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# Fused Thiophene-Pyrrole-Containing Ring Systems up to a Heterodecacene[**]

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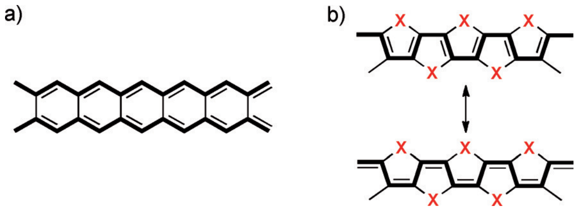
*In memory of Michael Bendikov*

**Abstract:** *A new class of π-conjugated polycyclic hydrocarbons that promises interesting electronic properties is presented. The synthesis and extension of the S,N-heteroacene series consisting of only five-membered heterocyclic rings up to a very long, stable, and still soluble decacene SN10 is realized by multiple Pd-catalyzed aminations of halogenated thiophene precursors as key reactions. These novel heteroacenes were characterized by optical spectroscopy and electrochemistry providing interesting structure–property relationships. Nearly complete bond-length equalization in the inner part of the conjugated backbone and an unusual herringbone packing in the solid state underline the structural features of these novel systems.*



*Scheme 1.* Structure of oligoacenes (a) and five-membered-ring heteroacenes (b).

Heteroacenes have recently emerged as promising alternatives to acenes.[1] Through the incorporation of electronegative heteroatoms, such as nitrogen, into the backbone of acenes to give in azacenes[2] or by fusion of five-membered rings, such as thiophenes, in (mixed) thienoacenes,[3] acenes can be stabilized.[4] Organic materials involving heteroacenes with highly interesting electronic properties were developed.[2,3] In comparison to oligoacenes, which are represented by two linked *trans*-polyacetylene chains,[5] five-membered heteroacenes can be regarded as a *cis-transoid* polyacetylene chain, which is stabilized on both sides by heteroatoms (X; Scheme 1).

Thienoacenes with up to eight linearly fused thiophene rings in an all-*anti* arrangement were realized, whereby the longer representatives are insoluble.[6] Mixed five-membered ring heteroacenes consisting of fused thiophene (X = S) and pyrrole units (X = NR), so-called S,N-heteroacenes, are advantageous over thienoacenes[6] because solubilizing substituents can be attached at the nitrogen atoms. Within the series of pure S,N-heteroacenes, dithieno[3,2-*b*:2′,3′-*d*]pyrrole (DTP) has been known for some time,[7] while different *N*-alkylated S,N-heteropentacenes **SN5** were presented only recently.[8] We pursued a similar concept and reported acceptor-functionalized S,N-heteropentacenes for application in different types of organic solar cells. Thus, acceptor-substituted **SN5** derivatives achieved efficiencies of as much as 6.5% in vacuum-processed solar cells,[9] up to 4.9% in solution-processed solar cells,[10] and up to 10.3% when used as hole transporters in Perovskite cells.[11] The to date longest S,N-heteroacene, heterohexacene **SN6**, was recently presented by our group and showed interesting optoelectronic properties as well as good charge-carrier mobility.[12]

Herein, we report the systematic extension of the S,N-heteroacene series up to a stable S,N-heterodecacene **SN10**. The syntheses of novel hexyl-substituted S,N-heteroacenes **SN4**, two **SN7** derivatives, **SN8**, **SN9**, and **SN10** in usable amounts is discussed. The strategy used for the syntheses is multiple Pd-catalyzed aminations of halogenated thiophene precursors which lead to the ring-closure of fused pyrroles and the construction of the final acene scaffold. Furthermore, the reactive terminal α-positions of the thiophene units are protected by triisopropylsilyl (TIPS) groups, which are efficiently removed in the final step. The characterization of the physical properties of the whole series should give meaningful structure–property relationships.

