

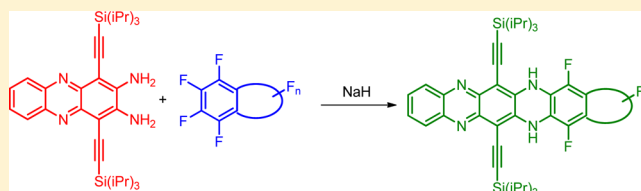
# Partially Fluorinated Tetraazaacenes by Nucleophilic Aromatic Substitution

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**S** Supporting Information

**ABSTRACT:** We report the sodium hydride-mediated reactions of a diethynylated diaminophenazine with perfluorobenzene, perfluoronaphthalene, and two octafluoroanthracene derivatives. In all of the cases, an *N,N*-dihydropyrazine ring is formed, and partially fluorinated tetraazapentacenes, tetraazahexacenes, and tetraazaheptacenes (in their respective *N,N*-dihydro forms) are easily prepared. In the case of the dihydrotetraazapentacenes and -hexacenes, oxidation with manganese dioxide is possible to give the desired, fully unsaturated tetraazaacenes; two molecules of the azahexacene undergo a Diels–Alder reaction in which an alkyne substituent in the conserved hexacene unit works as the dienophile while the tetraazahexacene participates as the diene to give an unsymmetrical dimer. All of the coupling targets were investigated by NMR and UV–vis spectroscopies, and several single-crystal structures of the *N,N*-dihydrotetraazaacenes and also that of the tetrafluorotetraazaacene were obtained.



## INTRODUCTION

We disclose a one-step reaction of an ethynyl-substituted diaminophenazine<sup>1</sup> with perfluorinated arenes in the presence of sodium hydride to give novel, partially fluorinated *N*-heteroacenes. The larger *N*-heteroacenes have experienced a revival in interest over the last couple of years. The first reports of their synthesis (diaz- and tetraazatetracenes) go back to the end of the 19th and the beginning of the 20th centuries.<sup>2</sup> These azaacenes of different size were obtained by comelting of aromatic diols with aromatic *o*-diamines. Much later, Leete and Zimmermann described oligoazapentacenes, which they obtained by the oxidation of *N,N'*-dihydroazapentacenes.<sup>3</sup> Until 2003, when Nuckolls and Miao demonstrated the hole-transporting properties of an *N,N'*-dihydrodiazapentacene, azaacenes were a backwater of organic chemistry.<sup>4</sup> Our own interest in this area was first aroused by the ambivalent aromatic/antiaromatic character of the *N*-acenes and their *N,N'*-dihydro derivatives.<sup>5</sup> Since then, a more systematic exploitation of this area of heterocyclic chemistry has been undertaken by us and others, and some tetraazapentacenes are now powerful electron-transporting materials for organic thin-film transistors.<sup>6</sup> Consequently, there is a drive to expand the structural diversity of the available larger *N*-heteroacenes to have access to a variety of substituted derivatives. One structurally particularly attractive class, as already described theoretically, are fluorinated *N*-heteroacene derivatives. Fluorine substituents are of particular interest because of solid-state packing effects and competing  $-I/+M$  effects.<sup>7–9</sup> This ambivalent character does not only influence the orbital energies. It also shows a distinct impact on the intensity and polarization of absorption bands dependent on the position of the substituents.<sup>10,11</sup> Although fluorination is a common

strategy to design *n*-type organic semiconductors, only Zhang's fluorinated azapentacene and Piers' perfluorinated *N*-phenyl-*N,N'*-dihydrophenazine are known members of the fluorinated azaacenes.<sup>12,13</sup> The latter heterocycle was an unwanted side product formed by a double nucleophilic aromatic substitution in hexafluorobenzene. We envisioned a modular synthesis of partially fluorinated *N*-heteroacenes by coupling *o*-diaminoarenes with perfluoroarenes in the presence of a strong base to give novel partially fluorinated *N,N'*-dihydrodiazacenes in one step to provide structural diversity for the design of new optoelectronic materials.

## RESULTS AND DISCUSSION

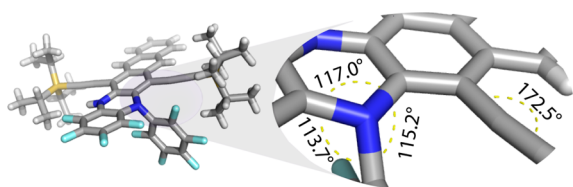
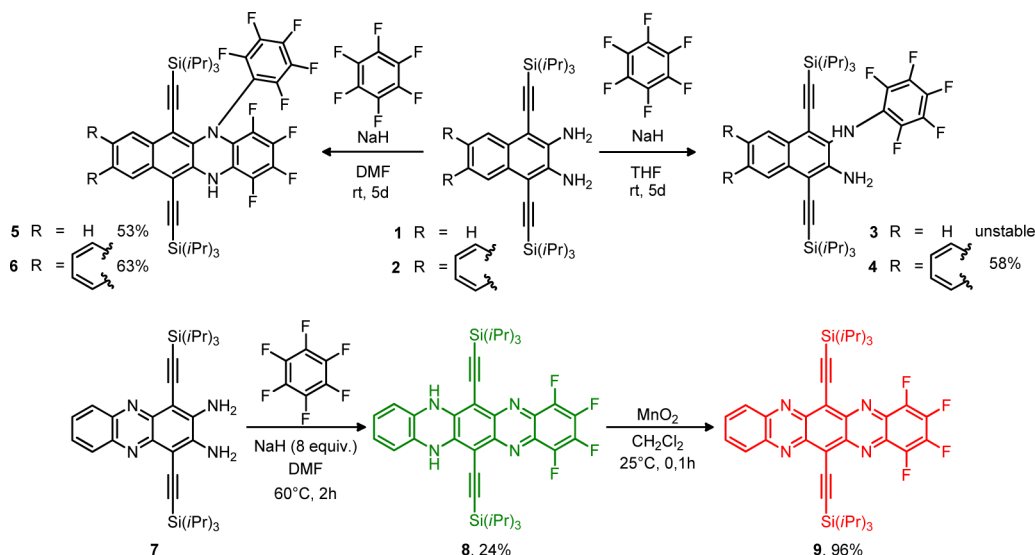
We treated the *o*-diamines **1** and **2** with hexafluorobenzene in the presence of NaH. Depending upon the solvent (DMF or THF), we obtained either the ring-closed heteroacenes **5** and **6** or the open, singly perfluorophenylated species **3** and **4**, respectively (Scheme 1). As we were not able to assign an unambiguous structure to **6**, a single-crystal X-ray structure of suitable specimen of **6** was obtained (Figure 1). The steric influence of the TIPS group forces the pentafluorophenyl group to bend out of plane.

While these results were promising, they were not what we wanted. Only when we employed diaminophenazine **7** as the starting material and reacted it with an equimolar amount of hexafluorobenzene in the presence of a 6-fold excess of NaH at 60 °C, did we isolate the desired coupling product **8** in 31% yield after chromatography and crystallization. As large amounts of black tarry materials also formed, we assume that

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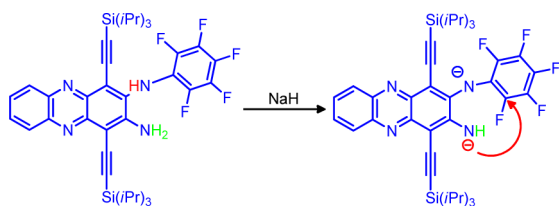
## Scheme 1. Nucleophilic Amination of Hexafluorobenzene To Form Dihydroazaacenes

Figure 1. Crystal structure of the *N*-phenylated dihydroazaacene 6.

the fluoride ion (a cofomed byproduct) desilylates the alkyne groups, giving rise to species that decompose under uncontrolled polymerization. For that reason, the best yields were achieved after 90 min, when consumption of 7 was not complete. Applying this procedure to 1 or 2 showed no success. In that case, only decomposition of the starting material was observed. The position of the NH groups in 8 is unexpected but supported by an X-ray crystal structure and theoretical studies, which identified 8 to be 4.64 kJ/mol more stable than the tautomer *iso*-8 (see the Supporting Information).

