Abstract: The synthesis, property evaluation, and single crystal X-ray structures of four 5,7,12,14-tetrafunctionalized diazapentacenes are presented. The synthesis of these compounds either starts from tetrabromo-N,N-dihydrodiapentacene or from a diazapentacene tetraketone. Pd-catalyzed coupling or addition of a lithium acetylide gave the precursors that furnish, after further redox reactions, the diazapentacenes as stable crystalline materials. The performance of the tetraphenyl-substituted compound as n-channel semiconductor was evaluated in organic field effect transistors.

Herein, we describe the synthesis of tetrasubstituted 6,13-diazapentacenes by using two different precursors. Azaacenes have aroused great interest, starting with the synthesis of the superb n-channel semiconductor TIPS-TAP. This interest was further stoked by new syntheses to construct azapentacenes to azaheptacenes, by using Pd-catalyzed formation of embedded N,N-dihydropyrazines, and the availability of several privileged, bis(tri-iso-propylsilylethynyl)-substituted aromatic ortho-diamines. These approaches lead to disubstituted azaacenes. The synthesis of higher substituted azaacenes (tetrasubstituted, hexasubstituted, etc.) is not common, although for their hydrocarbon analogues, some derivatives have been explored, including per-substituted species furnishing twistacenes. Herein, we decorate the diazapentacene framework either by fourfold Suzuki–Miyaura coupling or by fourfold addition of a lithium acetylide. Reaction of the literature known tetrabromide with different boronic acids under standard palladium catalysis conditions gave the crude N,N-dihydro-intermediates, which were not further characterized but immediately oxidized by MnO₂ into the target compounds 3a-c (53–79% overall yield). The dihydro-species is much more soluble (and does not re-oxidize the intermedi-ate formed Pd° species) than its oxidized heteroacene counterpart and was employed in our coupling reactions. Because 1 did not undergo Sonogashira reaction directly (see Scheme S1 in the Supporting Information for conditions), we obtained tetratetrayne 3d by reacting tetrato 4 with an excess of the lithium salt of TIPS acetylene and treatment of the intermedium with tin dichloride. Compound 5 was isolated in 26% yield. Oxidation with MnO₂ in acetonitrile then gave 3d in 95% yield. Note that the electron-withdrawing pyrazine units enable fourfold nucleophilic addition—TIPS acetylide only adds twice to the corresponding hydrocarbon tetraketone analogue.

Figure 1 displays the normalized absorption spectra of non-fluorescent 3a-d (see also Table 1). We note that 3a-c display almost identical UV/Vis spectra despite the significant electronic differences in the substituents of 3a-c. The substituents only exert an inductive effect but do not increase the conduction band, or vice versa, because the aren rings are heavily π-conjugated.

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twisted with respect to the diazapentacene backbone. Compound 3d with the four alkyne groups displays a 70–80 nm redshifted absorption at 743 nm, as a consequence of the strong conjugation of the four alkyne groups with the diazapentacene nucleus (Scheme 1).

Compounds 3a–d were investigated by cyclic voltammetry (Table 1). They can be both oxidized and reduced, suggesting ambipolar behavior. As was expected, 3d and c display the highest oxidation potential. The effect is particularly strong for 3c, featuring four CF3 groups. The same trend was observed for the reduction potentials, which are −1.14 V for 3c and −0.96 V for 3d. The electron affinity for 3c and d are estimated to be −3.7 and −3.8 eV, respectively. Although the alkyne substituents influence HOMO and LUMO position differently and lead to a decreased electrochemical and optical gap, electron withdrawing substituents on the aryl groups in 3c stabilize both frontier molecular orbitals (FMOs) similarly. In comparison to 5,7,12,14-tetraphenylpentacene, nitrogen substitution leads to decreased FMO energy levels, as was expected.

Compounds 3a–d form suitable specimens useful for X-ray single crystal analysis (Figure 2 and the Supporting Information). In compounds 3a–c, the diazapentacene backbone is planar, and the four aryl groups are oriented parallel to each other.

Table 1. Photophysical and electrochemical properties of 3a–d.

| Compound | Abs max [nm] | Eox1 [V] | Ered1 [V] | Ionization potential [eV] meas/[calcd] | Electron affinity [eV] meas/[calcd] | Gap [eV] meas/calcd/ opt |
|----------|--------------|----------|----------|---------------------------------------|------------------------------------|--------------------------|
| 3a       | 664          | 0.64     | −1.33    | −5.44/−5.08                           | −3.47/−2.98                        | 1.97/2.10/1.69            |
| 3b       | 668          | 0.63     | −1.32    | −5.43/−5.33                           | −3.48/−3.25                        | 1.95/2.08/1.72            |
| 3c       | 674          | 1.13     | −1.14    | −5.93/−6.27                           | −3.66/−4.23                        | 2.27/2.04/1.72            |
| 3d       | 743          | 0.77     | −0.96    | −5.57/−      | −3.84/−      | 1.73/−1.59                |
| 5,7,12,14-tetraphenylpentacene | 621 | −/− | −/− | −/− | −/− | −/−/1.88 |