The preparation of S,N-heteroacenes **SN4**, **SN7′**, and **SN8** started from central building block 2,3-dibromo-5-(triisopropyl)silyl thieno[3,2-*b*]thiophene and is illustrated in Scheme 2. Palladium-catalyzed Negishi couplings of the respective organozinc derivatives with multiply brominated thiophenes or thieno[3,2-*b*]thiophenes gave intermediates **3**–**5**. The following pyrrole ring closures with hexylamine in Pd-catalyzed Buchwald–Hartwig aminations gave TIPS-pro-

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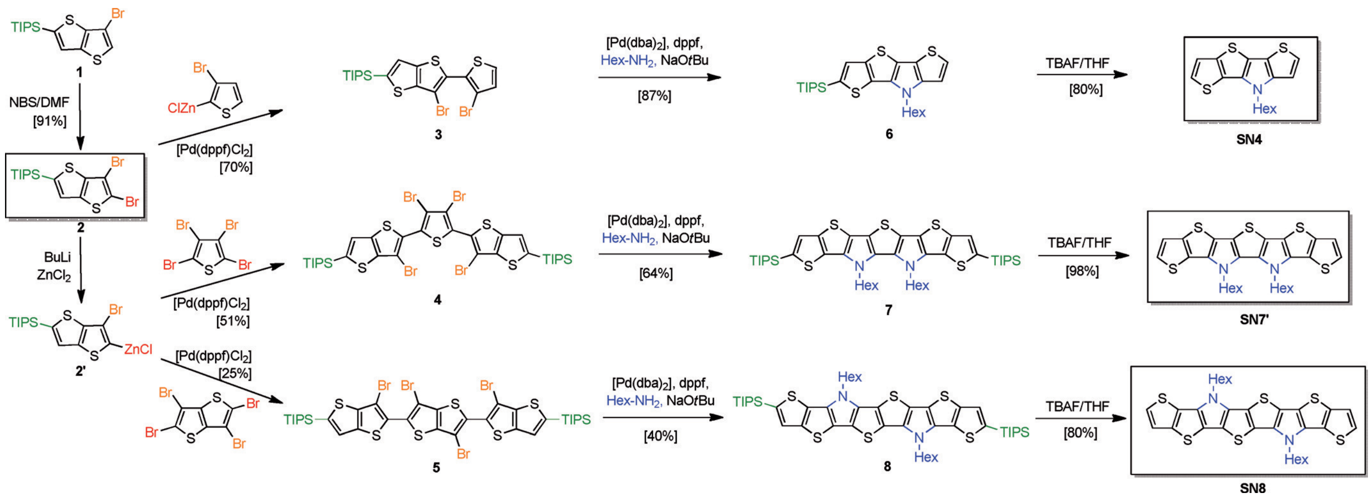
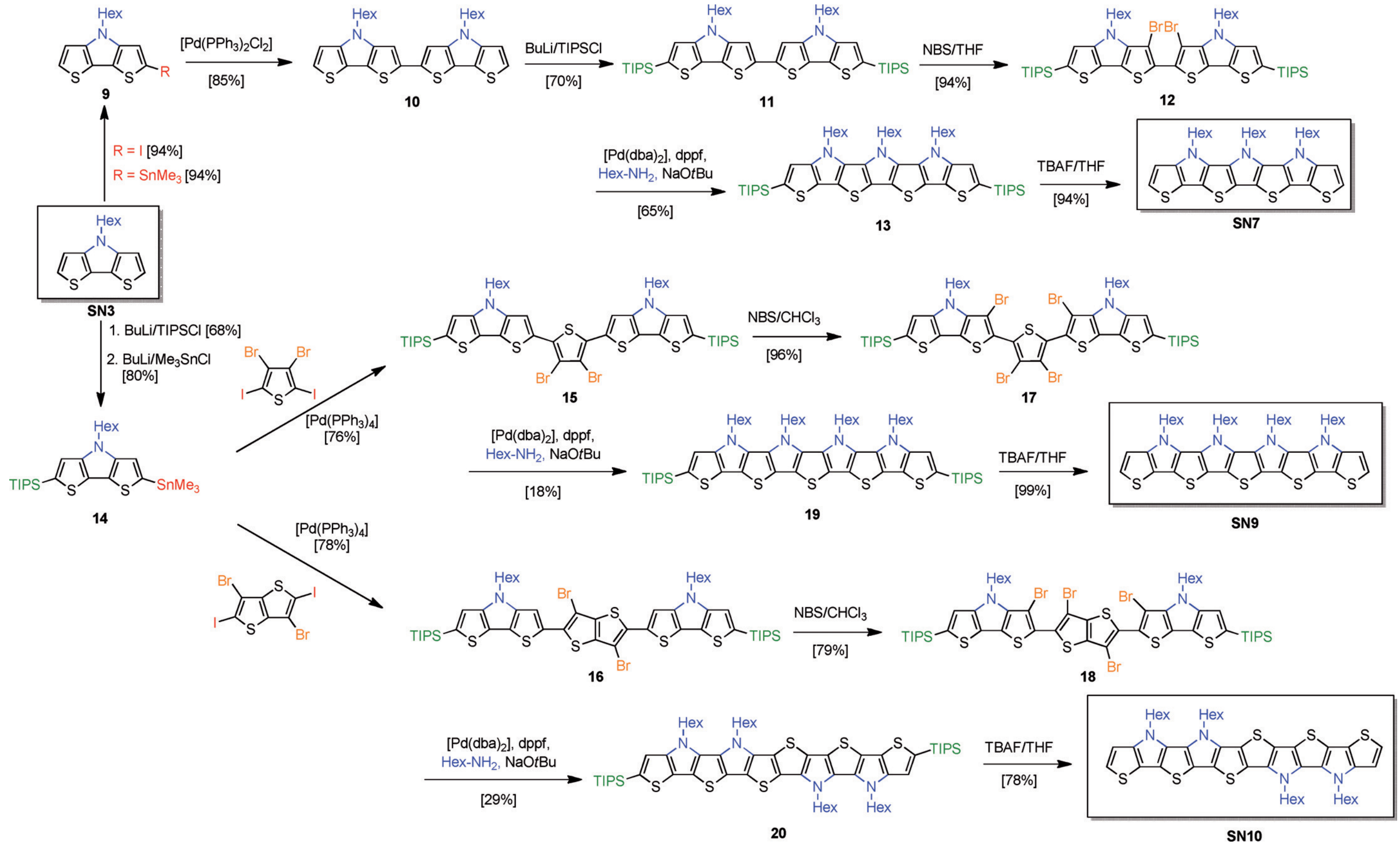