We assume that the ring closure of 7 into 8 is well feasible, as the amino groups in 7 are more acidic than those in 1 or 2, and therefore, perhaps the dianion of 7 forms and directly closes into the six-membered ring. Alternatively, the intermediate *N*-pentafluorophenylated derivative of 7 could be bis-deprotonated (Scheme 2), with the negative charge shown in blue

## Scheme 2. Reactivity Differences in the Anions



being sufficiently stabilized by both the phenazine and the pentafluorophenyl substituent that it is not able anymore to react with further hexafluorobenzene. Instead, the negative charge shown in red closes the ring, and the product tautomerizes into 8. Oxidation of 8 with MnO<sub>2</sub> then furnishes the tetrafluorotetraazacene 9 in excellent yield.

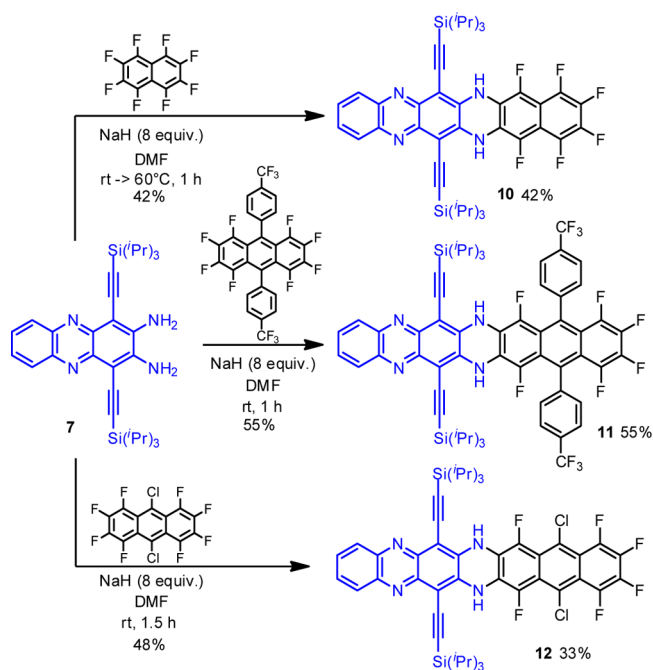
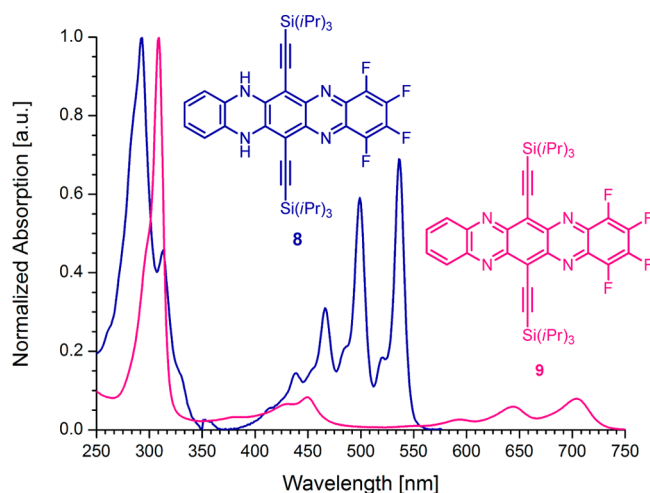
Scheme 3. Synthesis of *N,N'*-Dihydroheteroacenes 10–12 by Reaction of 7 with Larger Highly Fluorinated Arenes

Figure 2 depicts the absorption spectra of 8 and 9. The NH compound shows absorption at around 530 nm, while the oxidized tetraazapentacene displays a  $\lambda_{\text{max}}$  at around 710 nm, as expected for a pentacene derivative. In comparison with its nonfluorinated derivative, 9 shows a 24 nm red shift of the optical onset. The LUMO is more strongly affected by the electronegative fluorine substituents, as it is located on the acene core. In contrast, the HOMO is mainly located along the alkyne axes (Figure 3). Besides this red shift, the absorption spectra of 9 and the nonfluorinated derivative are similar in position and intensity (see the Supporting Information). In electrochemical experiments, azaacene 9 is easily reduced; according to cyclic voltammetry (CV), its first reduction potential occurs at  $-0.7$  V vs the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple, and a second reversible reduction occurs at  $-1.2$  V

Table 1. Experimentally and Computationally Determined Electronic Properties of 9

$E_{1/2}^{0/-}$ (V)	$E_{1/2}^{-1/2}$ (V)	$E_{\text{LUMO}}$ (eV)	$E_{\text{HOMO}}$ (eV)	opt. gap (eV)	HOMO–LUMO gap (eV)	theor. $E_{\text{HOMO}}$ (eV)	theor. $E_{\text{LUMO}}$ (eV)
$-0.7^a$	$-1.2^a$	$-4.1^b$	$-5.9^c$	$1.8^d$	$1.7^e$	$-5.9^e$	$-4.2^e$

<sup>a</sup>Cyclic voltammograms were recorded in THF using a Pt working electrode and  $\text{Bu}_4\text{NPF}_6$ . <sup>b</sup> $E_{\text{LUMO}}$  (in eV) =  $-4.8 \text{ eV} - (E_{1/2}^{0/-})$ . <sup>c</sup> $E_{\text{HOMO}}$  (in eV) =  $E_{\text{LUMO}}$  (in eV) –  $[\lambda_{\text{max}} \text{ (in eV)}]$ . <sup>d</sup>Gap obtained from the  $\lambda_{\text{max}}$  of the absorption in hexane. <sup>e</sup>Obtained by SPARTAN'10/Windows using DFT calculations with the B3LYP functional and the 6-311++G\*\* basis set. Calculations were run on molecules in which the TIPS groups were substituted with TMS groups.

Figure 2. Absorption spectra of 8 and 9 in *n*-hexane.

vs  $\text{Fc}/\text{Fc}^+$ . The calculated LUMO is at  $-4.2 \text{ eV}$  and the one extracted from the electrochemical measurements is at  $-4.1 \text{ eV}$  (Table 1), showing the calculations to give a good estimation of the electronic properties of 9.

An important issue for the potential usefulness of compounds such as 9 in organic thin-film transistors is their solid-state structure. The ORTEP model of 9 in Figure 4 shows that the molecular structure resolved from X-ray studies has an inversion center, where no distinction is made between the perfluorinated and nonfluorinated outer benzene rings. The perfluorinated moiety cannot be assigned periodically to one side of the acene core. Consequently, the fluorine substituents are disordered in the brick-wall solid-state structure. This is unusual, as the perfluorobenzene rings are considerably more electron-poor than the unsubstituted ones and one would expect a brick-wall stacking of 9 with a regular ABAB-type arrangement of the fluorinated and nonfluorinated outer rings.

The disordered molecules of 9, however, are arranged in a classic brick-wall motif similar to that of the unsubstituted bisalkynylated tetraazapentacene.<sup>14</sup> In this structure, the molecules pack parallel, and the  $\pi$  faces are  $3.33 \text{ \AA}$  apart from each other (i.e., considerably closer than the van der Waals radius).

