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Halogenated Symmetrical Tetraazapentacenes: Synthesis, Structures, and Properties

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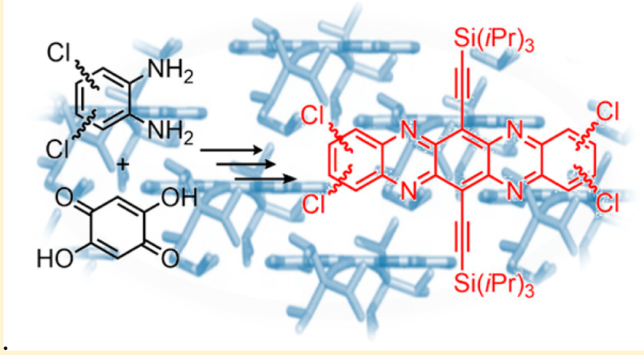
Ⓢ *Supporting Information*

ABSTRACT: We herein describe the synthesis and property evaluation of several brominated and chlorinated tetraazapentacenes. The targets were obtained by thermal condensation of 2,5-dihydroxyquinone with 4,5-dichloro-, 2,6-dichloro-, and 4,5-dibromo-1,2-phenylenediamine, followed by oxidation with hot acidic dichromate. Double alkynylation, reductive deoxygenation, and subsequent oxidation using MnO_2 furnishes the target compounds. Absorption spectra, electrochemistry, and single crystal structures of the targets are reported. The 1,4,8,11-tetrachlorotetraazapentacene (1,4,8,11-tetrachloroquinoxalino[2,3-*b*]phenazine) carrying its chlorine atoms in the peri-positions packs in a herringbone type arrangement, while the isomer (2,3,9,10-tetrachloroquinoxalino[2,3-*b*]phenazine, with the chlorine atoms in the east and west positions) packs in one-dimensional stacks. In all cases, the reduction potentials and the calculated LUMO-positions are decreased by the introduction of the halogen atoms.



INTRODUCTION

In this paper, we show the preparation of three halogenated symmetrical tetraazapentacenes and investigate their spectroscopic and structural properties. Azaacenes are an old class of compounds that have first been investigated more than 120 years ago by Fischer and Hepp.[1] A bit later, Hinsberg published an in depth study of azaacenes. He noted that *ortho*-dihydroxyarenes condense with *ortho*-diaminoarenes into azaacenes with three and four annelated six-membered rings. If five six-membered rings are formed, *N,N′*-dihydro compounds result, which could not be oxidized into azapentacenes.[2] Only much later, in 1967, the groups of Zimmermann and Leete prepared the first azapentacenes. They oxidized the dihydropyrazine compounds with lead dioxide or chloranil instead of acidic dichromate solution, which was normally used. Dichromate overoxidizes and gives the azapentacenequinones—also useful starting materials for other derivatives of the azaacenes.[3] In recent years, the chemistry and physics of the azaacenes have been pulled from the backwaters;[4] their properties as electron transporting materials have given them a privileged position as organic materials for electronics applications.[5] A series of reviews have been published dealing with the history of the field[6] and current developments,[7] but also applications beyond the azaacens' use as n-semiconducting, i.e., electron transporting materials.[8] Houk and Winkler first proposed that larger azaacenes with more than two nitrogen atoms in their perimeter should be attractive electron transport materials.[9] This is true for the symmetrical tetraazapentacene **1c**, which was synthesized in 2009 and has been employed by Miao et al. as a powerful electron transporting material in thin film transistors.[10] The electron affinity and the packing of **1c** in combination with the observed morphologies make **1c** attractive. However, the reported high electron mobilities with **1c** were achieved running the thin film transistors under vacuum. This prevents the formation of potential trap states by oxidation of intermediate anionic charge states with oxygen. One might suppress trap states also by increasing the electron affinity of the tetraazapentacenes. Therefore, suitable projected targets would be **1a,b** and **11**. In these tetraazapentacenes, the electron affinity is increased through the presence of the electron accepting halogen substituents, as calculated by Kuo et al.[11] While the attachment of electronegative substituents will not guarantee an increased device performance, it is still an important synthetic challenge to prepare such halogenated tetraazapentacenes.[12] Halogenated azaacens could also be used as building blocks for further elaboration of the azaacene nucleus, as halogen substituents should be easily substituted using common cross-coupling protocols.[13]

RESULTS AND DISCUSSION

Synthesis. Starting from the diamines **2a,b** thermal condensation with **3** either neat at 160 °C for the chloride or at 100 °C in acetic acid for the dibromide **2b** furnishes the coupling products; after thoroughly washing with water in the

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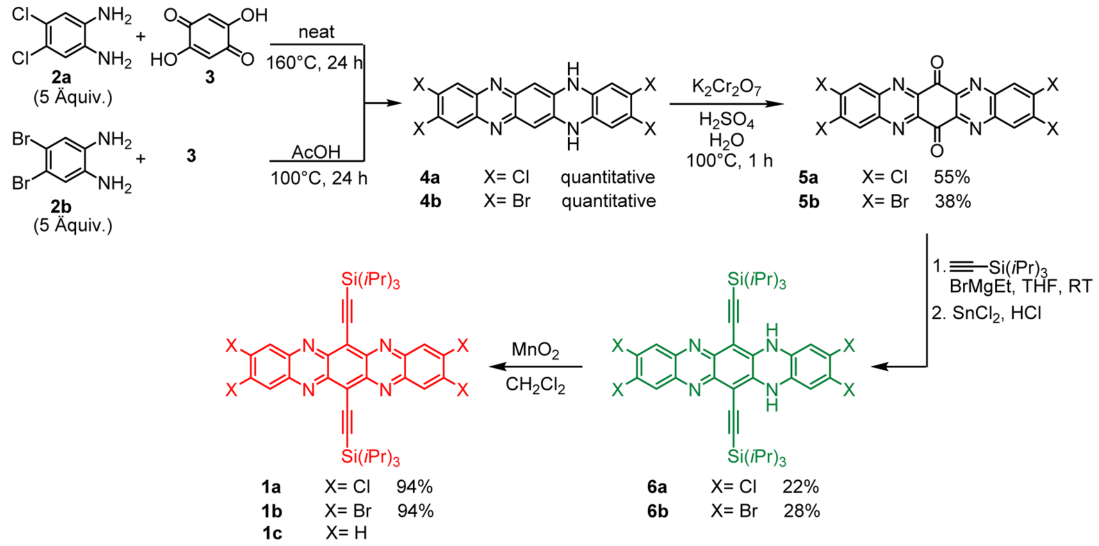
Scheme 1. Synthesis of the Tetrahalotetraazapentacenes 1a and 1b



case of **4b** and acetone, diethyl ether and THF the crude azaacenes **4a,b** were obtained in quantitative yields (Scheme 1). Washing was continued until the solutions of **4a,b** in sulfuric acid showed a deep blue color without a gray haze. Further oxidation, employing dichromate in dilute, hot sulfuric acid accesses **5a** in 55%, while **5b** only forms in 38% yield from **4b**. Reaction of **5a,b** with the Grignard reagent of TIPS-acetylene is followed by treatment with tin chloride, similar to the sequence described by Anthony et al. for the preparation of TIPS-pentacene.[14] The reaction works better if the tin chloride is used in the presence of HCl. The compounds **6a** and **6b** are isolated in a yield of 22% and 28% each. Facile oxidation with manganese dioxide delivers the targets **1a** and **1b** in excellent yields.

