JOC The Journal of Organic Chemistry

Article

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2-Bromotetraazapentacene and Its Functionalization by Pd(0)-Chemistry

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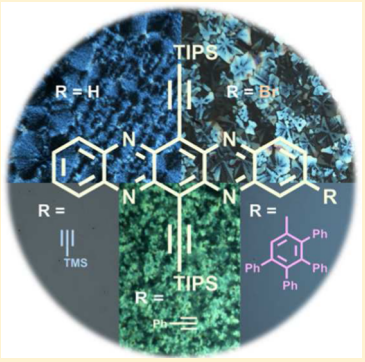
Supporting Information

ABSTRACT: We have synthesized a brominated *N,N′*-dihydrotetraazapentacene using a condensation route. Sonogashira reactions replace the Br-substituent by an alkynyl group, placed on the azaacene core. Sonogashira coupling of brominated dihydro tetraazapentacene $\mathbf{1H_2}$ with alkynes and subsequent oxidation afford several functionalized TIPS-tetraazapentacene derivatives with energetically stabilized FMOs. These TIPS-TAPs are either crystalline or amorphous, depending upon their substitution pattern.



INTRODUCTION

Here we describe the synthesis and characterization of substituted **TIPS-TAP**-derivatives and explore their properties. 6,13-Diethynyl-5,7,12,14-tetraazapentacene (**TIPS-TAP**), first synthesized in 2009,[1] is an excellent n-channel organic semiconductor (OSC) for organic field effect transistors (OFETs) (Figure 1); published electron mobilities reach 5.0 $cm^2\ V^{-1}\ s^{-1}$.[2]

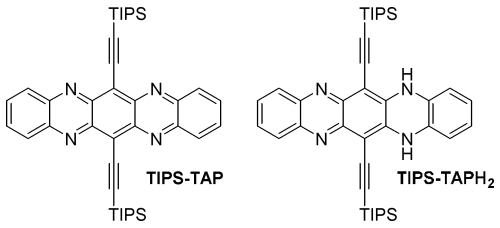


Figure 1. 6,13-Diethynyl-5,7,12,14-tetraazapentacene (**TIPS-TAP**) and its reduced *N,N′*-dihydro form $\mathbf{TIPS\text{-}TAPH_2}$.

In the following years, a number of large azaacenes were prepared by many methods, and their properties were investigated by different spectroscopic methods and by electrochemistry.[3−8] Azaacenes' performance in organic electronic devices and their capability for singlet fission were investigated.[2,9−13] To further tune the azaacenes' electrochemical properties, halogen atoms (F, Cl) were attached to their backbones.[14,15] Yet, with regard to potential applications as electroactive material, the parent, symmetrical bis-(triisopropylsilylethynyl)tetraazapentacene (**TIPS-TAP**) remains unchallenged in terms of stability and semiconductor performance.

While electronegative fluorine and chlorine substituents increase the electron affinity of arenes, the introduction of bromine or iodine atoms allows for further derivatization via Pd(0) chemistry. Halogenated azaacenes should be starting materials for a wide spectrum of new electron acceptors with tunable electronic properties and morphologies. For some advanced applications, breaking of the molecular symmetry may prove useful to control the materials microstructure; azaacenes might then be used as n-type materials in organic photovoltaics (OPV) or light emitting diodes (OLED), where π-interactions and the tendency to form large crystalline domains (present in most pentacene based materials) are generally harmful. Amorphous systems could allow better phase separation and processing and, in the case of OPV, therefore lead to improved charge separation.[16−18]

As **TIPS-TAP** is a superb small molecule n-channel material, we set out to prepare monobromo TIPS-TAP **1** and explore its substitution by Sonogashira cross-coupling reactions as well as the electrochemical and microstructural impact of the attachment of a substituent onto the TAP backbone.

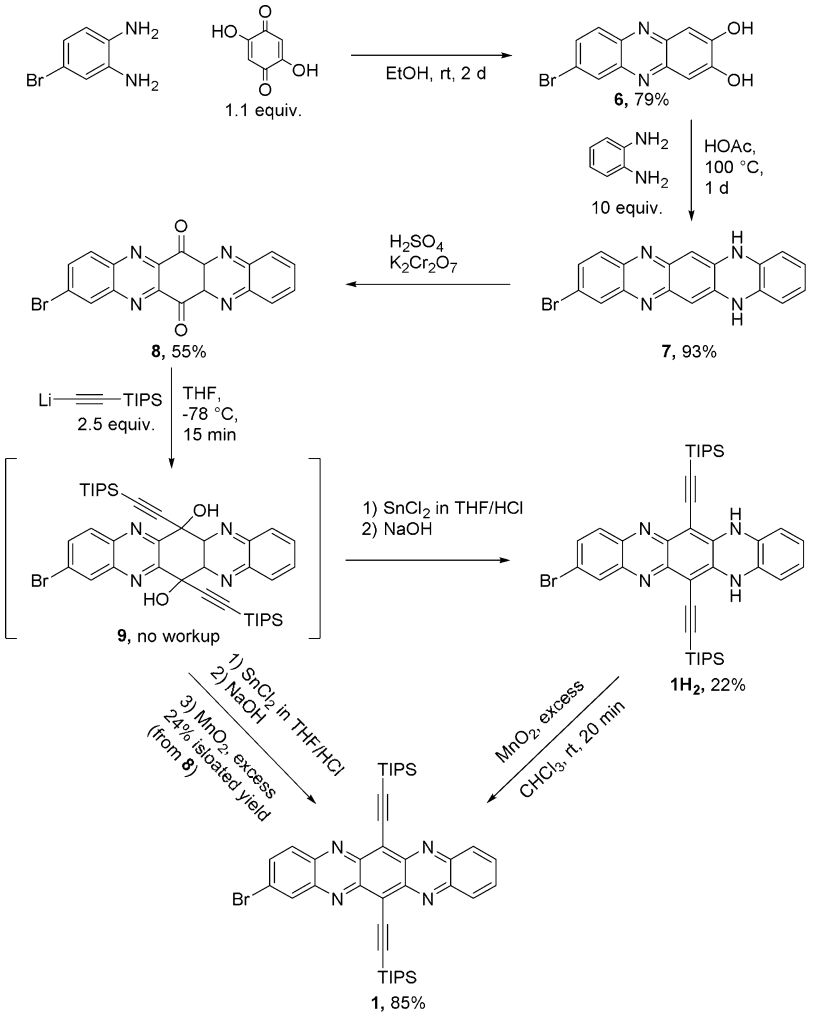
RESULTS AND DISCUSSION

Compound **1** was synthesized in a five step sequence (8% yield), starting from 4-bromophenylenediamine (Scheme 1). The first two condensation reactions to phenazine **6** and dihydro-tetraazapentacene **7** proceed smoothly in 73% yield. The tendency toward unspecific nucleophilic aromatic substitution in quinone **8** is increased, compared to that for the nonhalogenated tetraazapentacene quinone.[1] For the addition of the lithium acetylide to proceed selectively the

Received: September 9, 2015
Published: November 12, 2015

DOI: 10.1021/acs.joc.5b02115
J. Org. Chem. 2015, 80, 12166−12176

Scheme 1. Multistep Synthesis of the Monobrominated Tetraazapentacene 1



reaction temperature was lowered to −78 °C. After 15 min the reaction was complete. Reaction with the lithium acetylide led to higher yields than use of the analogous TIPS-ethynyl-Grignard. Following aqueous workup, diol **9** precipitated out. $SnCl_2$ in concentrated hydrochloric acid/THF transforms **9** into $\mathbf{1H_2}$, isolated in a total yield of 22% over two steps from quinone **8**. $\mathbf{1H_2}$ is oxidized with manganese dioxide into the brominated TIPS-TAP **1** in 85% yield. Larger batches are best oxidized without prior isolation of $\mathbf{1H_2}$, directly from the reduction mixture; the yield of **1** is then increased to 24% over the last three steps.

While iodoarenes are generally more reactive in Sonogashira reactions, electron-poor halogenated N-heteroarenes have an increased rate of the initial oxidative addition to the Pd(0) center. Even simple, brominated N-heteroarenes (e.g., bromopyridines, -quinolines, -phenazines) are reactive at room temperature under standard reaction conditions. One would expect monobromo **1** to couple smoothly to terminal alkynes under standard conditions at low temperature.

We reacted **1** with an excess of trimethylsilyl acetylene in the presence of tetrakis(triphenylphosphine)palladium(0) and copper(I) iodide as catalyst in THF/NEt_3 (ambient temperature). The dark green solution (typical color of **TIPS-TAP** and its derivatives in solution, compare Figure 3) changes to an intense red (typical color of the dihydro compounds; compare Supporting Information (SI)) within 1 h. Later, a solid precipitate (ammonium salt) indicates a productive Sonogashira coupling.