To extend the synthetic aspects of the delivery of fluorinated arenes to our diaminophenazine 7, we attempted reactions with 1,2,4,5-tetrafluorobenzol and with hexachlorobenzene under otherwise identical reaction conditions. Alas, we could not find the formation of the desired coupling products. Only when we employed larger, highly fluorinated or perfluorinated arenes such as perfluoronaphthalene we could induce reaction with metalated 7 (Scheme 3).<sup>15</sup> The  $N,N'$ -dihydroacenes 10–12 were isolated in yields between 33% and 55% as orange crystalline materials after chromatography and crystallization. These are all derivatives of  $N,N'$ -dihydrotetraazaheptacenes and  $N,N'$ -dihydrotetraazaheptacenes. Attempts to couple either 9 or 10 to a second molecule of lithiated 7 did not work; instead, reduction was observed for 9 and the starting materials were reisolated in the case of 10. As compound 10 was nicely crystalline, we obtained a single-crystal structure (Figure 5). The molecules are stacked on top of each other with a small interlayer distance of only  $3.29 \text{ \AA}$  (space group:  $P1$ ). They assume the typical brick-wall motif that is common to most but not all of the larger TIPS-ethynyl-substituted acenes and heteroacenes. In contrast, 11 forms pairwise-arranged one-dimensional stacks in the solid state (Figure 6) with an intralayer distance of  $3.33 \text{ \AA}$  and a strong lateral displacement (see the Supporting Information). These dimers form a zigzag pattern in which they are isolated (space group:  $P21/c$ ). We assume that this is due to the introduction of the trifluorotolyl substituents, strengthening the side-chain interactions within the dimer stacks.

Attempts to oxidize 10 into the heteroacene (Scheme 4) led to the unsymmetrical dimer 13. NMR data and UV–vis

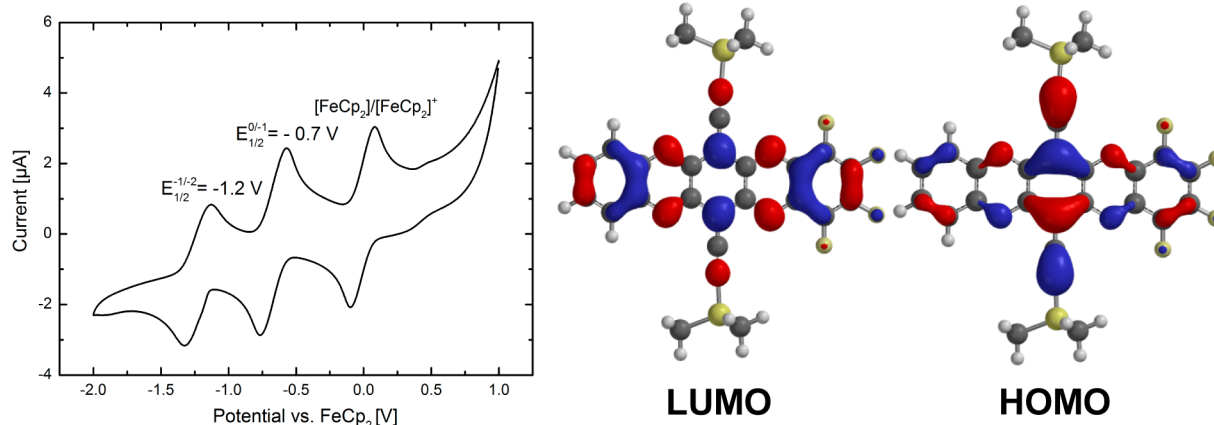
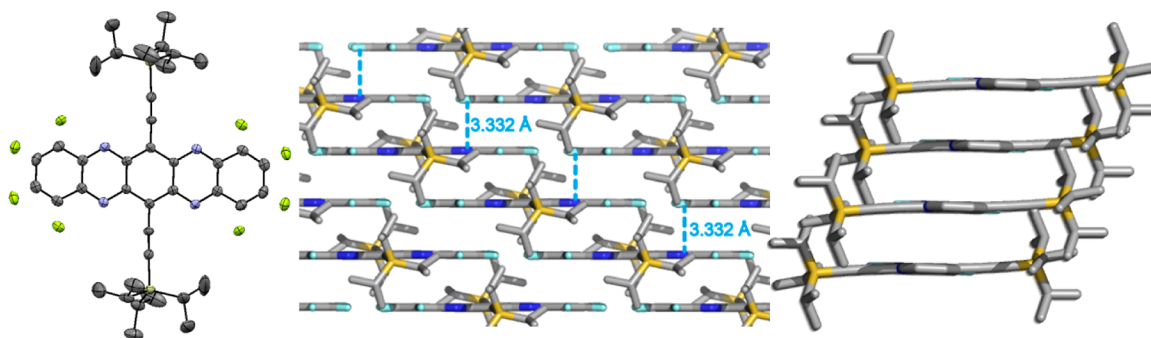
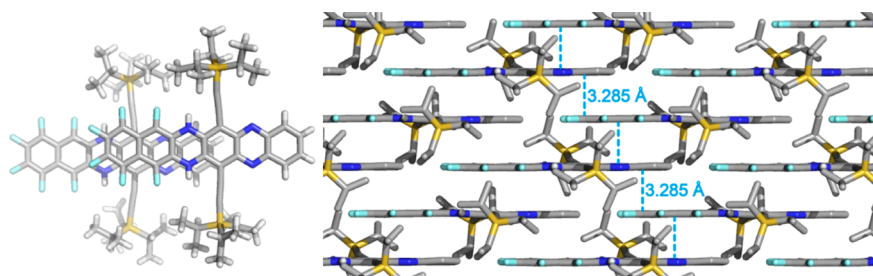


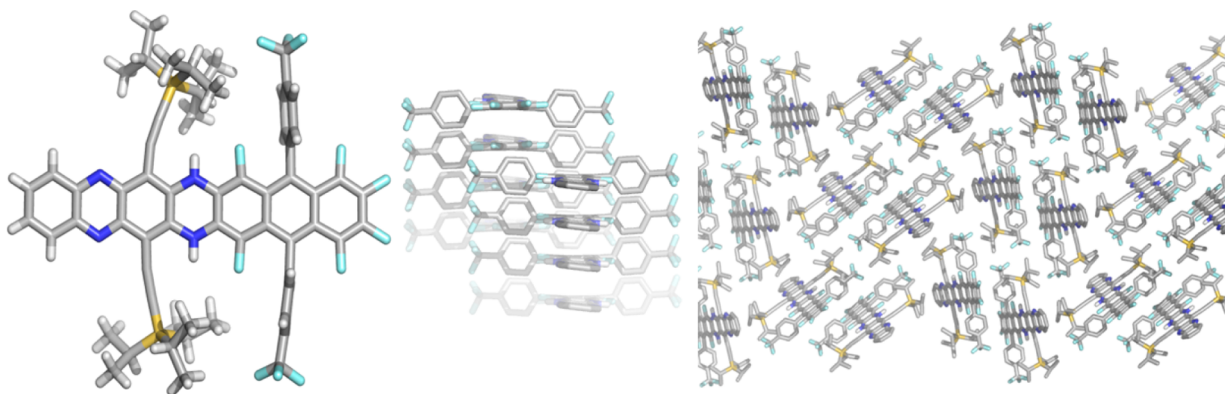
Figure 3. Cyclic voltammogram of 9 (left) and the frontier molecular orbitals of 9' (right).



**Figure 4.** Brick-wall-like disordered packing of **9** with an interlayer distance of 3.332 Å [cell parameters of **9**:  $a = 7.646(2)$  Å,  $b = 7.673(2)$  Å,  $c = 16.941(4)$  Å,  $\alpha = 89.462(5)^\circ$ ,  $\beta = 78.563(5)^\circ$ ,  $\gamma = 84.127(5)^\circ$ ,  $V = 969.0(4)$  Å<sup>3</sup>; cell parameters of nonfluorinated tetrazaacene:  $a = 7.533(2)$  Å,  $b = 7.570(2)$  Å,  $c = 16.802(3)$  Å,  $\alpha = 89.74(1)^\circ$ ,  $\beta = 79.12(1)^\circ$ ,  $\gamma = 82.49(1)^\circ$ ,  $V = 932.5(4)$  Å<sup>3</sup>].<sup>9</sup>