In an extension of this concept, we executed the synthesis of the isomeric tetrachloride **11** (Scheme 2). Here **7** is condensed with **3**. This reaction did work after careful optimization (Table 1) of the conditions. Microwave irradiation (200 °C) in the presence of 2.5 mol % TsOH for 2 h produced **8** in 73% after workup and purification. Acidic hot dichromate then oxidizes **8** into **9**. A modified Anthony-alkynylation with $SnCl_2$ under acidic conditions generates the *N*,*N*′-dihydrotetraazaacene **10**, which is oxidized by MnO_2 to give target molecule **11** in 66% yield. Overall not a high yield, but a serviceable route.

Scheme 2. Synthesis of the Isomeric Tetrachlorotetraazapentacene 11 Using Classical Condensation Methods

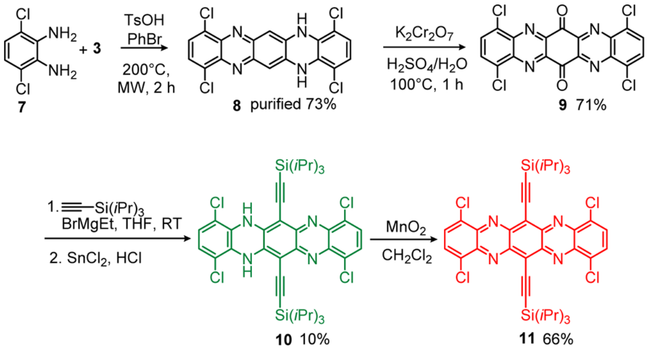


Table 1. Optimization of the Condensation of 7 to 4 under Microwave Conditions

	7 (equiv.)	TsOH (mol %)	time (min)	temperature (°C)	c(7) (mmol/L)	yield[a] (%)
1	2.5	70	60	250	62.5	0
2	4	100	90	250	125	0
3	4	300	60	150	62.5	0
4	4	300	240	200	62.5	51
5	4	20	90	200	62.5	38
6	4	5	240	200	62.5	48
7	2.5	5	120	200	83.3	60

[a] Raw yield after washing with ethyl ether.

Optical Properties. Figure 1 displays the absorption and emission spectra of the three *N*,*N*′-dihydrotetrazapentacenes **10**, **6a**, and **6b**. The compounds are fluorescent and show a small Stokes shift. Their absorption maxima is around 520–540 nm, with **6a,b** showing similar optical properties. Compound **11** displays somewhat blue-shifted optical features. Table 2 shows all of the optical and electronic properties of **6a,b** and **11** in condensed form.

Upon oxidation into **1a–c** and **11**, the fluorescence disappears, and the azaacenes form dark green solutions. The halogen substituents induce a significant effect upon the optical properties of the tetraazapentacene-nucleus (Figure 2). All three of the halogenated tetraazaacenes, **1a,b** and **11** (Figure 3) show a red-shifted absorption compared to that of the simple tetraazapentacene **1c.** Table 3 shows an overview over the optical and electrochemical measurements and the DFT calculations. Optical and electrochemical data are well correlated. Comparison of the experimental and the quantum chemical results do not give the correct trend. As the differences in the electronic properties between the three target molecules are only subtle, and the differences do not exceed 0.1 eV, one should neglect them. For example, from simple DFT-calculations the optical gap for **11** is calculated to be a tad larger than that for **1a,b**, which are identical. Experimentally, **11** shows an absorption spectrum that is a bit red-shifted from that of **1a,b**, which are both very similar.

To investigate electronic ground-state interaction of these azaacenes in the solid state, we prepared thin films of **1a** and **11** and took their UV–vis spectra (Figure 4). Compound **1a** shows a

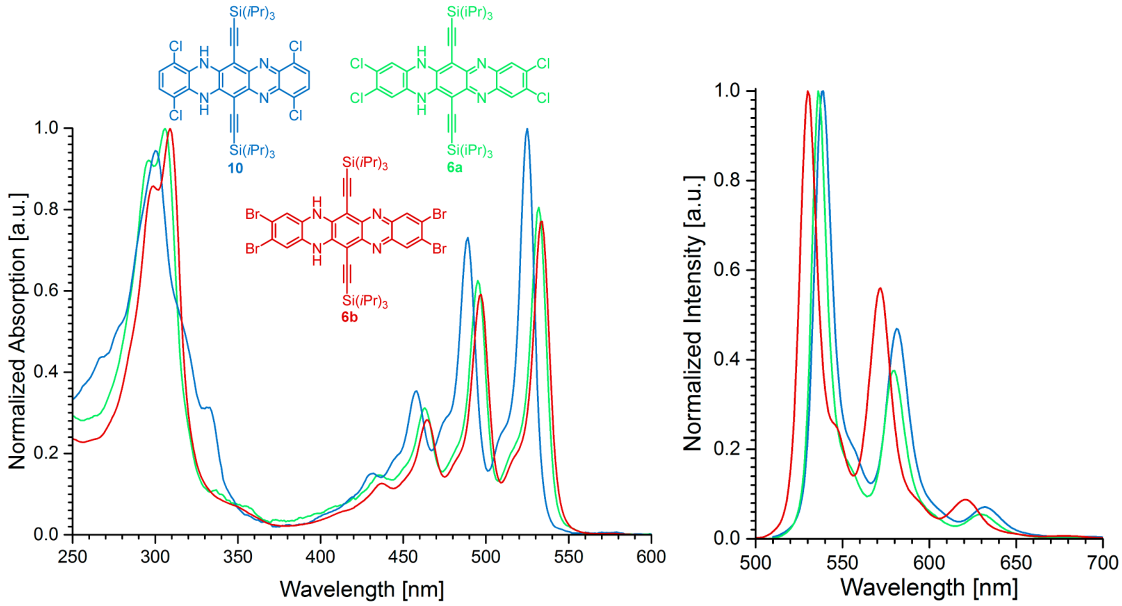


Figure 1. Absorption and emission spectra of the *N,N′*-dihydrotetraazaacenes.

Table 2. Electronic and Optical Properties of the *N,N′*-Dihydrotetraazaacenes 6a,b and 11

compound	opt. gap (nm/eV)	stokes shift (nm/cm^{-1})	theor. E_{HOMO} (eV)	theor. E_{LUMO} (eV)	theo. gap (eV)
6a	541/2.29	4	−5.7[a]	−3.0[a]	2.7[a]
6b	543/2.28	5	−5.7[a]	−3.0[a]	2.7[a]
11	534/2.32	5	−5.7[a]	−3.0[a]	2.7[a]

[a] B3LYP 6-31G*//6-311++G**; TIPS-groups were substituted by TMS-groups.

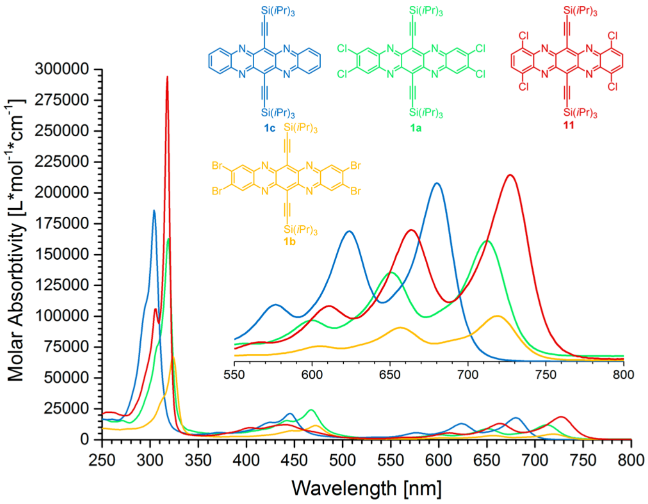


Figure 2. Absorption spectra of the compounds **1a**–**c** and **11**. The UV–vis spectrum of **1c** is added for clarity.

larger red-shift in the long wavelength region of the absorption when going from solution into the solid state. The average bathochromic shift for **1a** is 25.7 nm (87.0 meV, 701 cm^{-1}) and for **1b** 9.3 nm (24.5 meV, 198 cm^{-1}). These results suggest an increased electronic interaction of the molecules of **1a** in the solid state, when comparing to molecules of **11** in thin films. In both cases, the relative absorption strength in the long wavelength region increases relatively in the solid state.