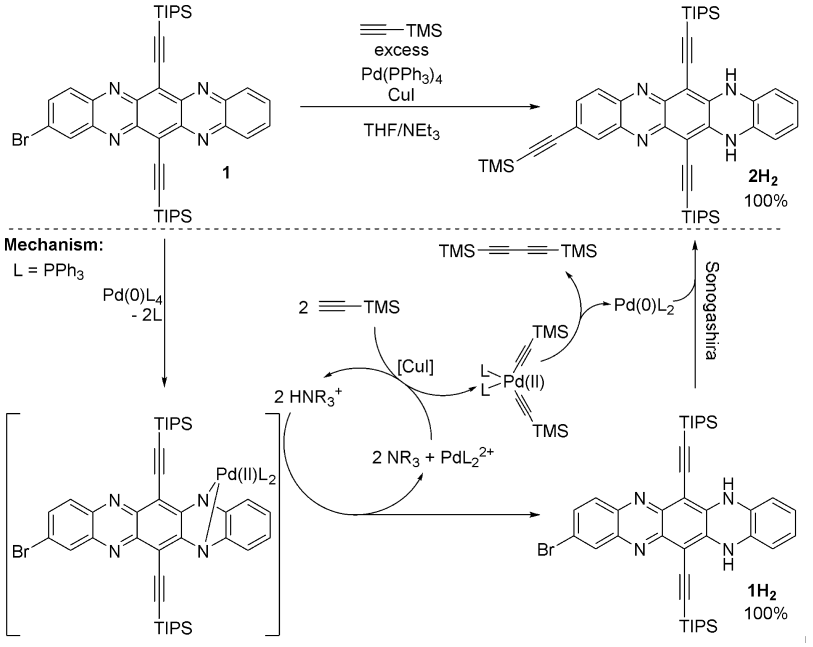
Apparently, **1** is first reduced to $\mathbf{1H_2}$, which then reacts with the alkyne. **1** must act as an oxidant (LUMO of −4.1 eV, Table 1). The reduction of the TAP-backbone under Sonogashira conditions is also observed using neat **TIPS-TAP**. Addition to a solution of alkyne in THF/NEt_3 slowly leads to reduced **TIPS-TAPH$_2$**, and even with the addition of CuI, the reduction proceeds within days rather than hours and is accompanied by the formation of side products (compare SI). On the other hand, the addition of a slight excess (1.1 equiv) of tetrakis(triphenylphosphine)palladium(0) to **TIPS-TAP** results

Table 1. Determination of Optical Band Gap and FMO-Energy Levels from UV−vis/CV and Quantum Chemical Calculations

compound	λ_{onset} [nm]	gap [eV] calcd/mes.	HOMO [eV] calcd/mes.	LUMO [eV] calcd/mes.
TIPS-TAP	718	−1.94/−1.73	−5.78/−5.72	−3.84/−3.99
1	724	−1.72/−1.71	−5.67/−5.79	−3.95/−4.08
2	726	−1.70/−1.71	−5.58/−5.82	−3.88/−4.11
3	731	−1.74/−1.70	−5.58/−5.73	−3.84/−4.03
4	730	−1.69/−1.70	−5.54/−5.82	−3.85/−4.12
10	725	−1.74/−1.71	−5.48/−5.68	−3.74/−3.97

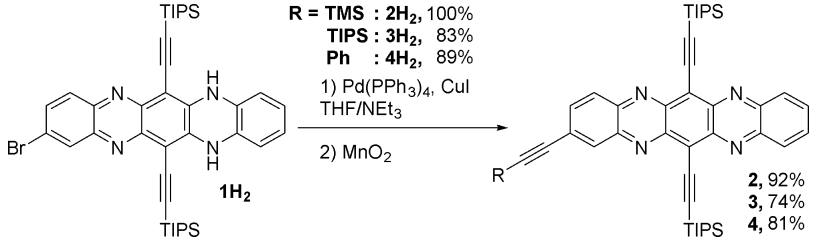
DOI: 10.1021/acs.joc.5b02115
J. Org. Chem. 2015, 80, 12166−12176

Scheme 2. Putative Mechanism of the Reductive Sonogashira Coupling of 1 with an Excess of Trimethylsilylacetylene to $2H_2$[a]



[a]Reductant is the terminal alkyne.

Scheme 3. Sonogashira Coupling of $1H_2$ with Simple Alkynes and Subsequent Oxidation with Manganese Dioxide to TAPs 2–4



in a red solution within minutes of stirring at room temperature; after quenching with dichloromethane/water only the dihydro compound $1H_2$ is isolated (see SI). These observations point to a Pd/Cu-catalyzed reduction of the TAP-backbone (Scheme 2). We hypothesize that Pd(0) is first oxidatively added to the azapentacene, which is concomitantly reduced. Ammonium salts generated by the copper acetylides and present under the coupling conditions protonate the nitrogen atoms and $1H_2$ and a catalytically inactive Pd(II) species is liberated. After the transmetalation of two alkynes to the Pd(II) center, a Glaser-type side reaction forms a butadiyne and the inactive Pd(II) is reverted back to a catalytically active Pd(0) species. Indeed, a large amount (1.3 equiv) of Glaser-type side product was isolated for a coupling carried out with **1**. While the amount of Glaser product is only circumstantial evidence for this mechanism, as it can also be generated during workup or from exposure to oxygen during the reaction, the high yields of the coupling prove that after the reduction of **1** to $1H_2$, the catalyst is still active. As the coupling of **1** with trimethylsilylacetylene to $2H_2$ is quantitative, the reduction from **1** to $1H_2$ must also be quantitative (Scheme 2).

$1H_2$ couples directly and quantitatively with trimethylsilylacetylene to $2H_2$. As it is not possible to generate oxidized alkynylated derivatives of **TIPS-TAP** directly by a Sonogashira coupling, the reaction of the dihydro compound $1H_2$ with terminal alkynes and subsequent oxidation into the respective tetraazapentacene is the most economical way to introduce an additional alkyne substituent into the TAP-backbone. $1H_2$ readily reacts with trimethylsilyl acetylene, triisopropylsilyl acetylene, and phenyl acetylene, applying tetrakis(triphenylphosphine)¬palladium(0) and CuI at room temperature in good to excellent yields (Scheme 3). The alkynylated derivatives $2H_2$-$4H_2$ are easily oxidized to the TAPs **2**–**4** in 74–92% yield.

Upon reduction of the TAP-system into the $TAPH_2$ system, it is energetically most favorable to reduce one pyrazine to a dihdyropyrazine unit.[19] Considering the unsymmetrical nature of the compounds $1H_2$-$5H_2$ and $10H_2$, this allows for two different dihydro tautomers. Both tautomers are easily identified spectroscopically for $2H_2$ (Figure S4) and $3H_2$ (Figure 2), due to the different chemical shifts the TMS- or TIPS-ethynyl groups possess if attached to either a phenazine ($2H_2$**a** and $3H_2$**a**) or to an *N,N′*-bis-arylphenylenediamine ($2H_2$**b** and $3H_2$**b**) (in the schemes and figures, dihydro compound **a** of a given $TAPH_2$ derivative is always depicted exemplary for the mixture of both tautomers if not indicated otherwise). Integration of the TMS respectively TIPS signals gives a ratio of nearly 1:1 for both isomers, pointing to their similar stability.

We expect for the brominated compounds $1H_2$**a** and $1H_2$**b** to have significantly different reactivities toward the oxidative addition. The dihydropyrazine unit disrupts the conjugation of

DOI: 10.1021/acs.joc.5b02115
J. Org. Chem. 2015, 80, 12166–12176

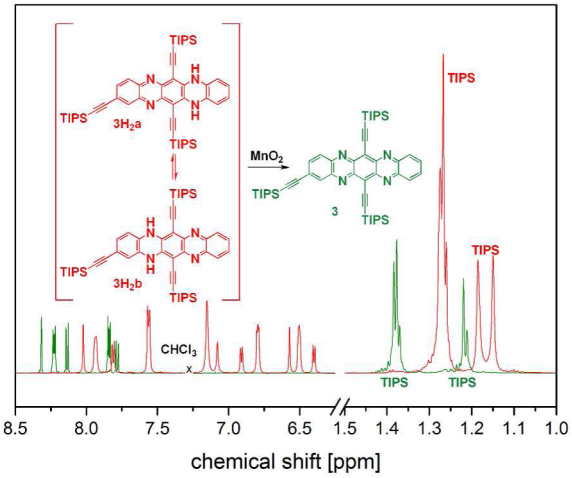


Figure 2. Proton NMR spectra ($CDCl_3$, 600 MHz, 25 °C) of **3** and $\mathbf{3H_2}$ visualizing the doubled aromatic and alkyl signals in $\mathbf{3H_2}$ (red). The integration of the doubled TIPS signal gives a 1:1 ratio for both isomers.

the π-system. $\mathbf{1H_2b}$ is electronically comparable to an electron-rich and thus unreactive *N,N′-bis*-aryl substituted phenylenediamine, while $\mathbf{1H_2a}$ is comparable to a reactive bromophenazine.

Breaking of symmetry usually has an impact on the macroscopic and microscopic solid state structure of a given compound. While **TIPS-TAP** and **TIPS-TAPH$_2$** are both crystalline solids, whose crystal structures were resolved by X-ray analysis,[1] the introduction of one bromine atom disturbs the microscopic order of the material. While **1** is a crystalline solid (Figure 5; it possesses long-range order, but short-range disorder), a single X-ray crystal structure cannot be determined, as in the crystalline state the bromine atom is statistically distributed over four different positions.

The trimethylsilyl derivative $\mathbf{2H_2}$ is deprotected with potassium carbonate into the terminal alkyne $\mathbf{5H_2}$ in surprisingly good yields (85%). $\mathbf{5H_2}$ can be stored under nitrogen or in high vacuum in a solid state, but decomposes during prolonged storage in solution, complicating its spectroscopic analysis. $\mathbf{5H_2}$ is a valuable starting material for further transformations.

Tetraphenylcyclopentadienone (tetracyclone) readily reacts with alkynes at high temperature, and through liberation of carbon monoxide, the primary reaction product aromatizes to a tetraphenyl substituted benzene ring.[20,21] Capping a terminal alkyne with a triisopropyl silyl group renders it sterically unable to react with tetracyclone;[22] thus high chemoselectivity was achieved for the initial Diels–Alder reaction. $\mathbf{5H_2}$ reacts with tetraphenylcyclopentadienone under ambient atmosphere in a microwave oven at 300 °C to give the tetraphenylphenyl-substituted TAPH$_2$ $\mathbf{10H_2}$ in 61% yield within 30 min. The compound was isolated and oxidized to the tetraphenylphenyl-TAP **10** (Scheme 4).

Reacting $\mathbf{5H_2}$ with $\mathbf{1H_2}$ via Sonogashira coupling affords the TIPS-TAPH$_2$-dimer $\mathbf{11H_4}$, which can be smoothly oxidized by manganese dioxide to dimer **11**, to our knowledge the first of its kind (Scheme 5).