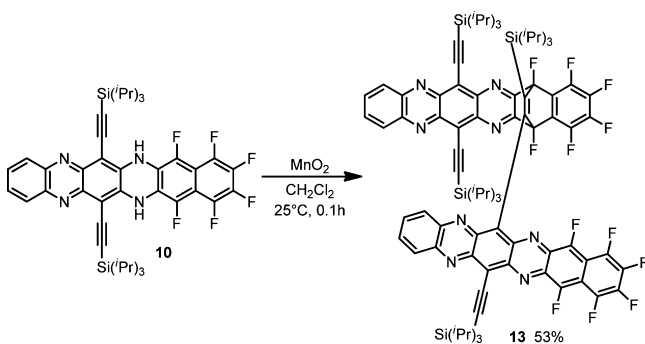


**Figure 5.** Crystal structure and packing arrangement of **10**.



**Figure 6.** Crystal structure and packing arrangement of **11**.

#### Scheme 4. Oxidative Dimerization of **10**



spectroscopy implied a Diels–Alder adduct as the only product of this oxidation (see the Supporting Information). The prominent  $\lambda_{\max}$  at 820 nm (Figure 7) is strongly suggestive that an intact tetraazahexacene unit is present in the molecule. Also, **13** is easily reduced ( $-0.5$  V vs Fc/Fc<sup>+</sup>) according to CV

(Figure 7). With that, the reduction of the intact tetraazahexacene core is quite facile. Unfortunately, we could not obtain any defined products from the oxidation of the *N,N'*-dihydrotetrazaheptacene derivatives **11** and **12**. Instead, when attempting to work up the oxidation reactions, dozens of compounds must have formed according to thin-layer chromatography.

#### CONCLUSIONS

Hexafluorobenzene, octafluoronaphthalene, and octafluoro derivatives of anthracene react with the lithiated diaminophenazine **7** producing *N,N'*-dihydrotetraazapentacenes, -hexacenes, and -heptacenes in one step and reasonably good yields as the only isolable products. Interestingly, only the 2,3-addition products formed in the case of the naphthalene and anthracene derivatives, perhaps because of steric hindrance and/or electronic effects. Both the *N,N'*-dihydrotetraazapentacene and -hexacene could be oxidized. While the former one, **9**, is stable, the latter one undergoes a Diels–Alder reaction in



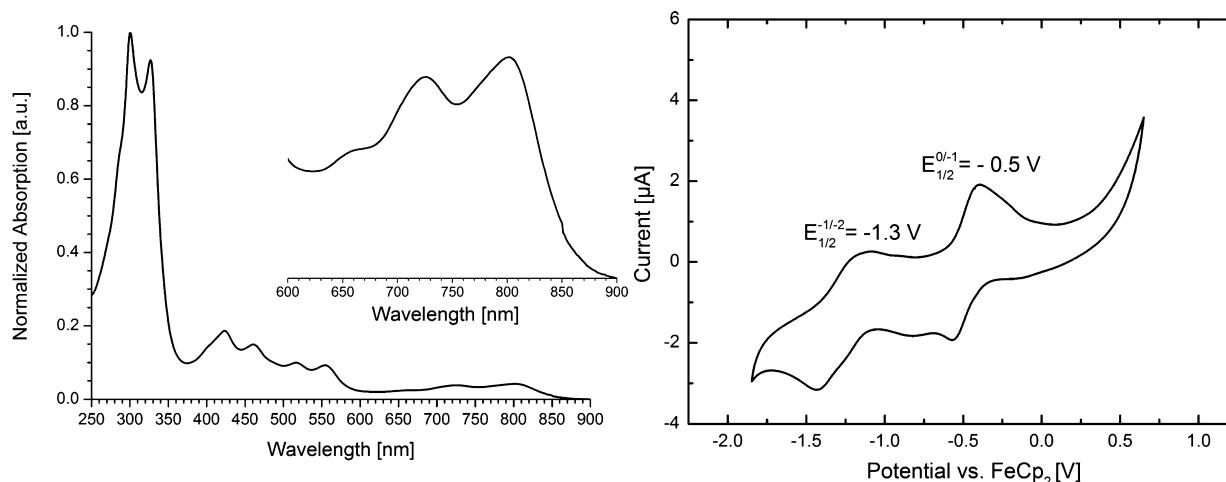


Figure 7. Absorption spectra and reduction characteristics of dimer 13.

which one of the TIPS-ethynyl groups acts as the dienophile and one hexacene unit as the diene to give stable 13.

Overall this reaction allows the rapid construction of *N,N*-dihydrotetraazapentacene and -heptacene cores by a simple one-step reaction without transition-metal catalysis. The highly activated large fluorinated arenes, which are commercially available, represent a significant part of the target molecules; therefore, despite the only moderate to good yields, this approach is powerful in its simplicity. Our method provides access to tetraazaacenes with hitherto-unavailable substitution patterns in synthetically useful amounts. In the future we will further explore this chemistry and report about the electrical characterization of these fascinating materials.

## EXPERIMENTAL SECTION

Reagents and solvents were obtained from commercial suppliers and were used without further purification, unless otherwise noted. THF 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. Functionalized diamionaphthalene 1, anthracene 2, and -phenazine 7 were prepared as reported previously.<sup>1,16</sup> Column chromatography was performed on silica gel (particle size: 0.04–0.063 mm) using mixtures of dichloromethane and petroleum ether or toluene and petroleum ether. Melting points were determined with a melting point apparatus and are uncorrected. <sup>1</sup>H NMR spectra were recorded on a 300, 500, or 600 MHz spectrometer, <sup>19</sup>F NMR spectra on a 282 or 471 MHz spectrometer, and <sup>13</sup>C NMR spectra on a 125 MHz spectrometer. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) relative to traces of CDCl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub>, toluene-*d*<sub>8</sub>, THF-*d*<sub>8</sub>, or C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> accordingly in the corresponding deuterated solvent.<sup>17</sup> MS spectra were recorded using matrix-assisted laser desorption/ionization or electrospray ionization methods with detection by FT-ICR techniques. Crystal structure analysis was accomplished using diffractometers with Mo *K* $\alpha$  radiation. Infrared (IR) spectra are reported in wavenumbers (cm<sup>-1</sup>) and were recorded in the solid state. Absorption spectra and emission spectra were recorded in hexane. Cyclic voltammetry was performed in dry and degassed THF using Bu<sub>4</sub>NPF<sub>6</sub> as the conducting salt.

**General Procedure 1 (GP1) for the Synthesis of Compounds 4–6.** In an oven-dried Schlenk tube under an atmosphere of argon, a mixture of *o*-diamino compound (193  $\mu$ mol), and hexafluorobenzene (578  $\mu$ mol, 3 equiv) was dissolved in dry DMF or THF (1 mL). After the mixture was cooled to 0 °C, sodium hydride (1.16  $\mu$ mol, 6 equiv) was added portionwise. The mixture was stirred for 5 days at room temperature. At this point, the reaction was quenched with aqueous NH<sub>4</sub>Cl (1 mL), and the mixture was extracted with diethyl ether (20 mL). Subsequently, the combined organic layers were washed with

aqueous NH<sub>4</sub>Cl (20 mL) and brine (5 mL). After drying over Na<sub>2</sub>SO<sub>4</sub> and evaporation under reduced pressure, flash column chromatography (silica gel, petroleum ether/dichloromethane) gave the clean product.