[a] Absorption peaks in DCM. [b] First oxidation and reduction potentials measured in CV using ferrocene/ferrocenium as the reference redox system and internal standard (−4.8 eV vs. vacuum). [c] Calculated from CV measurements (E_HOMO = −4.80 eV − E_{ox1}; E_LUMO = −4.80 eV − E_{red1}). [d] Calculated with Gaussian 09 B3LYP/6-311++G**/DFT/B3LYP/6-31+G**. [e] Estimated from E_HOMO and E_LUMO (E_{gap} = E_LUMO − E_HOMO). [f] Estimated from absorption onset recorded in DCM.

Scheme 1. Synthesis of substituted diazapentacenes 3a–d.
other and considerably twisted with respect to the diazapenta-
cene (dihedral angles: 63° and 65° for 3a; 57° and 61° for 3b
and 66° and 71° for 3c). The molecules of 3a and c pack in a
herringbone pattern with no π–π overlap between the mole-
cules. The molecules of 3b pack in π–π stacked dimers with
an interplanar distance of 3.60 Å, which are arranged in one-di-
ensional slipped stacks. In the case of 3d, the four TIPS-eth-
ynyl groups crowd each other. This leads to a twist of the dia-
zapentacene nucleus with an end-to-end torsion angle of 20°.

The steric crowding of the four TIPS groups also enforces a
bend in the alkynes away from each other, even though direct peri
interactions are not present due to the pyrazine unit inter-
spersed between the alkyne-carrying rings. Compound 3d also
packs in a herringbone motif; here also, as was expected,[21] π–π
overlap is absent. The observed packing suggests that larger
acenes, for example, diaazaheptacenes,[22] might be stabilized in
the solid state with the current substituent pattern and at the
same time display attractive solid-state ordering that would
allow their use in ambipolar transistors.

Next issue to address was stability of the diazapentacenes
compared to their hydrocarbon analogues. The stability of
5,7,12,14-tetraphenylpentacene was assessed through UV/Vis
measurements in dilute solution—it photooxidized in tolu-
enol[15] or dichloromethane[9] under ambient conditions (light
and air) in less than 20 minutes via endo-peroxide formation.
Nitrogen substitution protected the system. The absorption
profile of alkynylated 3d remains unchanged for 24 hours,
photooxidation of 3a–c depends on the electronic demand of
the aryl substituents. Electron-deficient trifluoromethyl groups
stabilize the system most (14% absorption loss after 24 h), but
even electron-rich, dimethoxy-substituted 3a was still fairly
stable (50% loss after 24 h).

To initially evaluate the potential of the newly synthesized
tetrasubstituted diazapentacenes as n-channel organic semi-
conductors, organic field-effect transistors (OFETs) were fabri-
cated by physical vapor deposition of 3b (for details regarding
the device fabrication, see the Supporting Information). The
compound showed n-type charge transport behavior with a maximum electron mobility of 3.2×10⁻³ cm²V⁻¹s⁻¹, threshold
voltage 30 V and on/off ratio on the level of 10⁴. The average
carrier mobility calculated for twelve transistors was
1.76×10⁻²±0.51 cm²V⁻¹s⁻¹. In contrast, for parent unsubstitu-
ted 6,13-diazapentacene hole mobilities in a range of 10⁻⁵
were reported.[24] This finding clearly highlights the beneficial
impact of the 5,7,12,14-substitution pattern on the n-channel
device performance and constitutes an asset for our future ef-
forts in this area.

In conclusion, we developed symmetrically tetrafunctional-
ized 6,13-diazapentacenes, either starting from bisquinone 4
or from the N,N’-dihydro-tetrambromide 1. Both routes work well
and give the expected products in reasonable yields. The com-
 pounds are stabilized with respect to photooxidation and the
tetraphenyl-substituted representative 3b shows n-channel be-
behavior. In future, we will expand this concept to 6,7,14,15-tet-
razaheptacene and to 7,16-diazapentacene. Herein, the solubi-
lity of the precursors might be a problem, but the prospect of
stable diazapentacenes is particularly attractive.[21]

**Experimental Section**

6,13-Di hydro-6,13-diazapentacene and 5,7,12,14-tet rah bromo-6,13-
dihydro-6,13-diazapentacene were synthesized by literature proce-
dure.[11,24]

**General synthesis procedure for 3a–c**

5,7,12,14-Tetra bromo-6,13-dihy dro-6,13-diazapentacene 1 (200 mg, 0.33 mmol), aryloboric acid (8.00 equiv), Pd(PPh₃)₄ (76.0 mg, 65.8 mmol, 0.20 equiv), and K₂CO₃ (462 mg, 3.34 mmol, 10.0 equiv) were added into the flask under N₂. 1,4-Dioxane (16 mL) and water (4 mL) were purged with N₂ for 20 min and then added into the flask. The resulting mixture was stirred at 70 °C for 4 days. After cooling to room temperature (rt), a pale green precipitate was formed. It was collected by filtration and washed with water and ethanol. The crude product was dissolved in DCM (20 mL), fol-
lowed by treatment with MnO₂ (872 mg, 10.0 mmol, 30.0 equiv) at rt for 6 h.