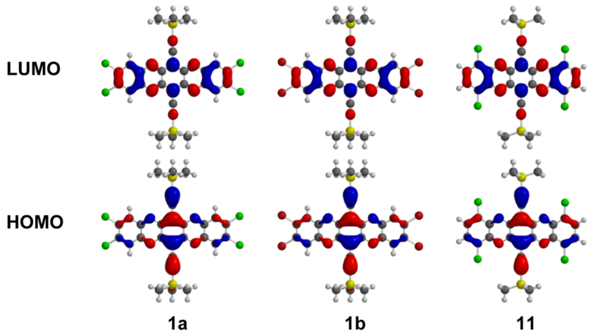


Figure 3. Frontier molecular orbitals (FMO) of **1a,b** and **11** (B3LYP 6-31G*//6-311++G**). The theoretically determined positions of the FMOs correlate well with the oxidation potentials and the reduction potentials of the tetraazapentacens.

Single Crystal X-ray Structures. Tables 4 and 5 and Figures 5–7 display the results of the single crystal X-ray structures of **6a,b** and **10** and **1a,b** and **11**. In the case of the dihydroazaacenes, we only discuss the structure of **10**. It is remarkable insofar as it has a relatively low density and incorporates crystal solvent. That is normally not observed. The chloroform molecules are located between the stacks. The ethynyle arms are strongly bent. Both observations suggest that the observed pseudobrick wall motif for **10** is hardly favored. On the contrary, the crystal structures of **6a,b** are roughly similar to that of TIPS-pentacene and show both a brick wall motif, even though they are not equal (for illustrated structures see SI).

Upon oxidation, the compounds **1a,b** still pack in a brick wall motif, but the solid-state structure of the compound **11** changes. Similar to **6a** (FigureS 2), **1a** packs in a brick wall motif with intra stack distances of 3.34 and 3.36 Å (Figure 6). A smaller overlap but a shorter distance exists to neighboring molecules of a different stack (3.25 Å).[15] The interlayer distances within a stack increase to 3.42 and 3.44 Å when bromides are attached to the azaacene core in **1b**. Neighbor molecules from different stacks show a distance of 3.37 Å for **1b** (FigureS 1).

In crystals of the compound **11** (Figure 7), we do not find a brick wall motif but a tight herringbone packing. The face-to-face

Table 3. Optical and Electrochemical Properties of the Tetraazapentacenes 1a,b and 11

verb.	$E^{0/-1}$ (V)	$E^{-1/-2}$ (V)	opt. gap (nm/eV)	exp. E_{LUMO} (eV)	exp. E_{HOMO} (eV)	calcd. E_{LUMO} (eV)	calcd. E_{HOMO} (eV)	gap (eV)
1a	−0.6[a]	−1.2[a]	737/1.68	−4.2[b]	−5.8[c]	−4.2[d]	−5.9[d]	1.6[d]
1b	−0.7[a]	−1.2[a]	744/1.67	−4.1[b]	−5.8[c]	−4.2[d]	−5.9[d]	1.6[d]
11	−0.6[a]	−1.0[a]	752/1.65	−4.2[b]	−5.9[c]	−4.1[d]	−5.9[d]	1.8[d]

[a] Cyclic voltammetry was performed in THF with a Pt work electrode and Bu_4NPF_6 as conducting salt. [b] E_{LUMO} (in eV) = −4.8 eV − ($E^{0/-1}$). [c] E_{HOMO} (in eV) = E_{LUMO} (in eV) − [λ_{max} (in eV)]. [d] B3LYP 6-31G*//6-311++G**; TIPS-groups were replaced by TMS-groups.

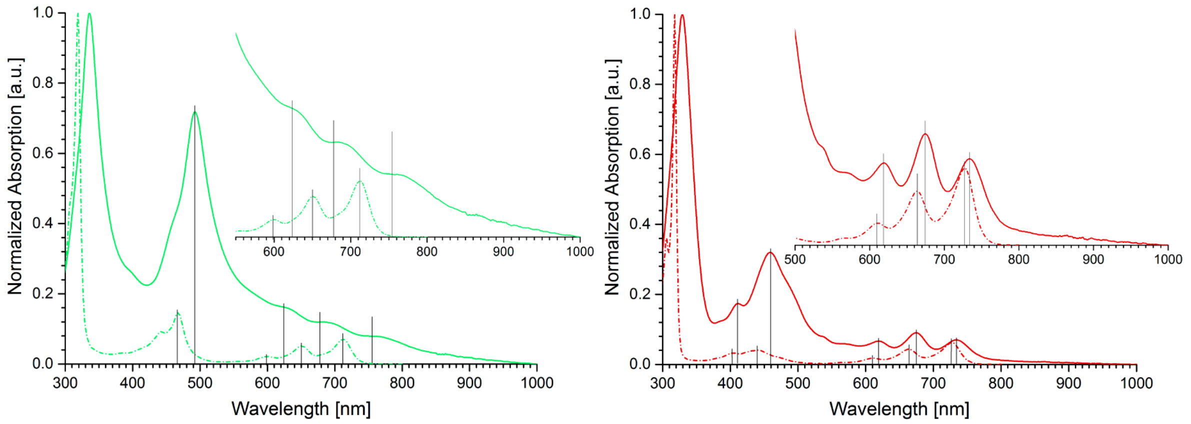


Figure 4. UV−vis spectra in thin films of **1a** (left) and **11** (right) as solid lines; for comparison, the solution-state spectra are shown as dashed lines.

Table 4. Unit Cell Data of the Halogenated Dihydro Species 6a,b and 10

cpd.	space group.	*a* (Å)	*b* (Å)	*c* (Å)	*α* (deg)	*β* (deg)	*γ* (deg)	*V* (Å^3)	*V*/*Z* (Å^3)
6a	$P\bar{1}$	10.10	12.39	17.94	97.22	102.46	101.81	2112.5	1056.2
6b	$P\bar{1}$	7.20	8.97	17.43	81.59	82.05	77.79	1082.2	1082.2
10	$P\bar{1}$	8.78	8.82	29.94	88.07	87.81	76.75	2253.0	1126.5

Table 5. Unit Cell Data of the Azaacenes 1a,b and 11

cpd.	space group.	*a* (Å)	*b* (Å)	*c* (Å)	*α* (deg)	*β* (deg)	*γ* (deg)	*V* (Å^3)	*V*/*Z* (Å^3)
1a	$P\bar{1}$	10.07	12.36	17.96	96.91	102.29	102.70	2097.7	1048.9
1b	$P\bar{1}$	10.28	12.58	17.97	96.23	103.75	102.90	2168.4	1084.2
11	$P\bar{1}$	8.66	14.10	17.11	77.91	85.32	87.28	2034.0	1017.0