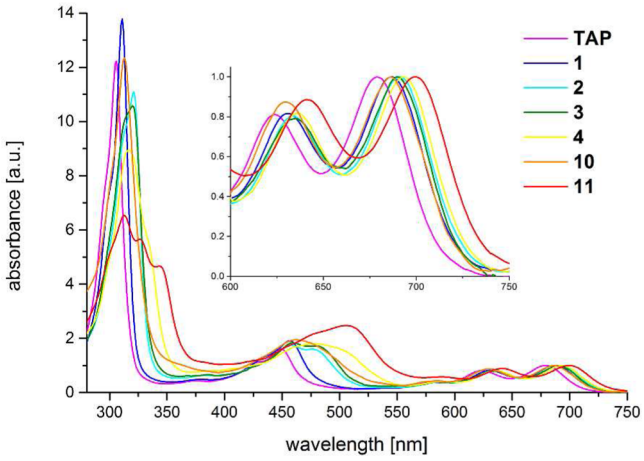
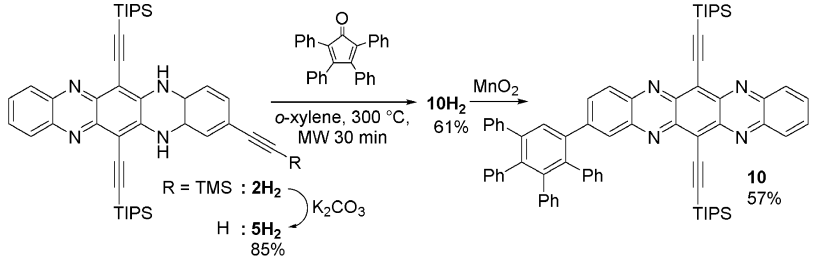


Figure 3. Normalized absorption spectra of the **TIPS-TAP** derivatives.

The oxidation of **TAPH$_2$** to **TAP** increases the conjugation in the azapentacene backbone, as evidenced by the absorption spectra (Figure 3). While the dihydro compounds possess their most bathochromic absorption maximum around 550 nm (SI), it is red-shifted for the **TIPS-TAP** derivatives to around 690 nm. Introducing an additional alkyne unit increases the conjugation of the π-system, and is expected to stabilize the frontier molecular orbitals (FMOs) and lower the optical band gap. While **TIPS-TAP** has a lowest-energy absorption maximum of 679 nm, it shifts to 691 nm for the introduction of a TMS-ethynyl moiety and, further enlarging the π-system, to 693 nm for phenyl ethynyl. Introducing the tetraphenylphenyl group only results in a shift to 686 nm. The most significant impact has a second **TIPS-TAP** unit in **11**; the red shifts in all absorption bands and an intensification of the more bathochromic bands are so pronounced that its solutions are dark brown rather than deep green as for all other TAP-derivatives known so far (λ_{max} at 700 nm).

Scheme 4. $\mathbf{2H_2}$ Can Be Deprotected to the Terminal Alkyne $\mathbf{5H_2}$ Which Can Be Subjected to a Cycloaddition with Tetraphenylcyclopentadienone To Yield $\mathbf{10H_2}$[a]



[a]Oxidation affords the tetraphenylphenyl substituted **TIPS-TAP**-derivative **10**.

DOI: 10.1021/acs.joc.5b02115
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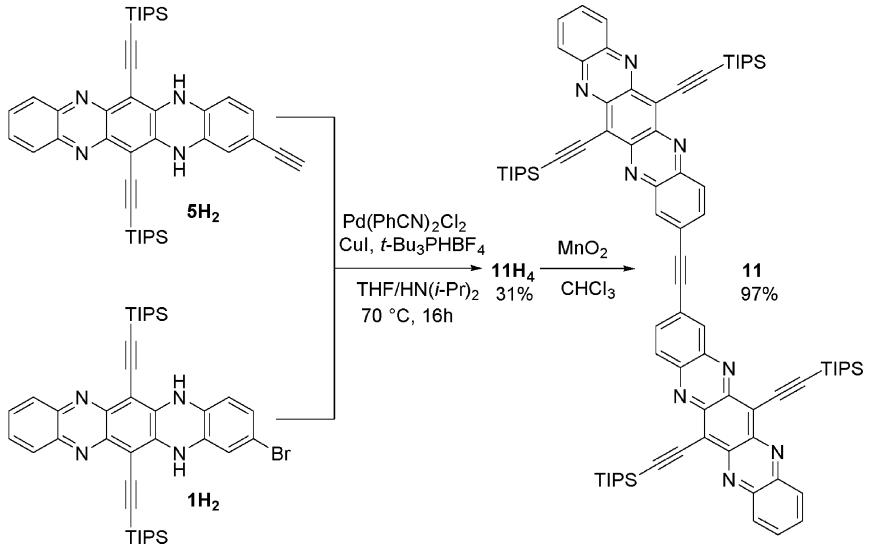
Scheme 5. Sonogashira Coupling of $5H_2$ with $1H_2$ to the Ethylene Bridged Dimer $11H_4$[a]



[a]The tetrahydro compound can be smoothly oxidized to the dimer **11**.

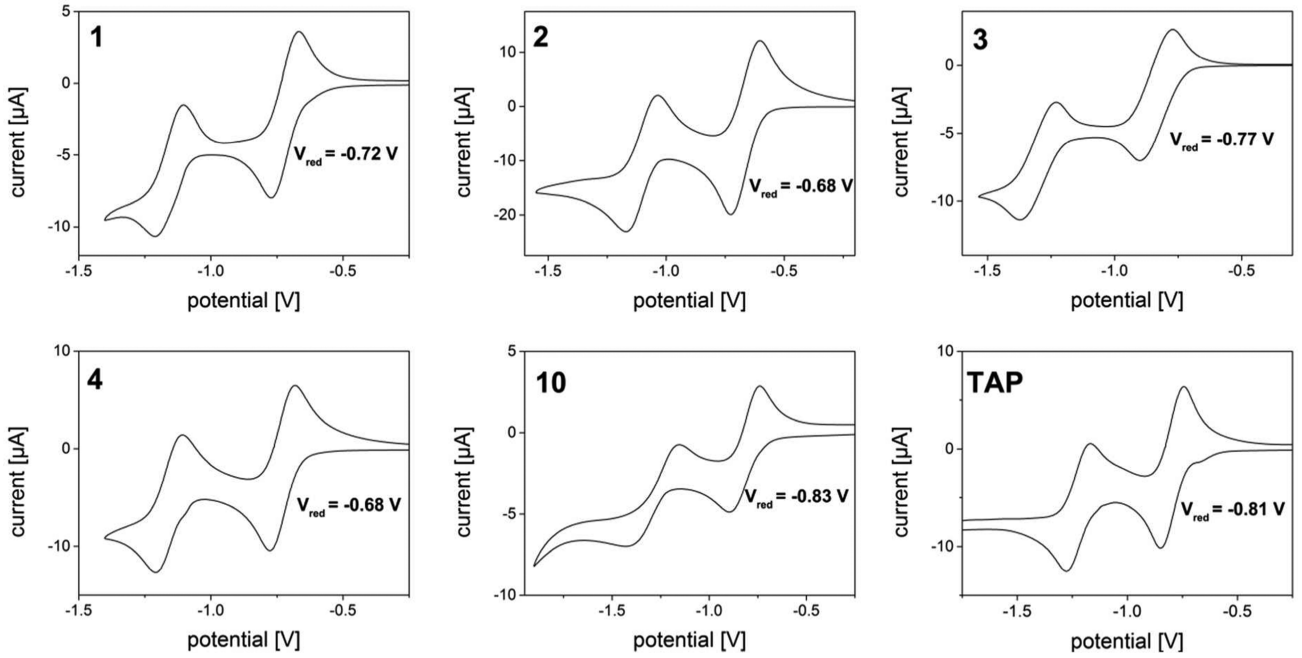


Figure 4. Cyclic voltammetry of compounds **1**–**4**, **10**, and **TIPS-TAP**. For estimations of the LUMO-energy levels, the measurements were carried out with ferrocene as an internal standard.

The monomeric tetraazapentacene derivatives **1**–**4** and **10** show reversible reduction waves in cyclovoltammetric (CV) measurements (Figure 4). From the CV and UV–vis spectra (solution), the HOMO/LUMO energy levels and optical band gap are estimated (Table 1). Additionally, the FMO-energies were determined using computational methods. Regarding applications as electron acceptor materials, the energy level of the LUMOs is of interest. The LUMO of unsubstituted **TIPS-TAP** is estimated to be −3.99 eV (calculated: −3.84 eV). Introducing a bromine atom lowers the band gap to −4.08 eV (calculated: −3.95 eV). Substituting the bromine atom by TMS-ethynyl further lowers it to −4.11 eV, evidencing the impact of expanding the π-system. This effect is apparently partially reversed by exchanging the TMS group with the more electron-rich TIPS group, as underlined by calculations (−3.84 eV) and CV measurements (−4.03 eV). Exchanging the TMS group with a phenyl ring lowers the LUMO energy level to −4.12 eV according to CV measurements.

All ethynyl substituents stabilize the FMOs. Due to steric hindrance, the tetraphenylphenyl substituent in **10** is distinctly non planar, prohibiting the increase of the pentacene-π-system over the additional phenyl rings. The substituent actually destabilizes the LUMO of the system to −3.97 eV (calculated: −3.74 eV).

The substituted TIPS-TAP derivatives **2**–**4** and **10** are well soluble in most common solvents. Their crystallinity and film forming properties were investigated by polarizing microscopy on drop cast and spin coated films (Figure 5).

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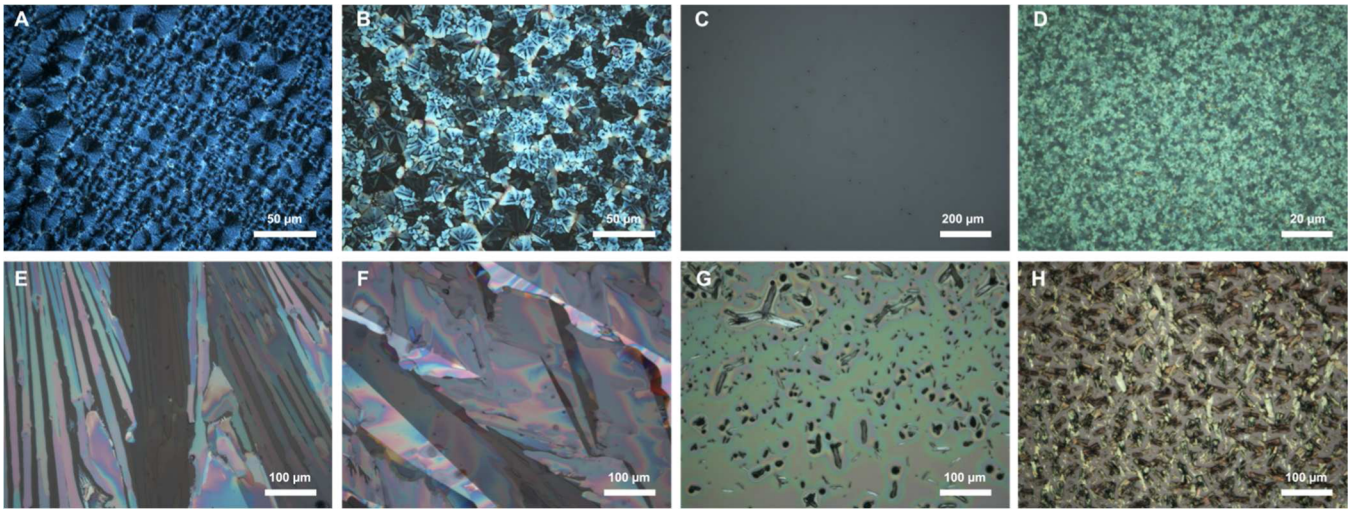

Figure 5. Drop cast films of (A) **TIPS-TAP**; (B) **1**; (C) **2**; (D) **4** and spin coated films of (E) **TIPS-TAP**; (F) **1**; (G) **2**; (H) **4** under cross-polarizers. Cast and coated from 10 mg/mL toluene solutions at room temperature on glass slides.

