8,15-Bis[[tri(propan-2-yl)silyl]ethynyl]-7,16-dihydrobenzo-[*g*]naphtho[2′,3′:6,7]quinoxalino[2,3-*b*]quinoxaline (2). Hünig base (5 mL) was placed under an argon atmosphere in a dried Schlenk tube that contained the diaminoanthracene (200 mg, 0.352 mmol), dichlorbenzoquinoxaline[6] (180 mg, 0.722 mmol), $Pd(dba)_2$ (16.0 mg, 27.8 μmol), and ligand **L** (18.0 mg, 38.6 μmol). The tube was sealed, and the reaction mixture was stirred for 20 h at 120 °C. Without any workup the mixture was purified by flash column chromatography (silica gel, petroleum ether/EtOAc, 95:8, 212 mg, 81%) to obtain the *N,N'*-dihydrocompound **2** as an orange solid (dec >350 °C): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.28−1.34 (m, 42H), 7.35−7.41 (m, 2H), 7.41−7.46 (m, 2H), 7.84−7.92 (m, 4H), 7.99 (s, 2H), 8.04 (brs, 2H), 8.57 (s, 2H); IR ν = 3375, 2942, 2864, 2143, 1581, 1488, 1408, 1447; UV−vis λ_{max}(hexane) 479 nm; ε(479 nm)= 51564 L·mol^{-1}·cm^{-1}; fluorescence λ_{max}(hexane) 481 nm; HR-FAB$^+$ (magnetic sector) *m*/*z* calcd for $C_{48}H_{56}N_4Si_2$ 744.4044, found 744.4011 (67.5). $^{13}C\{^1H\}$ NMR could not be received due to the low solubility of **2**. Crystallographic data: space group $P\overline{1}$, $Z = 2$, $a = 7.8787(1)$ Å, $b = 12.8918(1)$ Å, $c = 21.5552(2)$ Å, $\alpha = 93.602(1)°$, $\beta = 94.672(1)°$, $\gamma = 95.417(1)°$, $V = 2166.86(4)$ Å^3.

5,16-Bis[[tri(propan-2-yl)silyl]ethynyl]benzo[*g*]benzo[6,7]-quinoxalino[2,3-*b*]quinoxaline (3). Compound **1** (30.0 mg, 43.2 μmol) was diluted in CH_2Cl_2 (4 mL). The orange solution was treated with an excess of manganese dioxide and turned immediately dark green-brown. After 3 min, the reaction mixture was filtered through a pad of Celite. The solvent was evaporated and the crude product was purified by a quick flash column chromatography (silica gel, petroleum ether/EtOAc, 95:5, 21.1 mg, 70%) to yield the hexacene **3** as a brown, quickly decomposing solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.35−1.40 (m, 42H), 7.45−7.50 (m, 2H), 7.59−7.64 (m, 2H), 8.04−8.08 (m, 2H), 8.69−8.74 (m, 2H); UV−vis λ_{max} (hexane) 834 nm; HR-ESI (FT-ICR) *m*/*z* $[M + H]^+$ calcd for $C_{44}H_{53}N_4Si_2$ 693.38033, found 693.38051

14c,14d-Dichloro-9,14-bis[[tri(propan-2-yl)silyl]ethynyl]-14c,14d-dihydro-2a,6b,8a,14b-tetraazadicyclopenta[*fg*,*st*]-pentacene-1,2,7,8-tetrone (5). *N,N'*-Dihydropentacene **4** (100 mg, 0.155 mmol) was diluted in $(CO_2Et)_2$ (3 mL) and stirred under reflux for 4 h. The reagent was evaporated under reduced pressure (HVP), and the brownish crude product was purified by flash column chromatography (silica gel, petroleum ether/EtOAc, 9:1, 39.0 mg, 33%) to yield **5** as a yellow solid (dec >210 °C): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.17−1.23 (m, 42H), 7.54−7.60 (m, 2H), 7.73−7.80 (m, 2H), 8.16−8.23 (m, 2H), 8.52−8.58 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) 11.5, 18.8, 90.7, 98.0, 109.4, 118.2, 122.7, 122.8, 123.7, 127.3, 128.8, 129.5, 132.5, 150.6, 152.8; IR ν = 3369, 2942, 2862, 2129, 1576; UV−vis λ_{max}(hexane) 362 nm; ε(362 nm) = 5103 L·mol^{-1}·cm^{-1}; HR-EI (magnetic sector) *m*/*z* calcd for $C_{44}H_{50}{}^{35}Cl_2N_4O_4Si_2$ 824.2748, found 824.2726 (7.4). Crystallographic data: space group $P\overline{1}$, $Z = 2$, $a = 13.7684(2)$ Å, $b = 13.7850(2)$ Å, $c = 14.3419(2)$ Å, $\alpha = 102.149(1)°$, $\beta = 114.803(1)°$, $\gamma = 108.584(1)°$, $V = 2146.61(5)$ Å^3.