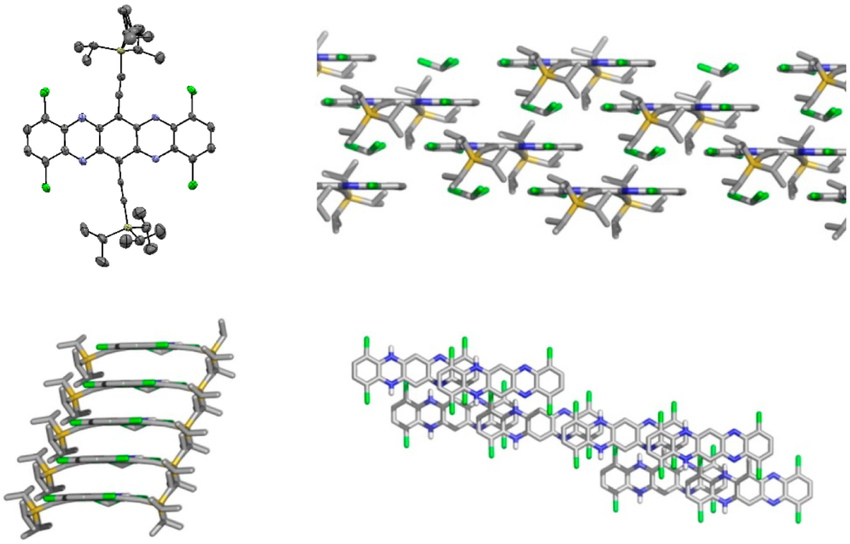


Figure 5. Compound **10** packs in one-dimensional stacks with relatively large distances between the stacks. Inclusion of chloroform is the consequence. The ellipsoid displacement shown at the 50% probability level.

distances of neighboring molecules are relatively short 3.34 and 3.37 Å.[15] The para substitution leads to one-dimensional stacks that are oriented with respect to each other like herringbones. This packing is very different from that observed for the similar

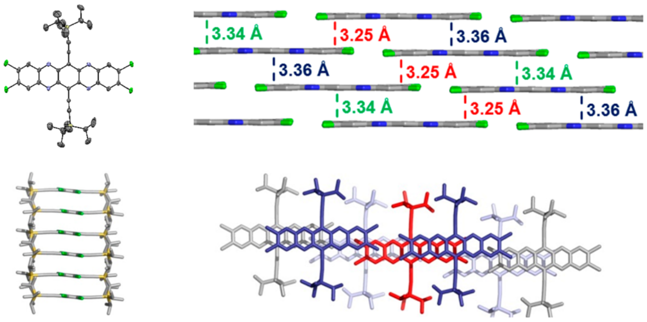


Figure 6. Compound **1a** packs in two-dimensional brick wall motif. The ellipsoid displacement shown at the 50% probability level.

1,4,8,11-tetramethyl(bistri-*iso*-propylsilylethynyl)pentacene, which shows an almost identical molecular shape but packs in 2D slipped stacks.[16]

■ CONCLUSIONS

In this contribution, we have shown that it is synthetically possible to attach four halogen atoms onto the perimeter of the symmetrical tetraazapentacene. The targets are obtained by a classic condensation/oxidation/alkynylation/deoxygenation/oxidation strategy, slightly modified from that of the synthesis of the parent tetraazapentacene. The targets are reasonably stable and show red-shifted absorption spectra and could be characterized using cyclic voltammetry and single crystal X-ray crystallography. Their solid-state structures look attractive for use in thin film transistors, and results of this investigation will be presented elsewhere. This classic method allows the synthesis of symmetrically substituted tetraazapentacenes in a well-controlled and easily expandable way—dependent only upon the availability of the necessary phenylenediamine building blocks. The lowering of the LUMO positions suggest that these targets are attractive candidates as electron transport materials for organic electronic devices.

■ 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. 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. ^{1}H NMR spectra were recorded on a 300, 400, or 600 MHz spectrometer and ^{13}C NMR spectra on a 100, 125, or 150 MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to traces of $CDCl_3$ or DMSO-d_6 accordingly in the corresponding deuterated solvent.[17] Mass spectra were recorded using electron impact ionization, direct analysis in real time or electrospray ionization methods with detection by FT-ICR techniques. Crystal structure analysis was accomplished using diffractometers with Mo Kα radiation. Infrared (IR) spectra are reported in wavenumbers (cm^{-1}) and were recorded in the solid state. Absorption spectra and emission spectra were recorded in hexane. Cyclic voltammetry was performed in dry and degassed THF using Bu_4NPF_6 as the conducting salt.

General Procedure 1 (GP1). In a heatgun-dried Schlenk tube purged with nitrogen tri-*iso*-propyle acetylene was dissolved in THF and cooled to 0 °C. A solution of EtMgBr in THF (0.77 M) was added slowly, and the mixture was warmed to ambient temperature. After being stirred for 1 h, the quinone was added forming a green suspension, which was stirred overnight (16 h). The reaction was quenched by adding a few drops of conc. HCl and diethyl ether (20 mL), the layers were separated, and the aqueous layer was extracted three times with diethyl ether. The combined organic layers were washed with aqueous NH_4Cl solution, water, and brine, and the solvents were evaporated until a solution with a total volume of about 20 mL was obtained. To the mixture was added a saturated solution of $SnCl_2$ in conc. HCl (2.5 mL) resulting in a dark blue solution which was stirred overnight (16 h). The solution was then neutralized via slow addition of an equimolar amount of 10 M NaOH and a small amount of saturated $NaHCO_3$ solution. This was followed by extraction with diethyl ether. The organic layers were combined, washed with water, saturated sodium bicarbonate solution, and brine. The solvents were removed under reduced pressure. The reaction mixture was purified by flash column chromatography yielding the desired product.

General Procedure 2 (GP2). The appropriate *N*,*N*′-dihydroazaacene was dissolved in dichloromethane (1.00 mL per 20.0 mg of the dihydroacene) and an excess (800 w% of the *N*,*N*′-dihydroazaacene) of MnO_2 was added. After 1 h, the reaction mixture was filtered through diatomaceous earth, and the filtrate was evaporated under reduced pressure. Flash column chromatography yielded the pure product.

*2,3,9,10-Tetrachloro-5,14-dihydroquinoxalino[2,3-b]phenazine (**4a**).* Under a nitrogen atmosphere in a Schlenk tube a finely ground mixture of compounds **2a** (2.94 g, 16.6 mmol, 4.00 equiv) and **3** (588 mg, 4.14 mmol, 1.00 equiv) was heated to 160 °C overnight (16 h). The resulting solid was ground with acetone and isolated by filtration. **4a** was obtained by washing of the filtration residue with aceton, diethyle ether, and THF until the filtrate was colorless. The product was yielded after drying *in vacuo* as a black solid (mp >350 °C, 1.75 g, 4.14 mmol, quant.). ^{1}H NMR (300.51 MHz, DMSO-d_6, 25 °C): δ = 6.71 (s, 2H), 6.94 (s, 2H), 7.11 (s, 2H), 7.28 (s, 2H). ^{13}C NMR: Due to insolubility no spectra could be recorded. IR-neat: ν [cm^{-1}] = 1609, 1574, 1514, 1481, 1448, 1427, 1398, 1394, 1301, 1286, 1268, 1217, 1204, 1109, 1083, 980, 937, 931, 846, 827, 667, 601. UV−vis: λ_{max} (DMF) = 558 nm. HR-MS (Electron impact ionization, EI): $[M]^+ = C_{18}H_8N_4{}^{35}Cl_4$ calcd. 419.9503 found 419.9534, correct isotope distribution.