TIPS-TAP and its brominated derivative **1** form crystalline films by both spin coating and drop casting (Figure 4 A,B,E,F and Figures S2, S3). Introducing the alkyne substituents lowers the film crystallinity. While for the TMS-ethynyl substituted **3** crystalline domains are found in some regions of the drop cast films (Figure 5 G), the spin-coated films (Figure 5C) are amorphous; substituting with TIPS-ethynyl as well as with tetraphenylbenzene results in amorphous films by drop casting or spin coating. Phenylethynyl substitution results in polycrystalline films (Figure 4E,F) with domain sizes in the micrometer region for spin coated films.

Measuring the thin-film absorption spectra gives insight into electronic interactions in the solid state. Comparing the absorption maxima for different processing methods unveils their influence on these interactions. Figure 6 visualizes the

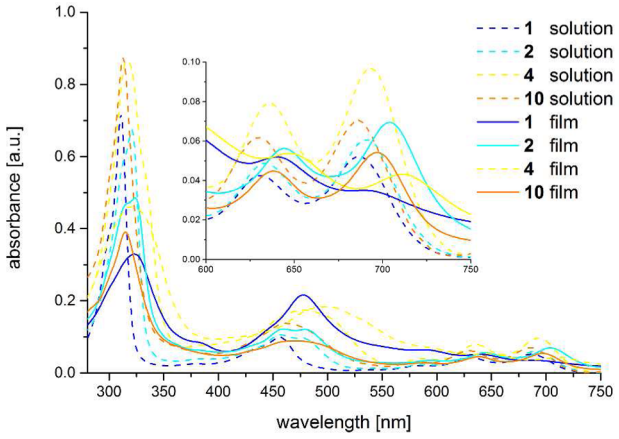

Figure 6. Comparison of solution and film (spin coated) UV−vis spectra of representative compounds.

absorption of some representative compounds in spin coated films (spectra from drop cast films and remaining compounds can be found in the SI). Table 2 summarizes the changes in the lowest energy absorption maxima, representing the electronic HOMO−LUMO transition. As expected, the ethynyl substituent impacts the solid state interaction of the materials. While the λ_{max} of bromide **1** shifts only 3 nm (spin coating) and

Table 2. Optical Properties of Thin Films from TIPS-TAP and Its Derivatives

compound	λ_{max} [nm] solution	λ_{max} [nm] spin coat	λ_{max} [nm] drop cast	$\Delta\lambda_{spin}/\Delta\lambda_{drop}$ [nm]
TIPS-TAP	679	685	694	6/15
1	687	690	696	3/9
2	691	704	702	13/11
3	690	703	701	13/11
4	693	711	713	18/20
10	686	697	695	11/9

9 nm (drop casting) from solution to solid state, it changes to 13 and 11 nm for the silylalkynylated compounds **2** and **3**, respectively. Surprisingly, the absorption shift is more pronounced for spin coated films and is more than twice the shift measured for spin coating neat **TIPS-TAP**. While the influence of the phenyl group in **4** on the measured and calculated FMO-energies is minor (in comparison to **2**,**3**), its impact on the solid state interactions is more pronounced and λ_{max} shows a red shift of 18/20 nm in the solid state. So this is an interesting case, as even in nonordered thin films there is some electronic coupling between the molecules in the ground state.

While all monomeric **TIPS-TAP** derivatives are soluble and solution processable, dimer **11** proved, to our surprise, to be nearly insoluble in most solvents at room temperature. After its oxidation from the soluble **11H$_4$**, **11** is soluble, but soon it precipitates upon longer storage. ^{1}H NMR spectroscopy was performed at elevated temperature in deuterated toluene; for optical spectroscopy the solubility in dichloromethane is sufficient. For these reasons, cyclic voltammograms of **11** could not yet be obtained and the study of its electronic properties relies solely on computational methods and optical measurements. The absorption spectra point to a further lowering of the optical band gap (λ_{onset} 735 nm, 1.69 eV). Optimization of the molecular geometry (DFT, TVZP using TurboMol) gives a planar conformation (Figure 7). This geometry should allow for strong $\pi-\pi$-stacking, thus explaining the observed low solubility and precipitation of the compound.

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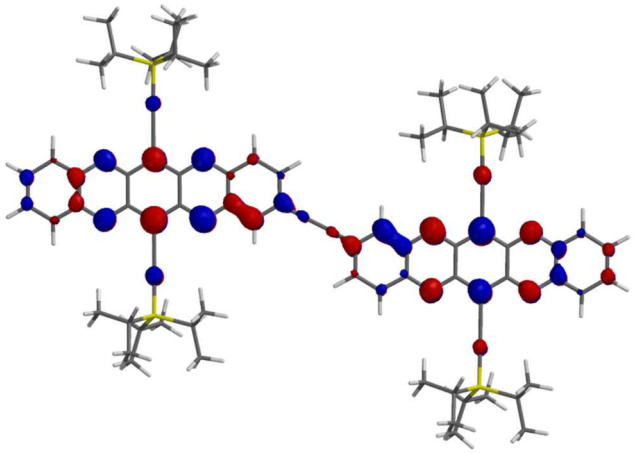

Figure 7. Optimized geometry of dimer **11**. The distribution of the LUMO was calculated using a single-point energy approach using Spartan 10 with the B3LYP 6-31G* basis set.

CONCLUSIONS

The reductive Sonogashira coupling of **1** or the direct coupling of $\mathbf{1H_2}$ and subsequent oxidative aromatization allows for the efficient functionalization of **TIPS-TAP**. Through alkynylation of **TIPS-TAP**, its solid state morphology is controlled, while the FMOs are stabilized. Depending on the substituent, the size of the crystalline domains in thin films is significantly decreased and even amorphous films result. Yet, even the amorphous derivatives show pronounced electronic ground state interactions in the solid state, as evidenced by the red-shifted absorption spectra upon going from solution into thin films. This ground state electronic coupling is similar or even larger than in films of the crystalline **TIPS-TAP**.

Overall, our approach opens up the synthesis of novel functionalized **TIPS-TAP** derivatives and also yields powerful modules for further functionalization. Applying these principles we aim to explore the chemistry of larger oligomeric **TIPS-TAP** derivatives, as well as the performance of the alkynylated compounds in OPV and related applications.

EXPERIMENTAL SECTION

All reagents and solvents were obtained from commercial suppliers and were used without further purification. For chromatography, the 40−60 °C petrol ether fraction was used. Preparation of air- and moisture-sensitive materials was carried out in flame-dried flasks under an atmosphere of nitrogen by using Schlenk techniques. For reactions carried out in a microwave, a microwave synthesis reactor was used. For column chromatographical purifications, an automated chromatography system capable of UV−vis based automated fractioning operated with self-packed columns or manual column chromatography (SiO_2, grain size 0.04−0.063 mm) was used. Melting points are reported uncorrected. Polarized microscopy was performed on an optical microscope fitted with cross polarizers and integrated digital imaging. ^{1}H (^{13}C) NMR spectra were recorded on 300 MHz (75 MHz), 400 MHz (100 MHz), 500 MHz (125 MHz), or 600 MHz (150 MHz) spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) relative to traces of [H_1] solvent in the corresponding deuterated solvent. Mass spectra were recorded using high resolution matrix assisted laser desorption ionization (HR-MALDI), high resolution electrospray ionization (HR-ESI), and high resolution electron impact ionization (HR-EI) detected by magnetic sector and FT-ICR (Fourier transform ion cyclotron resonance) techniques. Infrared (IR) spectra are reported in wavenumbers (cm^{-1}) and were recorded neat. Computational studies were carried out using DFT calculations. Geometry optimization was carried out at the BP-86/def2-TZVP level. Using this geometry the absolute energy and FMO energies were assigned by a single-point approach by employing B3LYP/6-311++G**. Thin films from the tetraazapentacenes were prepared by drop casting or spin coating a 10 mg/mL solution in toluene of the respective substance on glass slides. Spin coating was carried out at a speed of 1500 rpm, with an acceleration of 1500 rpm/s, for 32 s.

7-Bromophenazine-2,3-diol (6). In a 250 mL round-bottom flask, 4-bromophenylenediamine (5.00 g, 26.7 mmol) and 2,5-dihydroxy-*p*-benzoquinone (4.12 g, 29.4 mmol, 1.10 equiv) were dissolved in 150 mL of ethanol. The flask was closed (clamp), and the dark red mixture was stirred for 2 d at room temperature. The suspension was cooled to −20 °C, and the precipitate was filtered and washed with some cold (4 °C) ethanol to afford a dark red material that was dried *in vacuo* and used in the subsequent condensation reaction without further purification. Yield: 6.11 g (21.0 mmol), 79%. Mp: decomposition >273 °C. ^{1}H NMR (300.51 MHz, d_6-DMSO, 25 °C): δ (ppm) = 8.27 (brs, 1H); 8.05−7.96 (m, 1H); 7.88−7.80 (m, 1H); 7.26 (brs, 2H). Insufficient solubility for ^{13}C NMR-spectroscopy. IR: ν (cm^{-1}) = 2965, 2753 (broad), 1621, 1507, 1469, 1365, 1185. HR-MS (EI$^+$): *m*/*z* calcd for $C_{12}H_7{}^{79}BrN_2O_2$: $[M]^+$ 289.9691, found: 289.9709; $C_{12}H_7{}^{81}BrN_2O_2$: $[M]^+$ 291.9670, found: 291.9637, correct isotope distribution.