16c,16d-Dichloro-3,8-bis[[tri(propan-2-yl)silyl]ethynyl]-16c,16d-dihydro-2a,8b,10a,16b-tetraazadicyclopenta[*hi*,*uv*]-hexacene-1,2,9,10-tetrone (6). *N,N'*-Dihydrohexacene **1** (100 mg, 0.144 mmol) was diluted in $(CO_2Et)_2$ (3 mL) and stirred under reflux for 6 h. The reagent was evaporated under reduced pressure (HVP), and the light-brown crude product was purified by flash column chromatography (silica gel, petroleum ether/EtOAc, 9:1, 89.0 mg, 83%) to yield **6** as a light-brown solid (dec >250 °C): ^{1}H NMR (600 MHz, $CDCl_3$) δ = 1.19−1.25 (m, 42H), 7.65−7.69 (m, 2H), 7.75−7.79 (m, 2H), 7.98−8.02 (m, 2H), 8.54−8.58 (m, 2H) 8.67 (s, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) 11.5, 18.9, 90.9, 100.0, 109.5, 118.2, 120.7, 122.1, 123.6, 127.4, 128.4, 128.5, 129.5, 131.8, 132.5, 150.6, 158.8; IR ν = 2943, 2868, 1780, 1461, 1350; UV−vis λ_{max}(hexane) 362 nm; ε(362 nm) = 21646 L·mol^{-1}·cm^{-1}; HR-EI (magnetic sector) *m*/*z* calcd for $C_{48}H_{52}{}^{35}Cl_2N_4O_4Si_2$ 874.2904, found 874.2953 (rel int 1.00), calcd for $C_{48}H_{52}{}^{35}Cl^{37}Cl\ N_4O_4Si_2$ 876.2875, found 876.2914 (rel int 0.98), calcd for $C_{48}H_{52}{}^{37}Cl_2N_4O_4Si_2$ 874.2845, found 878.2877 (rel int 0.27), correct isotope distribution. Crystallographic data: space group $P2_1/c$, $Z = 4$, $a = 7.214(2)$ Å, $b = 21.153(6)$ Å, $c = 33.108(9)$ Å, $a = 90°$, $\beta = 95.674(7)°$, $\gamma = 90°$, $V = 5028(2)$ Å^3.

18c,18d-Dichloro-11,18-bis[[tri(propan-2-yl)silyl]ethynyl]-18c,18d-dihydro-2a,8b,10a,18b-tetraazadicyclopenta[*hi*, *yz*]-heptacene-1,2,9,10-tetrone (7). *N,N'*-Dihydroheptacene **2** (100 mg, 0.134 mmol) was diluted in $(CO_2Et)_2$ (8 mL) and stirred at 60 °C for 30 min. The reaction mixture was cooled to room temperature and poured slowly into ice−water. The yellow solid was filtered off and was purified by flash column chromatography (silica gel, petroleum ether/EtOAc, 5:1, 71.0 mg, 57%) to yield 7 as a yellow solid (decomp. >210 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.24−1.30 (m, 42H), 7.61−7.66 (m, 2H), 7.66−7.71 (m, 2H), 7.98−8.03 (m, 2H), 8.05−8.11 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) 11.6, 18.9, 90.9, 100.4, 110.1, 118.4, 120.6, 122.0, 123.0, 127.3, 127.67, 128.4, 128.5, 128.8, 129.2, 131.8, 133.3, 150.5, 152.8; IR ν = 2942, 2867, 1774, 1461, 1304; UV−vis λ_{max}(hexane) 438 nm; ε(438 nm)= 7294 L·mol^{-1}·cm^{-1}; Fluorescence λ_{max}(hexane) 444 nm; HR-EI (magnetic sector) *m*/*z* calcd for $C_{52}H_{54}{}^{35}Cl_2N_4O_4Si_2$: 924.3060, found 924.3079 (14.3).