*2,3,9,10-Tetrachloroquinoxalino[2,3-b]phenazine-6,13-dione (**5a**).* **4a** (1.75 g, 4.14 mmol, 1.00 equiv) was dissolved in a mixture of water and sulfuric acid (35 mL/145 mL), and potassium dichromate (5.85 g, 19.9 mmol, 4.80 equiv) was added under vigorous stirring. The

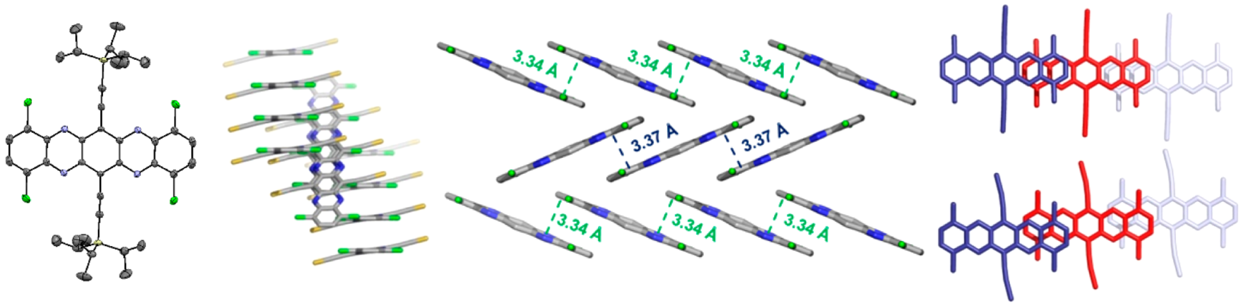


Figure 7. Compound **11** packs in a tight herringbone motif in the solid, crystalline state (side groups are omitted for clarification). The ellipsoid displacement shown at the 50% probability level.

solution was heated to reflux for 1 h, then poured onto ice and isolated by filtration. The filtration residue was washed with water and acetone and dried in vacuo. Compound **5a** was obtained as a brown solid (mp >350 °C, 1.03 g, 2.29 mmol, 55%). ^{1}H NMR (300.51 MHz, DMSO-d_6, 25 °C): $\delta = 8.86$ (s, 4H). ^{13}C NMR: Due to insolubility no spectra could be recorded. IR-neat: ν [cm^{-1}] = 3074, 1716, 1589, 1535, 1441, 1417, 1391, 1346, 1331, 1172, 1103, 1058, 982, 880. HR-MS (Electron impact ionization, EI): $[M]^+ = C_{18}H_4O_2N_4{}^{35}Cl_4$ calcd. 447.9083 found 447.9117, correct isotope distribution.

*2,3,9,10-Tetrachloro-6,13-bis[(tripropan-2-ylsilyl)ethynyl]-5,14-dihydroquinoxalino[2,3-b]phenazine (**6a**).* **GP1** was carried out with quinone **5a** (100 mg, 222 μmol, 1.00 equiv), tri-*iso*-propylsilyl acetylene (97.6 g, 530 μmol, 2.40 equiv) and EtMgBr (0.86 M in THF, 541 μL, 466 μmol, 2.10 equiv) in THF (4 mL). The purified product **6a** was obtained after flash column chromatography (R_f (**6a**) = 0.17 (PE/CH_2Cl_2 = 3:1), silica gel, PE/CH_2Cl_2) as red solid material (decomp. > 180 °C, 37.9 mg, 48.4 μmol, 22%).

^{1}H NMR (300.51 MHz, $CDCl_3$, 25 °C): $\delta = 1.23-1.27$ (m, 42H), 6.53 (s, 2H), 7.06–7.10 (s, 2H), 8.00 (s, 2H). ^{13}C {^{1}H} NMR (125.76 MHz, $CDCl_3$, 25 °C): $\delta = 11.5$, 19.0, 98.2, 98.5, 106.2, 115.1, 126.3, 127.8, 129.5, 132.9, 138.9, 141.0, 144.0. IR-neat: ν [cm^{-1}] = 3378, 3606, 2955, 2936, 2888, 2862, 2132, 1597, 1576, 1455, 1415, 1388, 1367, 1287, 1197, 1112, 1019, 992, 916, 875, 844, 757, 699, 675, 646, 623, 572, 523, 493, 482, 455. UV–vis: λ_{max} (hexane) = 532 nm, Extinction coefficient: ε(532 nm) = 12 929 L·mol^{-1}·cm^{-1}, Fluorescence: λ_{max} (hexane) = 536 nm. HR-MS (Electrospray ionization, ESI): $[M + H]^+ = C_{40}H_{49}{}^{35}Cl_3{}^{37}ClN_4Si_2$ calcd. 783.2215 found 783.2222, correct isotope distribution. Crystal data: CCDC number 1439300, red crystal (plate), dimensions 0.45 × 0.29 × 0.04 mm^3, crystal system triclinic, space group $P\bar{1}$, Z = 2, $a = 10.1041(12)$ Å, $b = 12.3922(14)$ Å, $c = 17.938(2)$ Å, $\alpha = 97.224(2)°$, $\beta = 102.464(2)°$, $\gamma = 101.810(2)°$, V = 2112.5(4) Å^3, $\rho = 1.237$ g/cm^3, $T = 200(2)$ K, $\theta_{max} = 25.68°$, 34291 reflections measured, 8016 unique ($R_{int} = 0.0708$), 4758 observed ($I > 2\sigma(I)$), $\mu = 0.37$ mm^{-1}, $T_{min} = 0.85$, $T_{max} = 0.99$, 484 parameters refined, hydrogen atoms were treated using appropriate riding models, except of those at the partially occupied crystal water, which were not considered in the model, goodness of fit 1.04 for observed reflections, final residual values $R1(F) = 0.058$, $wR(F^2) = 0.117$ for observed reflections, residual electron density −0.33 to 0.24 eÅ^{-3}.

*2,3,9,10-Tetrachloro-6,13-bis[(tripropan-2-ylsilyl)ethynyl]-quinoxalino[2,3-b]phenazine (**1a**).* **GP2** was carried out with dihydroazaacene **6a** (50.0 mg, 63.9 μmol). The purified product **1a** was obtained after flash column chromatography (R_f (**1a**) = 0.84 (PE/EE = 9:1), silica gel, PE/CH_2Cl_2) as dark green solid (mp >230 °C decomp., 47.0 mg, 60.2 μmol, 94%). ^{1}H NMR (300. Thirteen MHz, $CDCl_3$, 25 °C): $\delta = 1.34-1.37$ (m, 42H), 8.35 (s, 2H). ^{13}C {^{1}H} NMR (125.76 MHz, $CDCl_3$, 25 °C): $\delta = 11.8$, 19.1, 102.6, 114.6, 123.5, 130.5, 137.9, 143.2, 143.9. IR-neat: ν [cm^{-1}] = 3067, 2954, 2937, 2923, 2887, 2862, 1463, 1433, 1411, 1365, 1252, 1209, 1127, 1085, 1030, 992, 918, 871, 801, 756, 697, 673, 645, 557, 525, 490, 455, 433, 417, 406. UV–vis: λ_{max} (hexane) = 721 nm. Extinction coefficient: ε(721 nm) = 11278 L·mol^{-1}·cm^{-1}. Fluorescence: λ_{max} (hexane) = 724 nm. HR-MS (Electrospray ionization, ESI): $[M + H]^+ = C_{40}H_{47}{}^{35}Cl_3{}^{37}ClN_4Si_2$ calcd. 781.2058 found 781.2074, correct isotope distribution. Crystal data: CCDC number 1439298, green crystal (plate), dimensions 0.470 × 0.060 × 0.020 mm^3, crystal system triclinic, space group $P\bar{1}$, Z = 2, $a = 10.0700(13)$ Å, $b = 12.3582(16)$ Å, $c = 17.963(2)$ Å, $\alpha = 96.914(4)°$, $\beta = 102.292(4)°$, $\gamma = 102.701(4)°$, $V = 2097.7(5)$ Å^3, $\rho = 1.249$ g/cm^3, $T = 200(2)$ K, $\theta_{max} = 23.256°$, 19043 reflections measured, 6035 unique ($R_{int} = 0.0756$), 3507 observed ($I > 2\,\sigma\,(I)$), $\mu = 0.37$ mm^{-1}, $T_{min} = 0.86$, $T_{max} = 0.96$, 456 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.07 for observed reflections, final residual values $R1(F) = 0.072$, $wR(F^2) = 0.153$ for observed reflections, residual electron density −0.37 to 0.62 eÅ^{-3}.