*N*-(Pentafluorophenyl)-1,4-bis[(tripropan-2-ylsilyl)ethynyl]anthracene-2,3-diamine (4). GP1 was carried out with diaminoanthracene 2 in dry THF. The clean product 4 was obtained in a yield of 58% (82.6 mg, 112  $\mu$ mol) as a bright-yellow solid. *R*<sub>f</sub> = 0.44 (PE/EE = 9:1); mp >158 °C (decomp.). <sup>1</sup>H NMR (500.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$  8.81 (s, 1H), 8.66 (s, 1H), 7.90–7.96 (m, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 5.73 (s, 1H), 4.99 (s, 1H), 1.28–1.24 (m, 21H), 1.16–1.12 (m, 21H). <sup>19</sup>F NMR (282.76 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$  -157.21 to -157.08 (m, 2F), -164.88 (td, *J* = 20.8 Hz, 3.9 Hz, 2F), -170.02 (tt, *J* = 21.5 Hz, 5.2 Hz, 1F). <sup>13</sup>C{<sup>1</sup>H, <sup>19</sup>F} NMR (125.76 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$  145.3, 138.9, 138.5, 135.3, 133.0, 132.8, 132.2, 130.8, 130.5, 128.6, 128.0, 126.9, 126.5, 126.0, 125.3, 122.8, 121.5, 117.7, 114.1, 106.3, 104.2, 102.2, 100.9, 100.2, 19.0, 18.7, 11.8, 11.7. IR  $\nu$  (cm<sup>-1</sup>): 3486, 3376, 3053, 2941, 2890, 2864, 2134, 1601, 1517. UV–vis (hexane):  $\lambda_{\text{max}}$  = 446 nm,  $\epsilon$ (446 nm) = 10590 L·mol<sup>-1</sup>·cm<sup>-1</sup>. Fluorescence (hexane):  $\lambda_{\text{max}}$  = 654 nm. HR-ESI (FT-ICR) *m/z*: calcd for C<sub>42</sub>H<sub>52</sub>F<sub>5</sub>N<sub>2</sub>Si<sub>2</sub> [M + H]<sup>+</sup> 735.35837, found 735.35832 with correct isotope distribution.

1,2,3,4-Tetrafluoro-5-(pentafluorophenyl)-6,11-bis[(tripropan-2-ylsilyl)ethynyl]-5,12-dihydrobenzo[*b*]phenazine (5). GP1 was carried out with *o*-diamionaphthalene 1 in dry DMF. The clean product 5 was obtained in a yield of 53% (85.5 mg, 102  $\mu$ mol) as a bright-yellow solid. *R*<sub>f</sub> = 0.76 (PE/EE = 9:1); mp 187 °C. <sup>1</sup>H NMR (600.24 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  8.20 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.15–7.13 (bs, 1H), 1.25–1.21 (bs, 21H), 1.18–1.14 (bs, 21H). <sup>19</sup>F NMR (470.59 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  -137.35 (dd, *J* = 32.7 Hz, 20.3 Hz, 2F), -152.46 to -150.71 (m, 1F), -153.87 (t, *J* = 21.6 Hz, 1F), -161.38 (t, *J* = 20.1 Hz, 2F), -161.5 (t, *J* = 21.9 Hz, 1F), -164.63 (dt, *J* = 21.6 Hz, 6.2 Hz, 1F), -168.96 (td, *J* = 21.5 Hz, 4.9 Hz, 1F). <sup>13</sup>C{<sup>1</sup>H, <sup>19</sup>F} NMR (125.76 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  147.7, 141.9, 141.1, 138.7, 138.0, 137.6, 135.8, 134.7, 133.7, 131.4, 131.0, 127.8, 126.7, 125.5, 125.1, 122.6, 121.6, 117.5, 113.8, 108.3, 106.3, 102.7, 99.3, 99.1, 18.9, 18.7, 11.8, 11.4. IR  $\nu$  (cm<sup>-1</sup>): 3387, 3065, 2942, 2893, 2865, 2139, 1503. UV–vis (hexane):  $\lambda_{\text{max}}$  = 412 nm,  $\epsilon$ (412 nm) = 8402 L·mol<sup>-1</sup>·cm<sup>-1</sup>. Fluorescence (hexane):  $\lambda_{\text{max}}$  = 616 nm. HR-ESI (FT-ICR) *m/z*: calcd for C<sub>44</sub>H<sub>48</sub>F<sub>9</sub>N<sub>2</sub>Si<sub>2</sub> [M]<sup>+</sup> 831.32068, found 831.32201 with correct isotope distribution. Elemental analysis: calcd for C<sub>44</sub>H<sub>48</sub>F<sub>9</sub>N<sub>2</sub>Si<sub>2</sub> C 63.82, H 5.70, N 3.37; found C 63.59, H 5.89, N 3.16.

1,2,3,4-Tetrafluoro-5-(pentafluorophenyl)-6,13-bis[(tripropan-2-ylsilyl)ethynyl]-5,14-dihydronaphtho[2,3-*b*]phenazine (6). GP1 was carried out with *o*-diaminoanthracene 2 in dry DMF. The clean product 6 was obtained in a yield of 63% (107 mg, 122  $\mu$ mol) as a brown solid. *R*<sub>f</sub> = 0.74 (PE/EE = 9:1); mp >288 °C (decomp.). <sup>1</sup>H NMR (600.24 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$  8.80 (s, 1H), 8.56 (s, 1H),

7.91 (d,  $J = 8.3$  Hz, 1H), 7.85 (d,  $J = 8.3$  Hz, 1H), 7.47 (t,  $J = 7.4$  Hz, 1H), 7.43 (t,  $J = 7.4$  Hz, 1H), 7.33 (s, 1H), 1.31–1.26 (m, 21H), 1.25–1.20 (m, 21H).  $^{19}\text{F}$  NMR (282.76 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C):  $\delta$  -137.88 to -138.18 (m, 1F), -151.59 to -151.96 (m, 1F), -154.47 to -154.67 (m, 1F), -162.05 to -162.29 (m, 2F), -162.67 (t,  $J = 21.5$  Hz, 1F), -165.02 (ddd,  $J = 22.1$  Hz, 7.8 Hz, 5.2 Hz, 1F), -170.12 (td,  $J = 21.5$  Hz, 5.1 Hz, 1F).  $^{13}\text{C}\{^1\text{H}, ^{19}\text{F}\}$  NMR (125.76 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C):  $\delta$  147.9, 142.3, 141.1, 138.9, 138.3, 137.4, 136.1, 135.1, 134.9, 133.0, 131.7, 129.4, 129.2, 128.6, 128.0, 126.9, 126.2, 126.1, 123.5, 121.9, 121.5, 117.5, 112.8, 109.4, 107.1, 101.2, 99.8, 99.7, 19.0, 18.9, 12.1, 11.7. UV-vis (hexane):  $\lambda_{\text{max}} = 465$  nm,  $\epsilon(465 \text{ nm}) = 11477 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ . Fluorescence (hexane):  $\lambda_{\text{max}} = 638$  nm. IR  $\nu$  ( $\text{cm}^{-1}$ ): 3384, 3054, 2943, 2892, 2864, 2138, 1511. HR-ESI (FT-ICR)  $m/z$ : calcd for  $\text{C}_{48}\text{H}_{50}\text{F}_9\text{N}_2\text{Si}_2$   $[\text{M} + \text{H}]^+$  881.33825, found 881.33633. Elemental analysis: calcd for  $\text{C}_{48}\text{H}_{49}\text{F}_9\text{N}_2\text{Si}_2$  C 65.43, H 5.61, N 3.18; found C 65.58, H 5.82, N 2.96. Crystal data: yellow crystal (needle), dimensions 0.42 mm  $\times$  0.13 mm  $\times$  0.08 mm, crystal system triclinic, space group  $P\bar{1}$ ,  $Z = 2$ ,  $a = 8.6544(9)$  Å,  $b = 12.7016(13)$  Å,  $c = 21.437(2)$  Å,  $\alpha = 100.096(2)^\circ$ ,  $\beta = 96.605(2)^\circ$ ,  $\gamma = 103.513(2)^\circ$ ,  $V = 2225.6(4)$  Å<sup>3</sup>,  $\rho = 1.315 \text{ g}\cdot\text{cm}^{-3}$ ,  $T = 200(2)$  K,  $\Theta_{\text{max}} = 26.37^\circ$ , 26783 reflections measured, 9082 unique ( $R_{\text{int}} = 0.0481$ ), 5765 observed [ $I > 2\sigma(I)$ ],  $\mu = 0.15 \text{ mm}^{-1}$ ,  $T_{\text{min}} = 0.94$ ,  $T_{\text{max}} = 0.99$ , 550 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.03 for observed reflections, final residual values  $R_1(F) = 0.055$ ,  $wR(F^2) = 0.120$  for observed reflections, residual electron density -0.49 to 0.71 e/Å<sup>3</sup>.