1,1′-(7,12-Bis[[tri(propan-2-yl)silyl]ethynyl]benzo[*g*]-quinoxalino[2,3-*b*]quinoxaline-5,14-diyl)diethanone (9). *N,N'*-Dihydropentacene **4** (100 mg, 0.155 mmol) was placed under an argon-atmosphere in a dried Schlenk tube and was diluted in CH_2Cl_2 (5 mL). After cooling to 0 °C, the mixture was treated with NEt_3 (0.1 mL) and stirred for 10 min. Acetyl chloride (0.3 mL) was added, and the mixture was stirred at 0 °C for further 1.5 h. Subsequently, the reaction mixture was treated with water and the aqueous phase was extracted three times with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography (silica gel, petroleum ether/EtOAc, 95:5 → 9:1, 24.0 mg, 23%) to yield **9** as a yellow solid (dec >220 °C): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.22−1.29 (m, 42H), 2.80 (s, 6H), 7.29−7.37 (m, 2H), 7.68−7.74, (m, 2H), 7.97−8.03 (m, 2H), 8.65−8.71, (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) 11.7, 19.0, 25.6, 101.7, 106.9, 119.9, 125.5, 126.3, 127.6, 128.4, 131.0, 134.6, 137.3, 144.4, 169.2; IR ν = 3324, 2942, 2864, 1710, 1461, 1397; UV−vis λ_{max}(hexane) 482 nm; ε(482 nm) = 6378 L·mol^{-1}·cm^{-1}; fluorescence λ_{max}(hexane) 495 nm; HR-EI (magnetic sector) *m*/*z* calcd for $C_{44}H_{56}N_4O_2Si_2$ 728.3942, found 728.3966 (24.0).

1,1′-(8,15-Bis[[tri(propan-2-yl)silyl]ethynyl]benzo[*g*]-naphtha[2′,3′:6,7]quinoxalino[2,3-*b*]quinoxaline-6,17-diyl)-diethanone (10). *N*,*N*′-Dihydroheptacene **2** (140 mg, 0.188 mmol) was placed under an argon-atmosphere in a dried Schlenk tube and was diluted in CH_2Cl_2 (7 mL). After cooling down to 0 °C, the mixture was treated with NEt_3 (0.15 mL) and stirred for 10 min. Acetyl chloride (0.1 mL) was added, and the mixture was stirred at 0 °C for further 1.5 h. Subsequently, the reaction mixture was treated with water and the aqueous phase was extracted three times with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography (silica gel, petroleum ether/EtOAc, 95:5, 30.0 mg, 19%) to yield 10 as a redish solid (dec >230 °C): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.32−1.37 (m, 42H), 2.90 (s, 6H), 7.47−7.53 (m, 2H), 7.54−7.59 (m, 2H), 7.86−7.93 (m, 2H), 8.03−8.09 (m, 2H), 8.56 (s, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) 11.8, 19.1, 25.9, 102.5, 107.7, 119.8, 123.6, 126.7, 127.0, 127.1, 128.1, 128.7, 128.8, 131.19, 131.7, 133.0, 137.1, 144.3, 169.5; IR ν = 3051, 2940, 2862, 2131, 1713; UV−vis λ_{max}(hexane) 578 nm; ε(578 nm) = 10744 L·mol^{-1}·cm^{-1}; fluorescence λ_{max}(hexane) 586 nm; HR-ESI (FT-ICR) *m*/*z* $[M + H]^+$ calcd for $C_{52}H_{60}N_4O_2Si_2$ 829.43276, found 829.43015.

2,3-Dichlorobenzo[g]quinoxaline (11). 2,3-Naphthalenediamine (191 mg, 1.207 mmol) was placed under an argon atmosphere in a dried Schlenk tube and was diluted in diethyl oxalate (3 mL). The mixture was stirred under reflux for 15 h. After being cooled to ambient temperature, the suspension was filtered, and the residue was washed with EtOH. Without any further purification the brownish solid was dried under reduced pressure (176 mg, 69%). The intermediate product was diluted in $POCl_3$ and stirred for 16 h under reflux. After evaporating under reduced pressure the residue was dissolved in chloroforme and filtered. The organic solution was washed with water and brine. The combined organic layers were dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography (silica gel, chloroform) to yield **11** as a yellow solid (54.0 mg, 26%). The analytical data was in agreement with the literature.[10]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Further general methods, absorption spectra, emission spectra, ^{1}H and ^{13}C NMR spectra, Cartesian coordinates of theoretically treated molecules, and further crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

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

Author Contributions

‖These authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

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