*2,3,9,10-Tetrabromo-5,14-dihydroquinoxalino[2,3-b]phenazine (**4b**).* A finely ground mixture of diamino dibromobezene **2b** (3.00 g, 11.3 mmol, 4.00 equiv) and dihyroxy-*para*-quinone **3** (400 mg, 2.80 mmol, 1 equiv) was moistened with acetic acid (1.50 mL). The resulting mixture was heated to 100 °C for 20 h. After cooling to room temperature, washing several times with water, acetone, diethyl ether, and THF gave the product **4b** as black solid (mp >350 °C, 1.66 g, quant.)

^{1}H NMR (300.51 MHz, DMSO-d_6, 25 °C): $\delta = 6.38$ (s, 2H), 6.94 (s, 2H), 7.10 (s, 2H), 7.27 (s, 2H). ^{13}C NMR: Due to insolubility no spectra could be recorded. IR-neat: ν [cm^{-1}] = 3249, 1511, 1474, 1443, 1418, 1365, 1293, 1195, 1094, 1037, 941, 876, 837, 450. UV–vis: λ_{max} (DMF) = 564 nm. HR-MS (Direct Analysis in Real Time, DART): $[M + H]^+ = C_{18}H_9N_4{}^{79}Br_4$ calcd. 596.7555 found 596.7562, correct isotope distribution.

*2,3,9,10-Tetrabromoquinoxalino[2,3-b]phenazine-6,13-dione (**5b**).* **4b** (500 mg, 833 μmol, 1.00 equiv) was dissolved in a mixture of water and sulfuric acid (120 mL/40 mL), and potassium dichromate (1.18 g, 4.00 mmol, 4.80 equiv) was added under vigorous stirring. The solution was heated to reflux for 1 h, then poured onto ice and filtered. The filtration residue was washed with water until the filtate was colorless, acetone and dried in vacuo. Compound **5b** was obtained as a brown solid (mp >350 °C, 198 mg, 317 μmol, 38%). ^{1}H NMR: Due to insolubility no spectra could be recorded. IR-neat: ν [cm^{-1}] = 1707, 1626, 1441, 1389, 1326, 1123, 1082, 1050, 930, 876, 702, 605. HR-MS (Direct Analysis in Real Time, DART): $[M + H]^+ = C_{18}H_5N_4O_2{}^{79}Br_4$ calcd. 624.7141 found 624.7163, correct isotope distribution.

*2,3,9,10-Tetrabromo-6,13-bis[(tripropan-2-ylsilyl)ethynyl]-5,14-dihydroquinoxalino[2,3-b]phenazine (**6b**).* **GP1** was carried out with quinone **5b** (120 mg, 191 μmol, 1.00 equiv), tri-*iso*-propylsilyl acetylene (172 μL, 140 mg, 764 μmol, 4.00 equiv) and EtMgBr (778 μL, 0.86 M in THF, 669 μmol, 3.50 equiv) in THF (7 mL). The purified product **6b** was obtained after flash column chromatography ($R_f = 0.68$ (PE/EE = 9:1), silica gel, PE/CH_2Cl_2) as dark red solid material (decomp >350 °C, 37.9 mg, 484 μmol, 22%). ^{1}H NMR (300.51 MHz, $CDCl_3$, 25 °C); $\delta = 1.23-1.27$ (m, 42H), 6.53 (s, 2H), 7.06–7.10 (s, 2H), 8.00 (s, 2H). ^{13}C NMR: No feasible spectra could be obtained. IR-neat: ν [cm^{-1}] = 3366, 2939, 2889, 2863, 1576, 1454, 1286, 1196, 1109, 1080, 1019, 994, 877, 847, 753, 674. UV–vis: λ_{max} (hexane) = 534 nm. Extinction coefficient: ε(534 nm) = 44234 L·mol^{-1}·cm^{-1}. Fluorescence: λ_{max} (hexane) = 539 nm. HR-MS (Electrospray ionization, ESI): $[M + H]^+ = C_{40}H_{49}{}^{79}Br_2{}^{81}Br_2N_4Si_2$ calcd. 961.0183 found 961.0189, correct isotope distribution. Crystal data: CCDC number 1439301, gold crystal (needle), dimensions 0.370 × 0.040 × 0.020 mm^3, crystal system triclinic, space group $P\bar{1}$, Z = 1, $a = 7.200(3)$ Å, $b = 8.974(4)$ Å, $c = 17.429(7)$ Å, $\alpha = 81.590(11)°$, $\beta = 82.046(12)°$, $\gamma = 77.789(11)°$, $V = 1082.2(7)$ Å^3, $\rho = 1.474$ g/cm^3, $T = 200(2)$ K, $\Theta_{max} = 22.510°$, 7522 reflections measured, 2812 unique ($R_{int} = 0.1307$), 1492 observed (I > 2σ(I)), $\mu = 3.81$ mm^{-1}, $T_{min} = 0.70$, $T_{max} = 0.96$, 308 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.11 for observed reflections, final residual values $R1(F) = 0.121$, $wR(F^2) = 0.287$ for observed reflections, residual electron density −1.04 to 1.39 eÅ^{-3}.

*2,3,9,10-Tetrabromo-6,13-bis[(tripropan-2-ylsilyl)ethynyl]-quinoxalino[2,3-b] phenazine (**1b**).* **GP2** was carried out with dihydroazaacene **6b** (50.0 mg, 63.9 μmol). The purified product **1b** was obtained after flash column chromatography ($R_f = 0.61$ (PE/EE = 9:1), silica gel, PE/CH_2Cl_2) as dark green solid (mp >335 °C decomp., 47.0 mg, 60.2 μmol, 94%). ^{1}H NMR (600.24 MHz, $CDCl_3$, 25 °C): $\delta = 1.32-1.39$ (m, 42H), 8.56 (s, 4H). ^{13}C {^{1}H} NMR (150.93 MHz, $CDCl_3$, 25 °C): $\delta = 11.8$, 19.1, 102.7, 114.8, 123.6, 130.4, 134.1, 143.3, 144.2. IR-neat: ν [cm^{-1}] = 2942, 2892, 2865, 2060, 1472, 1457, 1433, 1363, 1073, 1062, 1031, 1018, 993, 881, 870, 801, 748, 676, 666, 662, 629. UV–vis: λ_{max} (hexane) = 719 nm. Extinction coefficient: ε (719 nm) = 4512 L·mol^{-1}·cm^{-1}. Fluorescence: λ_{max} (hexane) = 729 nm. HR-MS (Electrospray ionization, ESI): $[M + H]^+ = C_{40}H_{49}{}^{79}Br_2{}^{81}Br_2N_4Si_2$ calcd. 961.0183 found 961.0189, correct isotope distribution. Crystal data: CCDC number 1439299, green crystal (needle), dimensions 1.000 × 0.070 × 0.040 mm^3, crystal system triclinic, space group $P\bar{1}$, Z = 2, $a = 10.281(3)$ Å, $b = 12.582(4)$ Å, $c = 17.968(5)$ Å, $\alpha = 96.233(6)°$, $\beta = 103.750(7)°$, $\gamma = 102.897(6)°$, $V = 2168.4(11)$ Å^3, $\rho = 1.480$ g/cm^3, $T = 200(2)$ K, $\Theta_{max} = 26.373°$, 21140 reflections measured, 8850 unique ($R_{int} = 0.0314$), 6218 observed (l > $\sigma(I)$), $\mu = 3.80$ mm^{-1}, $T_{min} = 0.69$, $T_{max} = 0.89$, 483 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.03 for observed reflections, final residual values $R1(F)$ = 0.033, $wR(F^2)$ = 0.070 for observed reflections, residual electron density −0.48 to 0.37 $eÅ^{-3}$.