9-Bromo-*N*,*N*′-dihydro-5,7,12,14-tetraazapentacene (7). Powdered 7-bromophenazine-2,3-diol **6** (1.00 g, 3.44 mmol) and *o*-phenylenediamine (3.71 g, 34.4 mmol, 10 equiv) were added to a 50 mL round-bottom flask, and 5 mL acetic acid (glacial) were added. The flask was closed up (clamp), and the dark red, viscous slurry was heated to 100 °C overnight under rigorous stirring, then allowed to cool down, and taken up in dichloromethane. The solid material was centrifuged, and the dark brown solution was removed. The material was resuspended in acetone (20 mL), and the washing procedure was repeated three times. The solid, deep purple material was dried in air and kept under high vacuum overnight to remove residual solvent to yield 2-bromo *N*,*N*′-dihydrotetraazapentacene **7**. Yield: 1.16 g (3.19 mmol), 93%. Mp: >400 °C. Insufficient solubility for NMR-spectroscopy. IR: ν (cm^{-1}) = 3245, 3203, 3168, 3135, 3097, 3018, 2923, 1618, 1582, 1444, 809, 738. HR-MS (EI$^+$): material oxidizes to 9-bromo-5,7,12,14-tetraazapentacene in the spectrometer. *m*/*z* calcd for $C_{18}H_9{}^{79}BrN_4$: $[M]^+$ 360.0011, found: 360.0020; $C_{18}H_9{}^{81}BrN_4$: $[M]^+$ 361.9990, found: 361.9987, correct isotope distribution.

2-Bromo-5,7,12,14-tetraazapentacene-6,12-dione (8). Fine powdered **7** (3.50 g, 9.64 mmol, 1.00 equiv) was suspended in a mixture of water (350 mL) and sulfuric acid (92 mL). $K_2Cr_2O_7$ (13.6 g, 46.3 mmol, 4.80 equiv) was added in portions. The mixture was kept at reflux for 30 min. Over the course of the reaction a brown solid precipitated and was filtered off, after the reaction mixture was diluted with DI water (1 L) and cooled to room temperature. The solid was washed with DI water (500 mL) and acetone (2 L) to yield a yellow solid. Yield: 2.08 g (5.32 mmol), 55%. Mp: decomposition >170 °C. ^{1}H NMR (300 MHz, d-TFA, 295 K): δ (ppm) = 8.76 (s, 1 H), 8.67−8.50 (m, 2 H), 8.45−8.28 (m, 4H). ^{13}C NMR (75.5 MHz, d-TFA, 295 K): δ (ppm) = 181.6, 164.5, 164.3, 145.7, 145.3, 145.0, 144.8, 142.8, 139.3, 135.4, 134.1, 132.6, 131.7. IR: ν (cm^{-1}) = 3060, 3038, 1697, 1043. HR-MS (EI$^+$): *m*/*z* calcd for $C_{18}H_7{}^{79}BrN_4O_2$: $[M]^+$ 389.9752, found: 389.9785; $C_{18}H_7{}^{81}BrN_4O_2$: $[M]^+$ 391.9732, found: 391.9760, correct isotope distribution.

2-Bromo-6,13-(bis(triisopropylsilyl)ethynyl)-*N*,*N*′-dihydro-5,7,12,14-tetraazapentacene ($\mathbf{1H_2}$) and 2-Bromo-6,13-(bis(triisopropylsilyl)ethynyl)-5,7-12,14-tetraazapentacene (1). *Synthesis of* $\mathbf{1H_2}$ *by Reduction of* **1**. To a solution of **1** (50.0 mg, 69.3 μmol, 1.00 equiv) in THF (20 mL), a solution of $SnCl_2$ (130 mg, 693 μmol, 10 equiv) in HCl (10 mL) was added. The solution was stirred for 30 min at room temperature and quenched and neutralized by addition of saturated $NaHCO_3$ solution. The suspension was extracted with dichloromethane (3 × 100 mL), the combined organic layers were dried over $MgSO_4$, and the solvent was removed. The solid was purified by column chromatography using petrol ether/dichloromethane as below. Yield: 48.2 mg (66.6 μmol), 96%.

DOI: 10.1021/acs.joc.5b02115
J. Org. Chem. 2015, 80, 12166−12176

Synthesis of ***1*** *by Oxidation of* ***1H$_2$***. To a solution of **1H$_2$** (28.3 mg, 39.1 μmol) in $CHCl_3$ (5 mL), MnO_2 (136 mg, 1.56 mmol, 40 equiv) was added. The mixture was stirred for 20 min at room temperature while it changed its color from intense red to a dark green. The solid was filtered off, the solvent was evaporated, and the residual material was purified by column chromatography as below. Yield: 24.1 mg (33.4 μmol), 85%.

General Procedure for One-Step Synthesis of ***1H$_2$*** *from Quinone* ***8***. 2.00 g (5.11 mmol) of quinone **8** were suspended in 20 mL of dry tetrahydrofuran in a 100 mL Schlenk flask under a nitrogen atmosphere. In a separate Schlenk tube, triisopropylsilylacetylene (3.06 mL, 2.80 g, 15.3 mmol, 3 equiv) were dissolved in 10 mL of dry THF and cooled to −78 °C. A solution of *n*-butyl lithium in hexane (2.50 M, 5.11 mL, 12.8 mmol, 2.5 equiv) was added to the TIPS-acetylene solution, and the solution was stirred for 3 min at −78 °C and then allowed to warm to room temperature. The suspension of the tetraazapentacene quinone was cooled to −78 °C. Under intense stirring, the acetylide solution was slowly added (syringe) to the suspension to generate a dark green, homogeneous solution within 15 min of stirring at this temperature. The solution was poured into 400 mL of DI water (room temperature), and the solid was allowed to settle for 30 min. The reddish solid (diol compound **9**) was collected by filtration and allowed to dry in air overnight. The diol **9** can be identified by HR-MS. HR-MS (ESI$^+$): *m*/*z* calcd for $C_{40}H_{52}{}^{79}BrN_4O_2Si_2$: $[M + H]^+$ 755.28122, found: 755.28274; *m*/*z* calcd for $C_{40}H_{52}{}^{81}BrN_4O_2Si_2$: $[M + H]^+$ 757.27917, found: 757.28081. The filter was eluted with tetrahydrofuran until all soluble material was washed out. To this solution (ca. 300 mL THF), 9.68 g of $SnCl_2$ (51.1 mmol, 10 equiv) in 30 mL of concentrated hydrochloric acid were added. The dark red solution turned dark blue within seconds and was stirred overnight at room temperature. For workup, 300 mL of dichloromethane and 200 mL of DI water were added to the solution and stirred for 5 min, the mixture was transferred into a separatory funnel, and the layers were separated. The aqueous layer was extracted twice with dichloromethane (100 mL each), and the combined organic layers were washed twice with a NaOH solution (40 g of NaOH per 400 mL of DI water, 2 × 200 mL for washing). After each washing step, the aqueous layer was extracted with another 100 mL of dichloromethane. The combined organic layers were washed with DI water (2 × 300 mL); again the aqueous layers were each extracted with 100 mL of dichloromethane. The combined organic layers were dried over $MgSO_4$ and filtered, and the intensely red and weakly fluorescent solution was evaporated to yield the crude dihydrotetrazapentacene **1H$_2$** as a dark red solid.

Isolation of the Dihydro-compound ***1H$_2$***. Crude **1H$_2$** can be purified by column chromatography on SiO_2, with petrol ether/dichloromethane 1:1, to yield the product as a red crystalline solid with an intense metallic glare. R_f (SiO_2, petrol ether/dichloromethane 1:1) = 0.72. Yield: 795 mg (1.10 mmol), 22%. Mp: 296 °C. NMR spectroscopy: Due to the dihydro tautomerism the aromatic signals are doubled, overlapping to complex multiplets. ^{1}H NMR (600 MHz, d_8-THF, 25 °C): δ (ppm) = 8.00−7.95 (m, H_{arom}), 7.86−7.82 (m, H_{arom}), 7.75−7.66 (m, H_{arom}), 7.64−7.57 (m, H_{arom}), 7.56−7.47 (m, H_{arom}), 7.46 (s, H_{arom}), 7.30 (s, H_{arom}), 6.91−8.85 (m, H_{arom}), 6.83−6.76 (m, H_{arom}), 6.65−6.60 (m, H_{arom}), 6.55−6.50 (m, H_{arom}), 1.30−1.26 (m, 42H). ^{13}C {^{1}H} NMR (150 MHz, d_8-THF, 25 °C): δ (ppm) = 145.7 (C_q), 145.4 (C_q), 144.9 (C_q), 143.6 (C_q), 143.2 (C_q), 143.1 (C_q), 141.8 (C_q), 141.5 (C_q), 141.2 (C_q), 140.4 (C_q), 140.1 (C_q), 132.2 (CH), 131.6 (CH), 131.2 (CH), 131.0 (C_q), 129.8 (CH), 129.3 (C_q), 129.2 (CH), 129.2 (CH), 128.8 (C_q), 126.4 (CH), 124.44 (CH), 124.36 (CH), 122.3 (C_q), 117.9 (CH), 116.4 (CH), 115.6 (C_q), 115.36 (CH), 115.35 (CH), 105.0 (C_q), 104.7 (C_q), 104.6 (C_q), 104.5 (C_q), 101.0 (C_q), 100.88 (C_q), 100.85 (C_q), 100.7 (C_q), 98.7 (C_q), 98.3 (C_q), 97.6 (C_q), 97.4 (C_q), 19.4 (CH/CH_3), 12.6 (CH/CH_3). IR: ν (cm^{-1}) = 3377, 2939, 2862, 2155, 1604, 1573, 1450, 746. HR-MS (ESI$^+$): *m*/*z* calcd for $C_{40}H_{52}{}^{79}BrN_4Si_2$: $[M + H]^+$ 723.29139, found: 723.29109; *m*/*z* calcd for $C_{40}H_{51}{}^{81}BrN_4Si_2$: $[M + H]^+$ 725.28934, found: 725.28893.