*Scheme 2.* Synthesis of S,N-heteroacenes **SN4**, **SN7′**, and **SN8** starting from 3-bromo-5-tri(isopropyl) thieno[3,2-*b*]thiophene **1**.

tected heteroacenes **6–8**, which could be deprotected to give the target compounds upon treatment with tetrabutyl ammonium fluoride (TBAF).

The syntheses of the other novel representatives, **SN7**, **SN9**, and **SN10** started from **SN3** as central building block and are illustrated in Scheme 3. Similar to the synthesis of the above derivatives, for the preparation of the longest representatives, **SN9** and **SN10**, a TIPS-protected monostannylated **SN3 14** was treated with multiply halogenated thiophene and thieno[3,2-*b*]thiophene building blocks by Pd-catalyzed Stille cross-coupling reactions to obtain intermediates **15** and **16**. Subsequent bromination at the inner positions of the **SN3** blocks using *N*-bromosuccinimide gave **17** and **18**. The following multiple Pd-catalyzed aminations with hexylamine yielded TIPS-protect heterononacene **19** and heterodecacene **20**, which were deprotected using TBAF to achieve the longest representatives, **SN9** and **SN10**. For the preparation of the slightly shorter heteroheptacene **SN7**, which like **SN3**,



*Scheme 3.* Synthesis of S,N-heteroacenes **SN7**, **SN9**, and **SN10** starting from *N*-hexyl dithieno[3,2-*b*;2′,3′-*d*]pyrrole **SN3**.

**SN5**, and **SN9** consists of alternating thiophene and pyrrole units, a synthetic route using the **SN3**-dimer **10** was applied.[13] This was first protected by TIPS-groups to yield **11**, which in the next step was selectively brominated with NBS at the inner positions of the **SN3** moieties in **11** to obtain **12**. The bromination is selective, because the outer β-positions of the **SN3** units are sterically blocked by the bulky TIPS-groups. Subsequent amination with hexylamine provided the hepta-fused heteroacene **13**, which was deprotected with TBAF to obtain heteroheptacene **SN7**.