*1,4,8,11-Tetrachloro-5,14-dihydroquinoxalino[2,3-b]phenazine (**8**).* In a microwave vial equipped with stirring bar diaminodichlorobenzene **7** (450 mg, 2.54 mmol, 2.50 equiv), dihydroxy-*para*-quinone **3** (140 mg, 1.00 mmol, 1.00 equiv) and *para*-toluenesulfonic acid (9.20 mg, 50.0 μmol, 5.00 mol %) was suspended in chlorobenzene (12.0 mL). After heating in a microwave reactor for 2 h at 200 °C a dark purple suspension was formed. The crude product was isolated by filtration and washed subsequently with acetone, diethyl ether and THF. The pure product **8** (mp >350 °C, 308 mg, 730 μmol, 73%) was dissolved in sulfuric acid forming a blue solution. This is an indication for the clean product.

^{1}H NMR: Due to insolubility no spectra could be recorded. IR-neat: ν [cm^{-1}] = 3384, 3082, 1840, 1593, 1504, 1445, 1294, 1211, 1171, 95. UV−vis: λ_{max} (DMF) = 549 nm. HR-MS (Electron impact ionization, EI): $[M]^+$ = $C_{18}H_8N_4{}^{35}Cl_4$ calcd. 419.9503 found 419.9503, correct isotope distribution.

*1,4,8,11-Tetrachloroquinoxalino[2,3-b]phenazine-6,13-dione (**9**).* **8** (750 mg, 1.78 mmol, 1.00 equiv) was dissolved in a mixture of water and sulfuric acid (125 mL/85 mL) at 0 °C, forming a blue solution. Potassium dichromate (4.85 g, 16.6 mmol, 9.3 equiv) was added slowly while vigorously stirring. The solution was heated to reflux for 40 min, then poured onto ice and filtrated. The filtration residue was washed with water until the filtate was colorless, acetone and dried in vacuo. Compound **9** was obtained as a brown solid (mp >350 °C, 571 mg, 1.27 mmol, 71%). ^{1}H NMR (300.51 MHz, DMSO-d_6, 25 °C): δ = 8.37 (s, 4H). ^{13}C NMR: Due to insolubility no spectra could be recorded. IR-neat: ν [cm^{-1}] = 3095, 1717, 1525, 1455, 1373, 1329, 1212, 1101, 1067, 1058, 932, 864, 603, 591. HR-MS (Direct Analysis in Real Time, DART): $[M + H]^+$ = $C_{18}H_4O_2N_4{}^{35}Cl_4$ calcd. 448.91611 found 448.91624, correct isotope distribution.

*1,4,8,11-Tetrachloro-6,13-bis[(tripropan-2-ylsilyl)ethynyl]-5,6a,12a,14- tetrahydroquinoxalino[2,3-b]phenazine (**10**).* **GP1** was carried out with quinone **9** (640 mg, 1.43 mmol, 1.00 equiv), tri-*iso*-propylsilyl acetylene (1.3 mL, 1.05 g, 5.72 mmol, 4.00 equiv) and EtMgBr (0.86 M in THF, 6.4 mL, 5.50 mmol, 3.80 equiv) in THF (25.0 mL). The purified product **10** was obtained after flash column chromatography (R_f = 0.74 (PE/EE = 9:1), silica gel, PE/CH_2Cl_2) as green solid material (mp >280 °C decomp., 117 mg, 149 μmol, 10%). ^{1}H NMR (400.18 MHz, $CDCl_3$, 25 °C): δ = 1.22−1.26 (m, 42H), 6.76 (s, 2H), 7.59 (s, 2H), 7.65−7.68 (bs, 2H). ^{13}C {^{1}H} NMR (100.63 MHz, $CDCl_3$, 25 °C): δ = 11.5, 19.0, 98.0, 99.1, 106.7, 117.2, 123.1, 126.6, 127.9, 131.8, 139.3, 139.6, 144.1. IR-neat: ν [cm^{-1}] = 3351, 2943, 2889, 2863, 2140, 1593, 1569, 1456, 1432, 1291, 1219, 1090, 1032, 882, 757, 661, 617. UV−vis: λ_{max} (hexane) = 525 nm. Extinction coefficient: ε(525 nm) = 59640 $L\cdot mol^{-1}\cdot cm^{-1}$.Fluorescence: λ_{max} (hexane) = 530 nm. HR-MS (Electrospray ionization, ESI): $[M + H]^+$ = $C_{40}H_{49}{}^{35}Cl_4N_4Si_2$ calcd. 781.2244 found 781.2261, correct isotope distribution. Elemental Analysis: $C_{40}H_{48}Cl_4N_4Si_2$ calcd. C 61.37, H 6.18, N 7.16; found C 61.42, H 6.19, N 7.28. Crystal data: CCDC number 1439302, orange crystal (plate), dimensions 0.160 × 0.140 × 0.070 mm^3, crystal system triclinic, space group $P\overline{1}$, Z = 2, a = 8.777(2) Å, b = 8.817(2) Å, c = 29.942(7) Å, α = 88.066(6)°, β = 87.812(6)°, γ = 76.754(6)°, V = 2253.0(9) $Å^3$, ρ = 1.330 g/cm^3, T = 200(2) K, Θ_{max} = 22.043°, 14606 reflections measured, 5565 unique (R_{int} = 0.0849), 3368 observed ($I > 2\sigma(I)$), μ = 0.53 mm^{-1}, T_{min} = 0.80, T_{max} = 0.96, 500 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.07 for observed reflections, final residual values $R1(F)$ = 0.080, $wR(F^2)$ = 0.148 for observed reflections, residual electron density −0.34 to 0.34 $eÅ^{-3}$.

*1,4,8,11-Tetrachloro-6,13-bis[(tripropan-2-ylsilyl)ethynyl]-quinoxalino[2,3-b] phenazine (**11**).* **GP2** was carried out with dihydroazaacene **10** (117 mg, 149 μmol). The purified product **11** was obtained after flash column chromatography (R_f = 0.68 (PE/EE = 9:1), silica gel, PE/CH_2Cl_2) as dark green solid (decomp. > 314 °C, 76.0 mg, 97.3 μmol, 66%). ^{1}H NMR (400.18 MHz, $CDCl_3$, 25 °C): δ = 1.32−1.38 (m, 42H), 7.90 (s, 4H). ^{13}C {^{1}H} NMR (100.63 MHz, $CDCl_3$, 25 °C): δ = 11.8, 19.1, 102.3, 115.9, 124.3, 130.8, 133.5, 142.4, 142.9. IR-neat: ν [cm^{-1}] = 3085, 2941, 2889, 2863, 1852, 1667, 1596, 1509, 1450, 1375, 1152, 1035, 995, 949, 920, 882, 833, 760, 678, 659, 616, 581. UV−vis: λ_{max} (hexane) = 727 nm. Extinction coefficient: ε(727 nm) = 18607 $L\cdot mol^{-1}\cdot cm^{-1}$. Fluorescence: λ_{max} (hexane) = 739 nm. HR-MS (Electrospray ionization, ESI): $[M + H]^+$ = $C_{40}H_{47}{}^{35}Cl_3{}^{37}ClN_4Si_2$ calcd. 781.2058 found 781.2073, correct isotope distribution. Elemental Analysis: $C_{40}H_{47}Cl_4N_4Si_2$ calcd. C 61.53, H 5.94, N 7.18; found C 61.33, H 6.03, N 6.95. Crystal data: CCDC number 1439303, green crystal (needle), dimensions 0.490 × 0.040 × 0.040 mm^3, crystal system triclinic, space group $P\overline{1}$, Z = 2, a = 8.6568(10) Å, b = 14.0971(17) Å, c = 17.111(2) Å, α = 77.906(3)°, β = 85.320(3)°, γ = 87.277(4)°, V = 2034.0(4) $Å^3$, ρ = 1.275 g/cm^3, T = 200(2) K, Θ_{max} = 25.147°, 26094 reflections measured, 7243 unique ($R(int)$ = 0.0630), 4884 observed ($I > 2\sigma(I)$), μ = 0.38 mm^{-1}, T_{min} = 0.84, T_{max} = 0.96, 451 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.05 for observed reflections, final residual values $R1(F)$ = 0.054, $wR(F^2)$ = 0.115 for observed reflections, residual electron density −0.35 to 0.40 $eÅ^{-3}$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02731.