Direct Oxidation of Crude ***1H$_2$*** *and Isolation of* ***1***. The crude dihydro compound **1H$_2$** was redissolved in 200 mL of dichloromethane, MnO_2 (10.7 g, 123 mmol, 24 equiv) was added, and the suspension was stirred for 10 min at room temperature while the color quickly changed from an intense red to a dark green. The solid material was filtered, and the solution was evaporated to yield the crude **1** as a dark green solid that was further purified by column chromatography (SiO_2, petrol ether/dichloromethane 1:1), R_f (petrol ether/dichloromethane 1:1) = 0.51, to afford the product as a black, crystalline solid. Yield: 877 mg (1.21 mmol), 24%. Mp: decomposition >291 °C. ^{1}H NMR (600 MHz, d_8-THF, 25 °C): δ (ppm) = 8.44−8.42 (m, 1H), 8.23−8.17 (m, 2H), 8.14−8.11 (m, 1H), 8.02−7.98 (m, 1H), 7.95−7.90 (m, 2H), 1.42−1.35 (m, 42 H). ^{13}C {^{1}H} NMR (150 MHz, d_8-THF, 25 °C): δ (ppm) = 146.7 (C_q), 146.6 (C_q), 146.2 (C_q), 145.0 (C_q), 144.3 (C_q), 144.0 (C_q), 143.9 (C_q), 143.8 (C_q), 136.9 (CH), 133.7 (CH), 133.6 (CH), 133.0 (CH), 132.8 (CH), 131.4 (CH), 131.3 (CH), 128.2 (C_q), 124.4 (C_q), 124.2 (C_q), 112.70 (C_q), 112.68 (C_q), 104.5 (C_q), 104.4 (C_q), 19.5 (CH/CH_3), 12.79 (CH/CH_3), 12.78 (CH/CH_3). IR: ν (cm^{-1}) = 3067, 2934, 2890, 2862, 1603, 1521, 1454, 1421, 1383, 1020, 747. HR-MS (ESI$^+$): *m*/*z* calcd for $C_{40}H_{50}{}^{79}BrN_4Si_2$: $[M + H]^+$ 721.27574, found: 721.27596. *m*/*z* calcd for $C_{40}H_{50}{}^{81}BrN_4Si_2$: $[M + H]^+$ 723.27369, found: 723.27414, correct isotope distributions.

2-((Trimethylsilyl)ethynyl)-6,13-bis((triisopropylsilyl)-ethynyl)-*N*,*N*′-dihydro-5,7,12,14-tetraazapentacene (2H$_2$). *Reductive Sonogashira Coupling of* ***1***. In a Schlenk tube, to a degassed 1:1 mixture of triethyl amine and tetrahydrofuran (4 mL) containing 55 mg (76.2 μmol) of **1**, 2.9 mg (15.2 μmol, 0.2 equiv) of CuI and 8.8 mg of $Pd(PPh_3)_4$ were added. To this dark green (typical color of TIPS-TAP-derivatives) solution, trimethylsilylacetylene (108 μL, 74.8 mg, 762 μmol, 10 equiv) was added. The color slowly changed from dark green to a bright red. The mixture was stirred overnight at room temperature and quenched by addition of 5 mL of DI water and 10 mL of dichloromethane. The layers were separated. The aqueous layer was extracted with dichloromethane (3 × 10 mL), and the combined organic layers were dried over $MgSO_4$. The solvent was then evaporated. The residual material was chromatographed on a gradient of dichloromethane in petrol ether to yield the product as a red compound with orange fluorescence in solution. Yield: 57.0 mg (76.2 μmol), quantitative.

Sonogashira Coupling of ***1H$_2$***. In a Schlenk tube **1H$_2$** (100 mg, 138 μmol) was kept under nitrogen. 5 mL of degassed 2:1 THF/NEt_3 containing CuI (2.63 mg, 13.8 μmol, 0.1 equiv) and $Pd(PPh_3)_4$ (7.98 mg, 6.91 μmol, 0.05 equiv) were added. To the stirred solution, trimethylsilyl acetylene (108 μL, 74.8 mg, 762 μmol, 10 equiv) was added. The mixture was stirred for 2 days at room temperature. 10 mL of dichloromethane and 30 mL of DI water were added, and the phases were separated. The aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over $MgSO_4$, the solvent was evaporated, and the residual solid material was taken up on Celite and chromatographed (automated chromatography, 50 g of SiO_2 self-packed column with a gradient of 20−80% dichloromethane in petrol ether). R_f (SiO_2, petrol ether/dichloromethane 1:1): 0.74. Red, foamy solid. Yield: 103 mg (138 μmol), quantitative. Mp: decomposition >250 °C. NMR spectroscopy: Due to the dihydro tautomerism the aromatic signals are doubled, overlapping to complex multiplets. The integral over all aromatic signals affords the expected ratio of $H_{arom}/H_{TIPS/TMS}$. ^{1}H NMR (600 MHz, d_8-THF, 25 °C): δ (ppm) = 7.89−7.87 (m, H_{arom}), 7.86−7.81 (m, H_{arom}), 7.75−7.72 (m, H_{arom}), 7.72−7.67 (m, H_{arom}), 7.55−7.50 (m, H_{arom}), 7.50−7.48 (m, H_{arom}), 7.45−7.36 (m, H_{arom}), 7.30 (s, H_{arom}), 6.86−6.83 (m, H_{arom}), 6.80−6.75 (m, H_{arom}), 6.72−6.70 (m, H_{arom}), 6.64−6.60 (m, H_{arom}), 6.57−6.53 (m, H_{arom}), 1.30−1.27 (m, 42 H_{TIPS}), 0.27 (s, H_{TMS}), 0.21 (s, H_{TMS}). ^{13}C {^{1}H} NMR (150 MHz, d_8-THF, 25 °C): δ (ppm) = 145.7 (C_q), 145.4 (C_q), 145.0 (C_q), 144.8 (C_q), 143.2 (C_q), 143.1 (C_q), 142.9 (C_q), 142.5 (C_q), 141.3 (C_q), 140.3 (C_q), 140.2, 133.04 (CH), 131.68 (CH), 129.94 (C_q), 129.41 (C_q), 129.30 (C_q), 129.26 (C_q), 129.26 (C_q), 129.16 (CH), 129.13 (CH), 128.10 (CH), 124.40 (CH), 124.35 (CH), 123.60 (C_q), 118.56 (C_q), 118.03 (CH), 115.34 (CH), 115.28 (CH), 115.00 (CH), 105.90 (C_q), 104.90 (C_q), 104.76 (C_q), 104.47 (C_q), 104.43 (C_q), 101.01 (C_q), 100.91 (C_q), 100.80 (C_q), 98.57 (C_q), 98.36 (C_q), 97.66 (C_q),

DOI: 10.1021/acs.joc.5b02115
J. Org. Chem. 2015, 80, 12166−12176

97.60 (C_q), 96.81 (C_q), 96.51 (C_q), 93.65 (C_q), 19.45 (CH/CH_3), 19.43 (CH/CH_3), 12.60 (CH/CH_3), 12.58 (CH/CH_3), 12.56 (CH/CH_3), 0.20 (CH/CH_3), 0.14 (CH/CH_3). IR: ν (cm^{-1}) = 3370, 3056, 2941, 2863, 2150, 1575, 861, 837, 744. HR-MS (ESI^+): m/z calcd for $C_{45}H_{61}N_4Si_3$ $[M + H]^+$: 741.42040, found: 741.42125, correct isotope distribution.

2-((Trimethylsilyl)ethynyl)-6,13-bis((triisopropylsilyl)-ethynyl)-5,7,12,14-tetraazapentacene (2). 2H$_2$ (27.6 mg, 37.2 μmol) was dissolved in 5 mL of chloroform, and MnO_2 (130 mg, 1.49 mmol, 40 equiv) was added. The suspension was stirred for 20 min at room temperature. The now green mixture was filtered, and the solvent was evaporated to yield a dark green material that was purified by column chromatography on silica (petrol ether/dichloromethane 1:1) to yield **2** as a dark/black solid. R_f (SiO_2, petrol ether/dichloromethane 1:1) = 0.56. Yield: 25.20 mg (92%). Mp: decomposition >250 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) = 8.32−8.29 (m, 1H), 8.25−8.20 (m, 2H), 8.16−8.12 (m, 1H), 7.86−7.82 (m, 2H), 7.80−7.76 (m, 1H), 1.42−1.5 (m, 42H_{TIPS}), 0.36 (s, 9H_{TMS}). ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$, 25 °C): δ (ppm) = 145.6 (C_q), 145.5 (C_q), 144.98(C_q), 144.91(C_q), 143.1 (C_q), 143.04 (C_q), 142.96 (C_q), 142.66 (C_q), 134.5 (CH), 133.7 (CH), 132.1 (CH), 130.6 (CH), 130.4 (CH), 129.9 (C_q), 132.0 (C_q), 123.0 (C_q), 112.9 (C_q), 112.6 (C_q), 104.3 (C_q), 103.0 (C_q), 102.9 (C_q), 101.4 (C_q), 18.97 (CH/CH_3), 18.95 (CH/CH_3), 11.7 (CH/CH_3), −0.2 (CH/CH_3). IR: ν (cm^{-1}) = 2941, 2863, 1614, 1433, 1021, 747. HR-MS (ESI^-): m/z calcd for $C_{45}H_{58}N_4Si_3$: $[M]^-$ 738.39693, found: 738.39664, correct isotope distribution.