**8,9,10,11-Tetrafluoro-6,13-bis[(tripropan-2-ylsilyl)ethynyl]-5,14-dihydroquinoxalino[2,3-*b*]phenazine (8).** In an oven-dried Schlenk tube under an atmosphere of argon, a mixture of *o*-diaminophenazine 7 (1.00 g, 1.75 mmol) and hexafluorobenzene (326 mg, 1.75 mmol, 1 equiv) was dissolved in dry DMF (10 mL). After the mixture was cooled to 0 °C, sodium hydride (340 mg, 14.2 mmol, 8 equiv) was added portionwise. Subsequently, the mixture was stirred at 60 °C for 90 min. When no further consumption was indicated by TLC (9:1 petroleum ether/ethyl acetate), the reaction was quenched with aqueous  $\text{NH}_4\text{Cl}$  (20 mL), and the mixture was extracted with diethyl ether (300 mL). Subsequently, the combined organic layers were washed with aqueous  $\text{NH}_4\text{Cl}$  (100 mL) and brine (50 mL). After drying over  $\text{Na}_2\text{SO}_4$  and evaporation under reduced pressure, flash column chromatography (silica gel, petroleum ether/dichloromethane) gave the clean product 8 (25% [corrected yield 31%], 319 mg, 445  $\mu\text{mol}$ ) as a red solid with a golden luster and the reisolated starting material 7 (184 mg, 322  $\mu\text{mol}$ ).  $R_f = 0.56$  (PE/EE = 9:1); mp >320 °C (decomp.).  $^1\text{H}$  NMR (300.51 MHz,  $\text{THF}-d_8$ , 25 °C):  $\delta$  7.65 (s, 2H), 6.85–6.78 (m, 2H), 6.70–6.63 (m, 2H), 1.27–1.24 (m, 42H).  $^{19}\text{F}$  NMR (470.59 MHz,  $\text{THF}-d_8$ , 25 °C):  $\delta$  -157.28 to -157.36 (m, 2F), -162.76 to -162.83 (m, 2F).  $^{13}\text{C}\{^1\text{H}, ^{19}\text{F}\}$  NMR (125.76 MHz,  $\text{THF}-d_8$ , 25 °C):  $\delta$  145.5, 141.8, 141.0, 140.3, 129.7, 128.7, 124.5, 115.4, 104.8, 99.6, 96.8, 19.0, 12.2. UV-vis (hexane):  $\lambda_{\text{max}} = 536$  nm,  $\epsilon(536 \text{ nm}) = 48017 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ . IR  $\nu$  ( $\text{cm}^{-1}$ ): 3373, 2923, 2141, 1458, 1458, 1434. Fluorescence (hexane):  $\lambda_{\text{max}} = 503$  nm. HR-ESI (FT-ICR)  $m/z$ : calcd for  $\text{C}_{40}\text{H}_{49}\text{F}_4\text{N}_4\text{Si}_2$   $[\text{M} + \text{H}]^+$  717.34264, found 717.34287 with correct isotope distribution. Elemental analysis: calcd for  $\text{C}_{40}\text{H}_{48}\text{F}_4\text{N}_4\text{Si}_2$  C 67.01, H 6.75, N 7.81; found C 66.44, H 6.79, N 7.59. Crystal data: gold crystal (needle), dimensions 0.41 mm  $\times$  0.05 mm  $\times$  0.04 mm, crystal system triclinic, space group  $P1$ ,  $Z = 1$ ,  $a = 7.5628(5)$  Å,  $b = 7.6610(6)$  Å,  $c = 17.1065(13)$  Å,  $\alpha = 89.004(2)^\circ$ ,  $\beta = 78.407(2)^\circ$ ,  $\gamma = 85.986(2)^\circ$ ,  $V = 968.52(12)$  Å<sup>3</sup>,  $\rho = 1.229 \text{ g}\cdot\text{cm}^{-3}$ ,  $T = 220(2)$  K,  $\Theta_{\text{max}} = 24.71^\circ$ , 13162 reflections measured, 6412 unique ( $R_{\text{int}} = 0.1405$ ), 4192 observed [ $I > 2\sigma(I)$ ],  $\mu = 0.14 \text{ mm}^{-1}$ ,  $T_{\text{min}} = 0.94$ ,  $T_{\text{max}} = 0.99$ , 479 parameters refined, hydrogen atoms were treated using appropriate riding models, Flack absolute structure parameter 0.5(2), goodness of fit 0.97 for observed reflections, final residual values  $R_1(F) = 0.082$ ,  $wR(F^2) = 0.187$  for observed reflections, residual electron density -0.35 to 0.33 e/Å<sup>3</sup>.

**1,2,3,4-Tetrafluoro-6,13-bis[(tripropan-2-ylsilyl)ethynyl]-quinoxalino[2,3-*b*]phenazine (9).** Starting material 8 (288 mg, 402  $\mu\text{mol}$ ) was dissolved in dichloromethane. An excess of  $\text{MnO}_2$  (1 g) was added to this solution. After 15 min, TLC (9:1 petroleum ether/ethyl acetate) showed full consumption. The solid  $\text{MnO}_2$  was removed

by filtration before evaporation of the solvent. The clean product 9 (92%, 265 mg, 371  $\mu\text{mol}$ ) was isolated as dark-green crystals by flash column chromatography (silica gel, petroleum ether/dichloromethane).  $R_f = 0.51$  (PE/EE = 9:1); mp >315 °C (decomp.).  $^1\text{H}$  NMR (300.51 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  8.17–8.10 (m, 2H), 7.82–7.76 (m, 2H), 1.30–1.25 (m, 2H).  $^{19}\text{F}$  NMR (470.59 MHz,  $\text{THF}-d_8$ , 25 °C):  $\delta$  -147.91 to -147.99 (m, 2F), -149.64 to -149.72 (m, 2F).  $^{13}\text{C}\{^1\text{H}, ^{19}\text{F}\}$  NMR (125.76 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  146.2, 143.6, 142.0, 141.7, 140.0, 133.3, 133.0, 130.8, 123.7, 114.9, 102.3, 19.0, 11.8. IR  $\nu$  ( $\text{cm}^{-1}$ ): 3066, 2942, 2893, 2863, 1458. UV-vis (hexane):  $\lambda_{\text{max}} = 704$  nm,  $\epsilon(704 \text{ nm}) = 16443 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ . HR-ESI (FT-ICR)  $m/z$ : calcd for  $\text{C}_{40}\text{H}_{47}\text{F}_4\text{N}_4\text{Si}_2$   $[\text{M} + \text{H}]^+$  715.32699, found 715.32854 with correct isotope distribution. Elemental analysis: calcd for  $\text{C}_{40}\text{H}_{46}\text{F}_4\text{N}_4\text{Si}_2$  C 67.19, H 6.48, N 7.84; found C 67.32, H 6.62, N 7.82. Crystal data: green crystal (plate), dimensions 0.14 mm  $\times$  0.13 mm  $\times$  0.06 mm, crystal system triclinic, space group  $P\bar{1}$ ,  $Z = 1$ ,  $a = 7.6461(17)$  Å,  $b = 7.6728(17)$  Å,  $c = 16.941(4)$  Å,  $\alpha = 89.462(5)^\circ$ ,  $\beta = 78.563(5)^\circ$ ,  $\gamma = 84.127(5)^\circ$ ,  $V = 969.0(4)$  Å<sup>3</sup>,  $\rho = 1.225 \text{ g}\cdot\text{cm}^{-3}$ ,  $T = 200(2)$  K,  $\Theta_{\text{max}} = 23.22^\circ$ , 9014 reflections measured, 2790 unique ( $R_{\text{int}} = 0.0530$ ), 1799 observed [ $I > 2\sigma(I)$ ],  $\mu = 0.14 \text{ mm}^{-1}$ ,  $T_{\text{min}} = 0.98$ ,  $T_{\text{max}} = 0.99$ , 244 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.06 for observed reflections, final residual values  $R_1(F) = 0.065$ ,  $wR(F^2) = 0.144$  for observed reflections, residual electron density -0.24 to 0.41 e/Å<sup>3</sup>.