^{1}H and ^{13}C NMR spectra of all of the newly synthesized compounds and atom coordinates of all of the calculated structures (CIF)

Details of the X-ray crystal structures and cif-files for **1a,b**, **6a,b**, **10**, and **11** (PDF)

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Author Contributions

J.E., V.V., F.P., and O.T synthesized all of the compounds and performed the spectroscopic measurements. M.S. performed quantum chemical caculations. F.R. performed X-ray-crystal structures. The experiments were conceived by U.B. and J.E., and the manuscript was written by U.B. and J.E. through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Fischer, O.; Hepp, E. *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 2789−2793.

(2) Hinsberg, O. *Justus Liebigs Ann. Chem.* **1901**, *319*, 257−286.

(3) (a) Leete, E.; Ekechukwu, O.; Delvigs, P. *J. Org. Chem.* **1966**, *31*, 3734−3739. (b) Badger, G. M.; Pettit, R. *J. Chem. Soc.* **1951**, 3211−3215. (c) Miao, S.; Appleton, A. L.; Berger, N.; Barlow, S.; Marder, S. R.; Hardcastle, K. I.; Bunz, U. H. F. *Chem. - Eur. J.* **2009**, *15*, 4990−499.

(4) (a) Engelhart, J. U.; Tverskoy, O.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2014**, *136*, 15166−15169. (b) Lindner, B. D.; Engelhart, J. U.; Tverskoy, O.; Appleton, A. L.; Rominger, F.; Peters, A.; Himmel, H.-J.; Bunz, U. H. F. *Angew. Chem., Int. Ed.* **2011**, *50*, 8588−8591. (c) Biegger, P.; Stolz, S.; Intorp, S. N.; Zhang, Y.; Engelhart, J. U.; Rominger, F.; Hardcastle, K. I.; Lemmer, U.; Qian, X.; Hamburger, M.; Bunz, U. H. F. *J. Org. Chem.* **2015**, *80*, 582−589. (d) Engelhart, J. U.; Lindner, B. D.; Tverskoy, O.; Rominger, F.; Bunz, U. H. F. *Chem. - Eur. J.* **2013**, *19*, 15089−15092. (e) Kohl, B.; Rominger, F.; Mastalerz, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 6051−6056. (f) Li, G.; Wu, Y. C.; Gao, J. K.; Wang, C. Y.; Li, J. B.;

Zhang, H. C.; Zhao, Y.; Zhao, Y. L.; Zhang, Q. C. *J. Am. Chem. Soc.* **2012**, *134*, 20298−20301. (g) Gu, P. Y.; Zhou, F.; Gao, J. K.; Li, G.; Wang, C. Y.; Xu, Q. F.; Zhang, Q. C.; Lu, J. M. *J. Am. Chem. Soc.* **2013**, *135*, 14086−14089. (h) He, Z.; Mao, R.; Liu, D.; Miao, Q. *Org. Lett.* **2012**, *14*, 4190−4193.

(5) (a) Liu, D.; Xu, X.; Su, Y.; He, Z.; Xu, J.; Miao, Q. *Angew. Chem., Int. Ed.* **2013**, *52*, 6222−6227. (b) Lindner, B. D.; Paulus, F.; Appleton, A. L.; Schaffroth, M.; Engelhart, J. U.; Schelkle, K. M.; Tverskoy, O.; Rominger, F.; Hamburger, M.; Bunz, U. H. F. *J. Mater. Chem. C* **2014**, *2*, 9609−9612. (c) Paulus, F.; Lindner, B. D.; Reiß, H.; Rominger, F.; Leineweber, A.; Vaynzof, Y.; Sirringhaus, H.; Bunz, U. H. F. *J. Mater. Chem. C* **2015**, *3*, 1604−1609. (d) Liu, Y.-Y.; Song, C.-L.; Zeng, W.-J.; Zhou, K.-G.; Shi, Z.-F.; Ma, C.-B.; Yang, F.; Zhang, H.-L.; Gong, X. *J. Am. Chem. Soc.* **2010**, *132*, 16349−16351. (e) Liang, Z.; Tang, Q.; Mao, R.; Liu, D.; Xu, J.; Miao, Q. *Adv. Mater.* **2011**, *23*, 5514−5518.

(6) (a) Bunz, U. H. F. *Pure Appl. Chem.* **2010**, *82*, 953−968. (b) Bunz, U. H. F. *Chem. - Eur. J.* **2009**, *15*, 6780−6789.

(7) (a) Bunz, U. H. F.; Engelhart, J. U.; Lindner, B. D.; Schaffroth, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 3810−3821. (b) Miao, Q. *Synlett* **2012**, *23*, 326−336. (c) Miao, Q. *Adv. Mater.* **2014**, *26*, 5541−5549. (d) Bunz, U. H. F. *Acc. Chem. Res.* **2015**, *48*, 1676−1686. (e) Richards, G. J.; Hill, J. P.; Mori, T.; Ariga, K. *Org. Biomol. Chem.* **2011**, *9*, 5005−5017.

(8) (a) Ye, Q.; Chi, C. Y. *Chem. Mater.* **2014**, *26*, 4046−4056. (b) Li, J.; Zhang, Q. *ACS Appl. Mater. Interf.* 2015, *7*, ASAP.

(9) Winkler, M.; Houk, K. N. *J. Am. Chem. Soc.* **2007**, *129*, 1805−1815.

(10) Liang, Z.; Tang, Q.; Xu, J.; Miao, Q. *Adv. Mater.* **2011**, *23*, 1535−1539.

(11) Li, C.-H.; Huang, C.-H.; Kuo, M.-Y. *Phys. Chem. Chem. Phys.* **2011**, *13*, 11148−11155.

(12) Seillan, C.; Brisset, H.; Siri, O. *Org. Lett.* **2008**, *10*, 4013−4016.

(13) Geyer, F. L.; Brosius, V.; Bunz, U. H. F. *J. Org. Chem.* **2015**, *80*, 12166−12176.

(14) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482−9483.

(15) Layer distances were determined by measuring the distances between the planes through all non-hydrogen aromatic core atoms of neighboring molecules.

(16) Llorente, G. R.; Dufourg-Madec, M.-B.; Crouch, D. J.; Pritchard, R. G.; Ogier, S.; Yeates, S. G. *Chem. Commun.* **2009**, 3059−3061.

(17) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176−2179.

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