5,7,12,14-Tetra(3,5-dimethoxyphenyl)-6,13-diazapentacene (3a): 3,5-Dimethoxyphenylboronic acid (487 mg, 2.56 mmol, 8.00 equiv) was employed. After reaction, DCM was evaporated under reduced pressure and the crude product was purified by flash column chro-
matography (SiO₂, ethyl acetate (EE) to give a dark green solid. Further washing with petroleum ether (PE) gave pure 3a. Yield: 146 mg, 0.18 mmol, 53%. Melting point (M.p.):
1128.7007; correct isotope distribution.

5,7,12,14-Tetra(3,5-bis(trifluoromethyl)phenyl)-6,13-diazapenta-
cene (3b): Phenylboronic acid (326 mg, 2.56 mmol, 8.00 equiv) was employed. After reaction, DCM was evaporated under reduced pressure, and the crude prod-
cut was purified by flash column chromatography (SiO₂, DCM) to give a dark green solid. Subsequent washing with EE gave pure 3b. Yield: 116 mg, 0.20 mmol, 59%. M.p.: >400 °C (decomp).

5,7,12,14-Tetra(3,5-dimethoxyphenyl)-6,13-diazapentacene (3a): Calcd for C₄₄H₂₈N₄O₂: C, 83.71; H, 4.94; N, 7.47. Found: C, 83.64; H, 5.01; N, 7.39.

5,7,12,14-Tetra(3,5-bis(trifluoromethyl)phenyl)-6,13-diazapenta-
cene (3b): Calcd for C₄₄H₂₈F₄N₄O₂: C, 77.49; H, 4.62; N, 7.43. Found: C, 77.31; H, 4.51; N, 6.93.

5,7,12,14-Tetra(3,5-bis(trifluoromethyl)phenyl)-6,13-diazapenta-
cene (3c): Calcd for C₄₄H₂₆F₄N₄O₂: C, 77.36; H, 4.42; N, 7.42. Found: C, 77.27; H, 4.38; N, 7.29.

5,7,12,14-Tetrakis(trisopropylsilylacetylene)-6,13-dihydro-6,13-
diazapentacene (5): TIPS acetylene (3.63 mL, 16.2 mmol, 11.0 equiv) was dissolved in dry THF (30 mL). Subsequently, nBuLi (2.5 m in hexanes, 5.88 mL, 14.7 mmol, 10 equiv) of was added at

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The mixture was stirred for 2 h at –70 °C. After this time, 4 (500 mg, 1.47 mmol, 1.00 equiv) was added, and the reaction mixture was brought to room temperature, and stirred for 16 h. The solvent was removed under reduced pressure, and the precipitate was filtered through a SiO₂ pad first with PE and afterwards with EE. The solvent of the EE fraction was removed under reduced pressure, and the resulting colorless solid was dissolved in acetonitrile (5 mL), and SnCl₂·2H₂O (4.00 g) was added. The reaction mixture was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and purification by column chromatography (SiO₂, PE/DCM 4:1) gave 387 mg (386 µmol, 26%) of 5 as a yellow solid. M.p. > 350 °C (decomp). 1H NMR (CDCl₃, 400 MHz, 295 K): δ = 7.98–7.96 (m, 4H), 7.28 (s, 2H), 7.28–7.26 (m, 4H), 1.31–1.17 (m, 84H). 13C{1H} NMR (CDCl₃, 100 MHz, 295 K): δ = 132.5, 130.8, 125.7, 125.3, 106.0, 100.6, 100.5, 19.1, 12.5 ppm. IR: ν = 3370, 2940, 2862, 2124, 1550, 1526, 1468, 1425, 1407, 1381, 1349, 1254, 1154, 1070, 996, 917, 881, 753, 674, 658, 640, 526, 502 cm⁻¹. MS (DART–) m/z: [M+H]+: calcd for C₃₀H₂₃Ni₂S₄: 1003.6567; found 1003.6514; correct isotope distribution.

Crystallographic data: CCDC 1957020 (3a), 1958306 (3b), 1957021 (3c), and 1957022 (3d) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre

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Conflict of interest

The authors declare no conflict of interest.

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