**8,9,10,11,12,13-Hexafluoro-6,15-bis[(tripropan-2-ylsilyl)ethynyl]-7,14-dihydrobenzo[*b*]quinoxalino[2,3-*i*]phenazine (10).** In an oven-dried Schlenk tube under an atmosphere of argon, a mixture of *o*-diaminophenazine 7 (500 mg, 870  $\mu\text{mol}$ ) and perfluoronaphthalene (236 mg, 870  $\mu\text{mol}$ , 1 equiv) was dissolved in dry DMF (5 mL). After the mixture was cooled to 0 °C, sodium hydride (165 mg, 6.96 mmol, 8 equiv) was added portionwise. The mixture was stirred at room temperature for 30 min and subsequently at 60 °C for 30 min. When no further consumption was indicated by TLC (3:1 petroleum ether/dichloromethane), the reaction was quenched with aqueous  $\text{NH}_4\text{Cl}$  (20 mL), and the mixture was diluted with diethyl ether (20 mL). After extraction with dichloromethane (200 mL), the combined organic layers were washed with aqueous  $\text{NH}_4\text{Cl}$  (50 mL) and brine (30 mL). After drying over  $\text{Na}_2\text{SO}_4$  and evaporation under reduced pressure, flash column chromatography (silica gel, petroleum ether/dichloromethane) gave the clean product 10 (42%, 342 mg, 426  $\mu\text{mol}$ ) as brown crystals.  $R_f = 0.63$  (PE/EE = 9:1); mp >355 °C (decomp.).  $^1\text{H}$  NMR (500.13 MHz, toluene- $d_8$ , 353 K):  $\delta$  8.08–8.03 (m, 2H), 7.29–7.25 (m, 2H), 7.25–7.22 (bs, 2H), 1.36–1.31 (m, 42H).  $^{19}\text{F}$  NMR (470.59 MHz, toluene- $d_8$ , 353 K):  $\delta$  -148.75 to -148.96 (m, 2F), -151.21 to -151.43 (m, 2F), -159.51 to -159.61 (m, 2F).  $^{13}\text{C}\{^1\text{H}, ^{19}\text{F}\}$  NMR (125.76 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 393 K):  $\delta$  142.5, 142.3, 140.5, 138.0, 137.4, 135.1, 129.2, 129.0, 118.5, 107.2, 106.6, 101.7, 98.4, 18.6, 11.4. IR  $\nu$  ( $\text{cm}^{-1}$ ): 3375, 3057, 2942, 2892, 2863, 2145, 1664, 1575, 1479, 1442. UV-vis (hexane):  $\lambda_{\text{max}} = 486$  nm,  $\epsilon(486 \text{ nm}) = 53478 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ . Fluorescence (hexane):  $\lambda_{\text{max}} = 492$  nm. HR-ESI (FT-ICR)  $m/z$ : calcd for  $\text{C}_{44}\text{H}_{49}\text{F}_6\text{N}_4\text{Si}_2$   $[\text{M} + \text{H}]^+$  803.33945, found 803.34149 with correct isotope distribution. Elemental analysis: calcd for  $\text{C}_{44}\text{H}_{48}\text{F}_6\text{N}_4\text{Si}_2$  C 65.81, H 6.02, N 6.98; found C 65.68, H 6.23, N 6.38. Crystal data: brown crystal (plate), dimensions 0.11 mm  $\times$  0.10 mm  $\times$  0.02 mm, crystal system triclinic, space group  $P1$ ,  $Z = 2$ ,  $a = 7.7917(9)$  Å,  $b = 16.4403(19)$  Å,  $c = 17.186(2)$  Å,  $\alpha = 76.699(8)^\circ$ ,  $\beta = 89.404(9)^\circ$ ,  $\gamma = 84.780(8)^\circ$ ,  $V = 2133.5(4)$  Å<sup>3</sup>,  $\rho = 1.250 \text{ g}\cdot\text{cm}^{-3}$ ,  $T = 200(2)$  K,  $\Theta_{\text{max}} = 19.40^\circ$ , 11305 reflections measured, 5712 unique ( $R_{\text{int}} = 0.0865$ ), 2865 observed [ $I > 2\sigma(I)$ ],  $\mu = 0.14 \text{ mm}^{-1}$ ,  $T_{\text{min}} = 0.98$ ,  $T_{\text{max}} = 1.00$ , 1009 parameters refined, hydrogen atoms were treated using appropriate riding models, Flack absolute structure parameter 0.3(4), goodness of fit 1.02 for observed reflections, final residual values  $R_1(F) = 0.090$ ,  $wR(F^2) = 0.204$  for observed reflections, residual electron density -0.25 to 0.36 e/Å<sup>3</sup>.

**8,10,11,12,13,15-Hexafluoro-9,14-bis[4-(trifluoromethyl)phenyl]-6,17-bis[(tripropan-2-ylsilyl)ethynyl]-7,16-dihydronaphtho[2,3-*b*]quinoxalino[2,3-*i*]phenazine (11).** In an oven-dried Schlenk tube under an atmosphere of argon, a mixture of *o*-diaminophenazine 7 (100 mg, 175  $\mu\text{mol}$ ) and octafluoro-9,10-bis[4-

(trifluoromethyl)phenyl]anthracene (106 mg, 175  $\mu\text{mol}$ , 1 equiv) was dissolved in dry DMF (1 mL). After the mixture was cooled to 0 °C, sodium hydride (33.4 mg, 1.40 mmol, 8 equiv) was added portionwise. The reaction was stirred at room temperature for 2.5 h. When no further consumption was indicated by TLC (9:1 petroleum ether/ethyl acetate), the reaction was quenched with aqueous  $\text{NH}_4\text{Cl}$  (5 mL), and the mixture was extracted with dichloromethane (100 mL). The combined organic layers were washed with aqueous  $\text{NH}_4\text{Cl}$  (20 mL) and brine (10 mL). After drying over  $\text{Na}_2\text{SO}_4$  and evaporation under reduced pressure, flash column chromatography (silica gel, petroleum ether/dichloromethane) gave the clean product **11** (55%, 110 mg, 96.4  $\mu\text{mol}$ ) as an orange solid.  $R_f = 0.51$  (PE/EE = 9:1); mp >350 °C (decomp.).  $^1\text{H}$  NMR (500.13 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  8.02–7.98 (m, 2H), 7.73 (d,  $J = 8.0$  Hz, 4H), 7.66–7.62 (m, 2H), 7.54 (d,  $J = 8.0$  Hz, 4H), 7.52 (s, 2H), 1.14–1.08 (m, 42H).  $^{19}\text{F}$  NMR (470.59 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  –62.28 (s, 1F), –134.36 to –134.44 (m, 2F), –136.67 (s, 1F), –156.47 to –156.56 (m, 2F).  $^{13}\text{C}\{^1\text{H}, ^{19}\text{F}\}$  NMR (125.76 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 110 °C):  $\delta$  144.0, 142.5, 141.9, 139.7, 137.7, 134.7, 129.9, 129.2, 129.1, 129.0, 128.3, 124.2, 124.0, 119.2, 118.4, 117.7, 107.1, 101.8, 98.5, 18.4, 11.3. IR  $\nu$  ( $\text{cm}^{-1}$ ): 3361, 3060, 2944, 2890, 2866, 2127, 1443. UV–vis (hexane):  $\lambda_{\text{max}} = 507$  nm,  $\epsilon(507 \text{ nm}) = 45651 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ . Fluorescence (hexane):  $\lambda_{\text{max}} = 512$  nm. HR-ESI (FT-ICR)  $m/z$ : calcd for  $\text{C}_{62}\text{H}_{57}\text{F}_{12}\text{N}_4\text{Si}_2$  [ $\text{M} + \text{H}$ ] $^+$  1141.39247, found 1141.39588 with correct isotope distribution. Crystal data: orange crystal (needle), dimensions 0.250 mm  $\times$  0.030 mm  $\times$  0.020 mm, crystal system monoclinic, space group  $P21/c$ ,  $Z = 4$ ,  $a = 9.873(4)$  Å,  $b = 14.973(6)$  Å,  $c = 38.333(14)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 91.692(12)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 5664(4)$  Å $^3$ ,  $\rho = 1.338 \text{ g}/\text{cm}^3$ ,  $T = 200(2)$  K,  $\Theta_{\text{max}} = 19.587^\circ$ , 20734 reflections measured, 4979 unique ( $R_{\text{int}} = 0.1569$ ), 2393 observed [ $I > 2\sigma(I)$ ],  $\mu = 0.15 \text{ mm}^{-1}$ ,  $T_{\text{min}} = 0.75$ ,  $T_{\text{max}} = 0.96$ , 747 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.01 for observed reflections, final residual values  $R_1(F) = 0.073$ ,  $wR_2(F^2) = 0.176$  for observed reflections, residual electron density –0.33 to 0.34  $\text{e}/\text{Å}^3$ .