Finally, a series of S,N-heteroacenes ranging from a trimer to a decamer with increasing number of conjugated double bonds or chain lengths is now available which was completely characterized by NMR spectroscopy and mass spectrometry[14] (Figure 1). Based on their structural characteristics, the S,N-heteroacenes can be divided into the following subgroups: **SN3**, **SN5**, **SN7**, and **SN9** contain alternating thiophene and pyrrole rings and have $C_{2V}$ symmetry; **SN4**, **SN6**, **SN7′**, **SN8**, and **SN10** contain thienothiophene units, among which **SN6**, **SN8**, and **SN10** have $C_{2h}$ symmetry. Heteroheptacenes **SN7** and **SN7′** allow the investigation of two species which have the same chain length, but a different sequence of heteratoms.

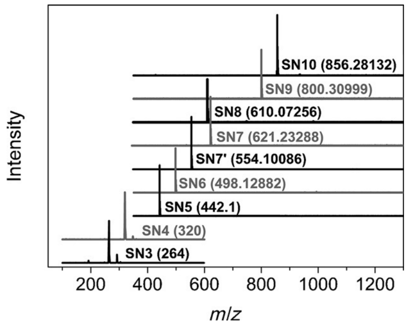


***Figure 1.*** MALDI mass spectra of S,N-heteroacenes **SN5–SN10** and CI mass spectra of **SN3** and **SN4**, that contain the typical ethyl cation adducts.

Single crystals of heteroheptacene **SN7′**, which were suitable for X-Ray structure analysis, were obtained. The unit cell of the triclinic space group $P\bar{1}$ contained two pairs of equivalent molecules (Figure 2 a).[14] The bond-length analysis showed a peculiarity of these fused systems: In comparison to oligothiophenes, the bond-length alternation in the inner part of the fused system is reduced to 0.01 Å. The molecules exhibited a planar structure and arrange themselves in dimers that are stabilized by multiple sulfur–sulfur dipolar interactions at distances of 3.18–3.31 Å (Figure 2 b) far below the sum of van der Waals radii (3.60 Å). The hexyl side chains, which showed slight polymorphism at their termini, are identically directed out of plane of the conjugated backbone by an angle of 35°. This arrangement enables a herringbone packing motif, which is quite unusual for functionalized oligoacenes. The π systems of the molecules interact perpendicular to the dimer plane through very short S-atom–π interactions of 3.34–3.46 Å (Figure 2 b). In contrast, the one-ring-shorter derivative **SN6** stacks by π–π interactions.[12]