2-((Triisopropylylsilyl)ethynyl)-6,13-bis((triisopropylsilyl)-ethynyl) *N,N′*-Dihydro-5,7,12,14-tetraazapentacene (3H$_2$). In a Schlenk tube **1H$_2$** (100 mg, 138 μmol) was kept under an inert gas. 5 mL of degassed 2:1 THF/NEt_3 containing CuI (2.63 mg, 13.8 μmol, 0.1 equiv) and $Pd(PPh_3)_4$ (7.98 mg, 6.91 μmol, 0.05 equiv) were added. To the stirred solution, 310 μL (10 equiv) of triisopropylsilyl acetylene were added. The mixture was stirred for 2 d at room temperature. 10 mL of dichloromethane and 30 mL of DI water were added, the phases were separated, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over $MgSO_4$, the solvent was evaporated, and the residual solid material was taken up on Celite and chromatographed (automated chromatography, 50 g of SiO_2 self-packed column with a gradient of 20−80% dichloromethane in petrol ether). Red, film forming solid. R_f (petrol ether/dichloromethane 1:1) = 0.78. Yield: 94.3 mg (114 μmol), 83%. Mp: 106 °C. NMR spectroscopy: Due to the dihydro tautomerism the aromatic signals are doubled, overlapping to complex multiplets. The integral over all aromatic signals affords the expected ratio of H_{arom}/H_{TIPS}. Ratio of different H_{TIPS}/H_{TIPS} side chains is 42:21, the two tautomers are in a ratio of 10:11 according to the integrals of the TIPS side chain. ^{1}H NMR (600 MHz, d_8-THF, 25 °C): δ (ppm) = 8.02 (s, H_{arom}), 7.96−7.90 (m, H_{arom}), 7.84−7.76 (m, H_{arom}), 7.60−7.53 (m, H_{arom}), 7.20−7.05 (m, H_{arom}), 6.93−6.89 (m, H_{arom}), 6.84−6.76 (m, H_{arom}), 6.57 (s, H_{arom}), 6.58−6.47 (m, H_{arom}), 6.43−6.37 (m, H_{arom}), 1.31−1.25 (m, 42H_{TIPS}), 1.19 (s, H_{TIPS}), 1.15 (s, H_{TIPS}). ^{13}C {^{1}H} NMR (150 MHz, d_8-THF, 25 °C): δ (ppm) = 144.1 (C_q), 143.7 (C_q), 143.4 (C_q), 142.0 (C_q), 142.0 (C_q), 141.8 (C_q), 141.5 (C_q), 139.9 (C_q), 139.8 (C_q), 139.2 (C_q), 138.9 (C_q), 132.5 (CH), 131.3 (CH), 128.9 (CH), 128.7 (CH), 128.44 (CH), 128.41 (CH), 128.3 (C_q), 128.1 (C_q), 128.0 (C_q), 127.9 (C_q), 127.4 (CH), 123.5 (CH), 123.4 (CH), 123.1 (C_q), 118.1 (C_q), 117.0 (C_q), 113.92 (CH), 113.91 (CH), 113.5 (CH), 107.3 (C_q), 106.3 (C_q), 105.1 (C_q), 105.0 (C_q), 104.8 (C_q), 104.7 (C_q), 18.9 (CH/CH_3), 18.7 (CH/CH_3), 18.6 (CH/CH_3), 11.4 (CH/CH_3), 11.34 (CH/CH_3), 11.31 (CH/CH_3). IR: ν (cm^{-1}) = 3372, 2941, 2890, 2863, 2148, 1611, 1595, 1575, 1454, 745. HR-MS (ESI^+): m/z calcd for $C_{51}H_{73}N_4Si_3$ $[M + H]^+$: 825.51430, found: 825.51390.

2-((Triisopropylylsilyl)ethynyl)-6,13-bis((triisopropylsilyl)-ethynyl)-5,7,12,14-tetraazapentacene (3). 3H$_2$ (36.6 mg, 44.3 μmol) was dissolved in 5 mL of chloroform, MnO_2 (154 mg, 1.77 mmol, 40 equiv) was added, and the suspension was stirred for 20 min at room temperature. The now green mixture was filtered, and the green solution was evaporated to yield a dark green material that was purified by column chromatography on silica (petrol ether/dichloromethane 1:1) to yield **3** as a dark green film. R_f (SiO_2 petrol ether/dichloromethane 1:1) = 0.64. Yield: 26.7 mg (32.4 μmol), 74%. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) = 8.34−8.30 (m, 1H), 8.25−8.20 (m, 2H), 8.16−8.12 (m, 1H), 7.87−7.82 (m, 2H), 7.81−7.77 (m, 1H), 1.42−1.35 (m, 42H), 1.24−1.20 (m, 21H). ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$, 25 °C): δ (ppm) = 145.6 (C_q), 145.5 (C_q), 145.0 (C_q), 144.9 (C_q), 143.2 (C_q), 144.0 (C_q), 143.0 (C_q),142.7 (C_q), 134.6 (CH), 133.7 (CH), 132.1 (CH), 130.6 (CH), 130.4 (CH), 127.3 (C_q), 123.0 (C_q), 122.9 (C_q), 112.9 (C_q), 112.6 (C_q), 106.5 (C_q), 103.0 (C_q), 102.9 (C_q), 98.5 (C_q), 19.0, 18.7, 11.7, 11.3. IR: ν (cm^{-1}) = 2941, 2863, 1614, 1526, 1459, 747. HR-MS (ESI^-): m/z calcd for $C_{51}H_{70}N_4Si_3$ $[M]^-$: 822.49083; found: 822.49082.

2-(Phenylethynyl)-6,13-bis((triisopropylsilyl)ethynyl)-*N,N′*-dihydro-5,7,12,14-tetraazapentacene (4H$_2$). In a Schlenk tube **1H$_2$** (100 mg, 138 μmol) was kept under an inert gas. 5 mL of degassed 2:1 THF/NEt_3 containing CuI (2.63 mg, 13.8 μmol, 0.1 equiv) and $Pd(PPh_3)_4$ (7.98 mg, 6.91 μmol, 0.05 equiv) were added. To the stirred solution, 152 μL (1.38 mmol, 10 equiv) of phenyl acetylene were added. The mixture was stirred for 2 d at room temperature. 10 mL of dichloromethane and 30 mL of DI water were added, the phases were separated, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over $MgSO_4$, the solvent was evaporated, and the residual solid material was taken up on Celite, followed by column chromatography (automated chromatography, 50 g of SiO_2 self-packed column with a gradient of 20−80% dichloromethane in petrol ether). Dark red solid. R_f (SiO_2, petrol ether/dichloromethane 1:1): 0.64. Yield: 91.5 mg (123 μmol), 89%. Mp: 262 °C. NMR spectroscopy: Due to the dihydro tautomerism the aromatic signals are doubled, overlapping to complex multiplets. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) = 8.10−8.05 (m, H_{arom}), 7.98−7.91 (m, H_{arom}), 7.89−7.83 (m, H_{arom}), 7.66−7.50 (m, H_{arom}), 7.41−7.34 (m, H_{arom}), 7.21−7.13 (m, H_{arom}), 7.10−7.05 (m, H_{arom}), 6.99−6.94 (m, H_{arom}), 6.83−6.77 (m, H_{arom}), 6.61 (s, H_{arom}), 6.54−6.47 (m, H_{arom}), 6.47−6.42 (m, H_{arom}), 1.30−1.25 (m, H_{TIPS}). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) = 144.1 (C_q), 143.8 (C_q), 143.5 (C_q), 143.3 (C_q), 142.0 (C_q), 141.7 (C_q), 141.5 (C_q), 139.9 (C_q), 139.1 (C_q), 131.7 (CH), 131.5 (CH), 131.1 (CH), 128.8 (CH), 128.5 (CH), 128.42 (CH),128.36 (CH), 128.2 (C_q), 128.1 (C_q), 128.0 (C_q), 127.2 (CH), 126.6 (CH), 123.5 (CH), 123.13 (C_q), 123.05 (C_q), 122.9 (C_q), 117.9 (C_q), 116.3 (CH), 114.0 (CH), 113.7 (CH), 105.2 (C_q), 104.84 (C_q), 104.80 (C_q), 99.3 (C_q), 99.2 (C_q), 99.2 (C_q), 99.1 (C_q), 97.5 (C_q), 97.3 (C_q), 96.73 (C_q), 96.69 (C_q), 91.3 (C_q), 89.7 (C_q), 89.3 (C_q), 88.7 (C_q), 18.92 (CH/CH_3), 18.90 (CH/CH_3), 11.4 (CH/CH_3). IR: ν (cm^{-1}) = 3373, 3057, 2940, 2862, 2140, 1595, 1575, 1447, 746. HR-MS (ESI^+): m/z calcd for $C_{48}H_{57}N_4Si_2$ $[M + H]^+$: 745.41218, found: 745.41323, correct isotope distribution.

2-(Phenylethynyl)-6,13-bis((triisopropylsilyl)ethynyl)-5,7,12,14-tetraazapentacene (4). 4H$_2$ (60.0 mg, 80.1 μmol) was dissolved in 5 mL of dichloromethane, and MnO_2 (69.6 mg, 801 μmol, 10 equiv) was added. The suspension was stirred for 20 min at room temperature. The now green mixture was filtered, and the green solution was evaporated to yield a dark green material that was purified by column chromatography on silica (petrol ether/dichloromethane 1:1) to yield **3** as a dark solid. R_f (petrol ether/dichloromethane 1:1) = 0.47. Yield: (48.5 mg, 65.3 μmol, 81%). Mp: 249 °C. ^{1}H NMR (600 MHz, d_8-THF, 25 °C): δ (ppm) = 8.35−8.33 (m, 1H), 8.23−8.18 (m, 3H), 7.96−7.94 (m, 1H), 7.94−7.90 (m, 2H), 7.69−7.66 (m, 2H), 7.47−7.43 (m, 3H), 1.41−1.38 (m, 42H). ^{13}C {^{1}H} NMR (150 MHz, d_8-THF, 25 °C): δ (ppm) = 146.6 (C_q), 146.5 (C_q), 146.1 (C_q), 145.9 (C_q), 144.3 (C_q), 144.2 (C_q), 144.1 (C_q), 143.8 (C_q), 135.4 (CH), 133.7 (CH), 133.5(CH), 133.0 (CH), 131.7 (CH), 131.4 (CH), 130.4 (CH), 129.7 (CH), 128.5 (C_q), 124.18 (C_q), 124.15 (C_q), 123.5 (C_q), 112.6 (C_q), 112.3 (C_q), 104.6 (C_q), 104.5 (C_q), 96.5 (C_q), 99.0 (C_q), 19.57 (CH/CH_3), 19.55 (CH/CH_3), 12.8 (CH/CH_3). IR: ν (cm^{-1}) = 3064, 2939, 2890, 2862, 2205, 1615, 880. HR-MS (ESI^+): m/z calcd for $C_{48}H_{55}N_4Si_2$ $[M + H]^+$: 743.39653, found: 743.39766, correct isotope distribution.