**9,14-Dichloro-8,10,11,12,13,15-hexafluoro-6,17-bis-[(tripropyl-2-ylsilyl)ethynyl]-7,16-dihydro naphtho[2,3-*b*]quinoxalino[2,3-*f*]phenazine (12).** In an oven-dried Schlenk tube under an atmosphere of argon, a mixture of *o*-diaminophenazine **7** (101 mg, 175  $\mu\text{mol}$ ) and 9,10-dichlorooctafluoroanthracene (65.0 mg, 175  $\mu\text{mol}$ , 1 equiv) was dissolved in dry DMF (1.5 mL). After the mixture was cooled to 0 °C, sodium hydride (33.5 mg, 1.40 mmol, 8 equiv) was added portionwise. At this point, the reaction was stirred at room temperature for 90 min. When no further consumption was indicated by TLC (9:1 petroleum ether/ethyl acetate), the reaction was quenched with aqueous  $\text{NH}_4\text{Cl}$  (5 mL), and the mixture was extracted with diethyl ether (100 mL). The combined organic layers were washed with aqueous  $\text{NH}_4\text{Cl}$  (20 mL) and brine (10 mL). After evaporation under reduced pressure, the crude product was washed with pentane. Finally, flash column chromatography (silica gel, petroleum ether/toluene) gave the clean product **12** (34%, 54 mg, 58.6  $\mu\text{mol}$ ) as a red solid.  $R_f = 0.88$  (PE/toluene = 7:3); mp >350 °C (decomp.).  $^1\text{H}$  NMR (500.13 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 393 K):  $\delta$  8.14–8.08 (m, 2H), 7.87–7.82 (bs, 2H), 7.76–7.70 (m, 2H), 1.40–1.36 (m, 42H).  $^{19}\text{F}$  NMR (470.59 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 393 K):  $\delta$  –136.79 to –136.87 (m, 2F), –140.10 (s, 1F), –154.33 to –154.43 (m, 2F). Because of insolubility, no  $^{13}\text{C}$  NMR data were recorded. IR  $\nu$  ( $\text{cm}^{-1}$ ): 3370, 3056, 2940, 2888, 2863, 2145, 1667, 1597, 1572, 1497, 1442. UV–vis (hexane):  $\lambda_{\text{max}} = 511$  nm,  $\epsilon(511 \text{ nm}) = 68966 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ . Fluorescence (hexane):  $\lambda_{\text{max}} = 520$  nm. HR-ESI (FT-ICR)  $m/z$ : calcd for  $\text{C}_{48}\text{H}_{49}\text{Cl}_2\text{F}_6\text{N}_4\text{Si}_2$  [ $\text{M} + \text{H}$ ] $^+$  921.27715, found 921.27839 with correct isotope distribution.

**8,9,10,11,12,13-Hexafluoro-17-[8,9,10,11,12,13-hexafluoro-15-[(tripropyl-2-ylsilyl)ethynyl]-7,14-dihydrobenzo[*b*]quinoxalino[2,3-*f*]phenazin-6-yl]-18-(tripropyl-2-ylsilyl)-6,15-bis[(tripropyl-2-ylsilyl)ethynyl]-8,13-dihydro-8,13-ethenobenzo[*b*]quinoxalino[2,3-*f*]phenazine (13).** Starting material **10** (97.7 mg, 122  $\mu\text{mol}$ ) was dissolved in dichloromethane (80 mL). An excess of  $\text{MnO}_2$  (1 g) was added to this solution. After 1 h, TLC (9:1 petroleum ether/ethyl acetate) showed full consumption of the dihydro compound **10**. Excess  $\text{MnO}_2$  was removed by filtration

through a pad of silica gel. After removal of the solvent under reduced pressure, the pure dimer **13** (53%, 97.7 mg, 122  $\mu\text{mol}$ ) was obtained as a moderately stable brown solid with a metallic luster by flash column chromatography (silica gel, petroleum ether/dichloromethane).  $R_f = 0.70$  (PE/EE = 9:1); mp >295 °C (decomp.).  $^1\text{H}$  NMR (500.13 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C):  $\delta$  8.39–8.35 (m, 1H), 8.32–8.27 (m, 1H), 8.17 (d,  $J = 8.9$  Hz, 1H), 8.01–7.96 (m, 2H), 7.90–7.85 (m, 1H), 7.85–7.80 (m, 1H), 7.57 (d,  $J = 8.9$  Hz, 1H), 1.46–1.35 (m, 42H), 0.74–0.53 (m, 42H).  $^{19}\text{F}$  NMR (470.59 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C):  $\delta$  –123.18 to –123.70 (m, 2F), –143.85 to –144.07 (m, 1F), –144.28 to –144.51 (m, 2F), –145.50 to –145.71 (m, 1F), –151.54 to –151.67 (m, 1F), –152.08 to –152.20 (m, 1F), 152.74 (t,  $J = 19.6$  Hz, 1F), 153.33 (t,  $J = 19.6$  Hz, 1F), –185.61 to –185.73 (m, 1F), –192.86 to –192.96 (m, 1F).  $^{13}\text{C}\{^1\text{H}, ^{19}\text{F}\}$  NMR (125.76 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C):  $\delta$  153.3, 153.2, 150.6, 150.0, 149.9, 147.4, 147.3, 147.1, 146.6, 145.2, 144.5, 143.5, 143.4, 143.3, 142.9, 142.3, 141.6, 141.0, 140.8, 140.8, 140.7, 140.6, 138.8, 138.4, 134.5, 134.2, 134.0, 133.6, 132.6, 132.5, 132.4, 131.5, 131.1, 130.6, 130.6, 130.5, 130.1, 129.9, 125.5, 123.5, 123.1, 121.3, 120.6, 120.5, 116.8, 110.7, 110.0, 109.8, 109.4, 103.0, 101.9, 101.6, 19.1, 19.1, 19.0, 19.0, 18.9, 18.3, 18.2. IR  $\nu$  ( $\text{cm}^{-1}$ ): 3064, 2941, 2889, 2866, 1677, 1563, 1499, 1461. UV–vis (hexane):  $\lambda_{\text{max}} = 783$  nm,  $\epsilon(563 \text{ nm}) = 6389 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ . HR-MALDI (FT-ICR)  $m/z$ : calcd for  $\text{C}_{88}\text{H}_{92}\text{F}_{12}\text{N}_8\text{Si}_4$  [ $\text{M}$ ] $^+$  1600.63249, found 1600.63066; calcd for  $\text{C}_{88}\text{H}_{94}\text{F}_{12}\text{N}_8\text{Si}_4$  [ $\text{M} - \text{H}_2$ ] $^+$  1602.64814, found 1602.64212; calcd for  $\text{C}_{44}\text{H}_{46}\text{F}_6\text{N}_4\text{Si}_2$  [ $\text{M}/2 - \text{H}$ ] $^+$  801.32365, found 801.32380.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

All general methods, absorption spectra, emission spectra,  $^1\text{H}$  and  $^{13}\text{C}$  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>.

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### Notes

The authors declare no competing financial interest.

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