DOI: 10.1021/acs.joc.5b02115
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2-Ethynyl-6,13-bis((triisopropylsilyl)ethynyl)-*N*,*N*′-dihydro-5,7,12,14-tetraazapentacene (5H$_2$). **2H$_2$** (73.3 mg, 98.9 μmol) were dissolved in 20 mL of THF/MeOH 1:1, and the solution was degassed by bubbling N_2 through it. K_2CO_3 (68.3 mg, 494 μmol, 5 equiv) was added, and the suspension was stirred for 20 min. The reaction was quenched by addition of 30 mL of dichloromethane and 50 mL of DI water. The phases were separated, and the aqueous phase was extracted with dichloromethane (3 × 20 mL). The combined organic layers were dried over $MgSO_4$, the solvent was evaporated, and the residual red solid was purified by filtration over a short ALOX column (petrol ether/dichloromethane 1:1). R_f (SiO_2, petrol ether/dichloromethane 1:1) = 0.70. Yield: 56.1 mg (83.9 μmol), 85%. Mp: 240 °C. NMR spectroscopy: the compound is stable in solid form, but in solution it slowly decomposed to an unknown compound. Due to the dihydro tautomerism and generally large molecule, acquisition times were too long for an unambiguous ^{1}H NMR to be obtained. IR: ν (cm^{-1}) = 3381, 3310, 3061, 2941, 2864, 2143, 1612, 1596, 1575, 1576, 1452, 750. HR-MS (ESI$^+$): m/z calcd for $C_{42}H_{53}N_4Si_2$ [M + H]$^+$: 669.38088, found: 669.38166, correct isotope distribution.

2-(3′,6′-Diphenyl-[1,1′:2′,1″-terphenyl]-4′-yl)-6,13-bis((triisopropylsilyl)ethynyl)-*N*,*N*′-dihydro-5,7,12,14-tetraazapentacene (10H$_2$). **5H$_2$** (110 mg, 164 μmol) was dissolved in 4 mL of *o*-xylene and transferred to a microwave vessel. To this solution, tetraphenylcyclopentadienone (69.5 mg, 181 μmol, 1.10 equiv) and a stirring bar were added. The vessel was sealed (septum) and heated to 300 °C for 30 min under vigorous stirring. The solution was transferred to a round-bottom flask, the solvent was removed, and the residual material was subjected to column chromatography (SiO_2, petrol ether/dichloromethane 1:1). R_f (SiO_2, petrol ether/dichloromethane 1:1) = 0.75. Yield: 101 mg (164 μmol), 61%. NMR spectroscopy: Due to the tautomerism the aromatic signals are doubled, overlapping to complex multiplets. Due to the tetraphenylphenyl group, the signal pattern becomes too complex for separate signals to be distinguished. ^{1}H NMR (600 MHz, d_8-THF, 25 °C): δ (ppm) = 8.80−7.35 (m, 6H$_{arom}$), 7.25−6.15 (m, 26H$_{arom}$), 1.45−1.15 (m, 42H$_{TIPS}$). ^{13}C {^{1}H} NMR (150 MHz, d_8-THF, 25 °C): δ (ppm) = complex inseparable signal pattern in the aromatic region, 18.93 (CH/CH$_3$), 18.89 (CH/CH$_3$), 11.4 (CH/CH$_3$). IR: ν (cm^{-1}) = 3375, 3057, 3025, 2940, 2890, 2863, 2141, 1716, 1598, 1575, 1541, 1456, 1385, 1365, 1307, 1256, 1179, 1155, 1141, 1125, 1102, 1072, 1039, 1017, 996, 969, 918, 882, 864, 836, 806, 781, 760, 746. HR-MS (ESI$^+$): m/z calcd for $C_{70}H_{73}N_4Si_2$ [M + H]$^+$: 1025.53738, found: 1025.53521, correct isotope distribution.

2-(3′,6′-Diphenyl-[1,1′:2′,1″-terphenyl]-4′-yl)-6,13-bis((triisopropylsilyl)ethynyl)-5,7,12,14-tetraazapentacene (10). **10H$_2$** (77.5 mg, 75.6 μmol) was dissolved in 5 mL of chloroform. MnO_2 (263 mg, 3.02 mmol, 40 equiv) was added, and the mixture was stirred for 15 min at room temperature. The solid was filtered off, the solvent was evaporated, and the residual green material was subjected to column chromatography. R_f (SiO_2, petrol ether/dichloromethane 1:1) = 0.64. Yield: 43.8 mg (43 μmol), 57%. Mp: 187 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) = 8.27−8.20 (m, 3H), 8.14−8.07 (m, 1H), 7.86−7.81 (m, 3H), 7.45−7.41 (m, 1H), 7.26−7.17 (m, 5H), 7.04−6.81 (m, 15H), 1.45−1.32 (m, 42H). ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$, 25 °C): δ (ppm) = 146.7 (C$_q$), 145.5(C$_q$), 145.41 (C$_q$), 145.35 (C$_q$), 144.7 (C$_q$), 143.0 (C$_q$), 142.9 (C$_q$), 142.78 (C$_q$), 142.76 (C$_q$), 142.2 (C$_q$), 141.3 (C$_q$), 141.2 (C$_q$), 140.8 (C$_q$), 139.7 (C$_q$), 139.6 (C$_q$), 139.34 (C$_q$), 139.22 (C$_q$), 135.24 (CH), 134.21 (C$_q$), 131.94 (CH), 131.92 (CH), 131.6 (CH), 131.42 (CH), 131.40 (CH), 131.3 (CH), 130.53 (CH), 130.51 (CH), 130.0 (CH), 129.7 (CH), 129.5 (CH), 128.8 (CH), 127.7 (CH), 127.4 (CH), 127.0 (CH), 126.8 (CH), 126.5 (CH), 126.3 (CH), 125.8 (CH), 125.6 (CH), 122.8 (C$_q$), 122.7 (C$_q$), 112.3 (C$_q$), 112.1 (C$_q$), 103.0 (C$_q$), 103.0 (C$_q$), 19.00 (CH/CH$_3$), 18.95 (CH/CH$_3$), 11.7 (CH/CH$_3$). IR: ν (cm^{-1}) = 3059, 3026, 2940, 2924, 2891, 2863, 1721, 1620, 1601, 1577, 1530, 1495, 1462, 1441, 1384, 1364, 1327, 1311, 1266, 1250, 1225, 1172, 1149, 1135, 1115, 1073, 1021, 996, 963, 919, 882, 836, 818, 805, 794. HR-MS (ESI$^-$): m/z calcd for $C_{70}H_{70}N_4Si_2$ [M + H]$^+$: 1022.51390, found: 1022.51298, correct isotope distribution.

1,2-Bis(6,13-bis(triisopropylsilyl)ethynyl)-*N*,*N*′--5,7,12,14-tetraazapentacen-2-yl)ethyne (11H$_4$). Freshly prepared **5H$_2$** (91.6 mg, 137 μmol, 1.00 equiv) and **1H$_2$** (119 mg, 164 μmol, 1.20 equiv) were dissolved in 8 mL of dry THF and degassed. CuI (2.61 mg, 13.7 μmol, 0.20 equiv), $Pd(PhCN)_2Cl_2$ (5.25 mg, 13.7 μmol, 0.10 equiv), and HP(*t*-Bu)$_3$BF$_4$ (7.94 mg, 27.8 μmol, 0.20 equiv) were added to an oxygen-free mixture of THF/HN(*i*Pr)$_2$ 1:1 (8 mL) in this sequence. The catalyst solution was stirred for 5 min at room temperature and added to the educt solution. The mixture was stirred at 70 °C for 16 h. The reaction was quenched by addition of DI water (20 mL), and the mixture was extracted with dichloromethane (3 × 30 mL). The combined organic layers were dried over anhydrous $MgSO_4$, the solvent was evaporated, and the residual material was subjected to column chromatography (SiO_2, petrol ether/dichloromethane 2:3). R_f (SiO_2, petrol ether/dichloromethane 2:3) = 0.52. Yield: 56.0 mg (42.7 μmol), 31%. Due to the complex tautomerism, meaningful NMR spectroscopy is best carried out after oxidation to **11**. IR: ν (cm^{-1}) = 3375, 3061, 2940, 2889, 2862, 2141, 1727, 1596, 1574, 1447, 1383, 1366, 1339, 1309, 1290, 1259, 1221, 1099, 1073, 1014, 995, 919, 880, 829, 799, 747. HR-MS (MALDI$^+$): m/z calcd for [M − 2H + H]$^+$ ($C_{82}H_{101}N_8Si_4$): 1309.72263, found: 1309.72208.

1,2-Bis(6,13-bis(triisopropylsilyl)ethynyl)-5,7,12,14-tetraazapentacen-2-yl)ethyne (11). **11H$_4$** (25.1 mg, 19.1 μmol, 1.00 equiv) was dissolved in chloroform. MnO_2 (500 mg, 5.74 mmol, 300 equiv) was added, followed by stirring for 10 min at room temperature, and the solid residue was removed by filtration. The solvent was removed, and the residual dark material was subjected to column chromatography (SiO_2, petrol ether/dichloromethane 3:2). ^{1}H NMR (600 MHz, d_8-toluene, 70 °C): δ (ppm) = 8.59−8.54 (m, 2H), 8.17−8.07 (m, 6H), 7.55−7.48 (m, 2H), 7.28−7.23 (m, 4H), 1.62−1.50 (m, 82H). Solubility too low for ^{13}C NMR. IR: ν (cm^{-1}) = 3067, 2940, 2889, 2862, 1723, 1617, 1523, 1490, 1461, 1435, 1383, 1362, 1324, 1310, 1259, 1233, 1222, 1169, 1135, 1114, 1073, 1020, 994, 920, 881, 831, 816, 748. HR-MS (MALDI$^-$): m/z = 1306.70197, calcd for [M]$^-$ ($C_{82}H_{98}N_8Si_4$): 1306.6992.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02115.

Optical spectra (UV−vis, IR), electrochemical measurements, microscopical images, NMR spectra, and a closer investigation of the redox-coupling chemistry (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

F.L.G. thanks the Studienstiftung des Deutschen Volkes for support through a Ph.D-scholarship. U.B. thanks the Deutsche Forschungsgemeinschaft for generous financial support (DFG Bu771/7-1).

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