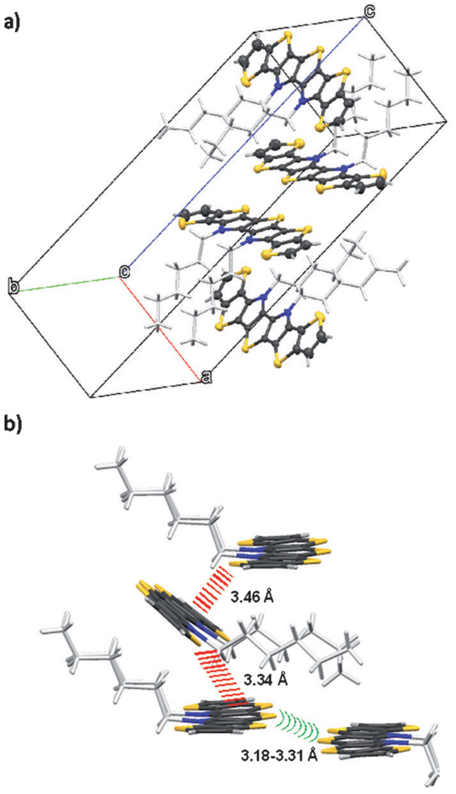


***Figure 2.*** a) The unit cell of **SN7′**; b) strongest intermolecular interactions (S–S green, S–π red lines).

The optoelectronic properties of the S,N-heteroacenes were investigated in view of structure–property relationships. Absorption and emission maxima, fluorescence quantum yields, Stokes shifts, optical gaps, oxidation potentials, and the calculated frontier orbital energies are summarized in Table 1. The absorption maxima in THF solutions are stepwise red-shifted from 298 nm for **SN3** to 436 nm for **SN10**. Simultaneously, the molar extinction coefficient increases with increasing conjugation length up to as much as 99800 $\text{M}^{-1}\,\text{cm}^{-1}$ for **SN10** (Figure 3 a). While **SN3** showed no fluorescence, the emission bands are shifted to lower energies going from **SN4** to **SN10** (Figure 3 b). The determination of the fluorescence quantum yields revealed that the shorter derivatives from **SN4** to **SN6** exhibit very low values while the longer representatives with seven or more fused rings exhibit remarkably higher values of up to 61 % for **SN9** which then decreases to only 6 % for **SN10**. Typical for such rigid systems are besides vibronic fine splitting in absorption and emission spectra the very small Stokes shifts caused by small structural differences in the ground and first excited state. A minimum of 664 $\text{cm}^{-1}$ was observed for **SN10**. The optical gap decreased from 3.90 eV for **SN3** to 2.74 eV for **SN10** and correlates linearly with the reciprocal number of conjugated double bonds (Figure 3 c).[15]

The redox potentials of the S,N-heteroacenes were determined by cyclic voltammetry (Figure 4 a). The shorter member of the series, **SN3** to **SN5**, exhibited an irreversible

***Table 1:*** Physical properties of S,N-heteroacenes **SN3**–**SN10**.

| Heteroacene | m.p. [°C] | $\lambda_{max}{}^{abs}$ [nm][a] | $\varepsilon$ [$M^{-1}\,cm^{-1}$][a] | $\lambda_{max}{}^{em}$ [nm][a] | $\phi^{em}$ [%][a] | Stokes shift [$cm^{-1}$] | $E_g{}^{opt}$ [eV][d] | $E_{ox1}$ [V][e] | $E_{ox2}$ [V][e] | $E_{HOMO}$ [eV][h] | $E_{LUMO}$ [eV][j] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **SN3**[k] | 46.7 | *298*, 310 | 24900 | – | – | – | 3.90 | 0.51[f] | – | −5.52 | −1.62 |
| **SN4** | 66.3 | *323*, 336 | 30700 | 364 | < 0.3[b] | 1513 | 3.55 | 0.39[f] | – | −5.39 | −1.84 |
| **SN5**[k] | 104.2 | 339, *356* | 42100 | 370 | 1[b] | 1142 | 3.37 | 0.11[f] | – | −5.12 | −1.75 |
| **SN6**[k] | 162.1 | 361, *379* | 54200 | 398 | < 0.3[c] | 1259 | 3.15 | 0.06 | 0.73 | −5.09 | −1.94 |
| **SN7** | 209.0 | 372, *391* | 58100 | 409 | 19[c] | 1125 | 3.04 | −0.16 | 0.35 | −4.88 | −1.84 |
| **SN7′** | 194.1 | 375, *395* | 58000 | 407 | 58[c] | 746 | 3.03 | 0.04 | 0.64 | −5.05 | −2.02 |
| **SN8** | 278.8 | 390, *413* | 72600 | 427 | 16[c] | 794 | 2.91 | 0.00 | 0.63 | −5.01 | −2.10 |
| **SN9** | 223.8 | 398, *420* | 77900 | 442 | 61[c] | 1031 | 2.82 | −0.21[g] | 0.22[g] | −4.82 | −2.00 |
| **SN10** | 295.8 | 420, *436* | 99800 | 452 | 6[c] | 664 | 2.74 | −0.26[g] | 0.12[g] | −4.79 | −2.05 |

[a] Measured in THF, maximum in italics. [b] Quantum yields referenced against anthracene in ethanol ($\phi^{em}=0.27$). [c] Quantum yields referenced against 9,10-diphenylanthracene in ethanol ($\phi^{em}=0.95$). [d] Calculated from the onset of the absorption band. [e] First oxidation potential in dichloromethane/0.1 м tetrabutyl ammonium hexafluorophosphate at 295 K, scan speed 100 mV s$^{-1}$, versus ferrocene/ferricenium (Fc/Fc$^+$). [f] Irreversible wave. [g] Measured in THF. [h] Calculated from the onset of the first oxidation wave and referenced against Fc/Fc$^+$ at −5.1 eV vs. vacuum. [j] Calculated with $E_{HOMO}$ and $E_g{}^{opt}$. [k] We synthesized and investigated these literature-known derivatives.

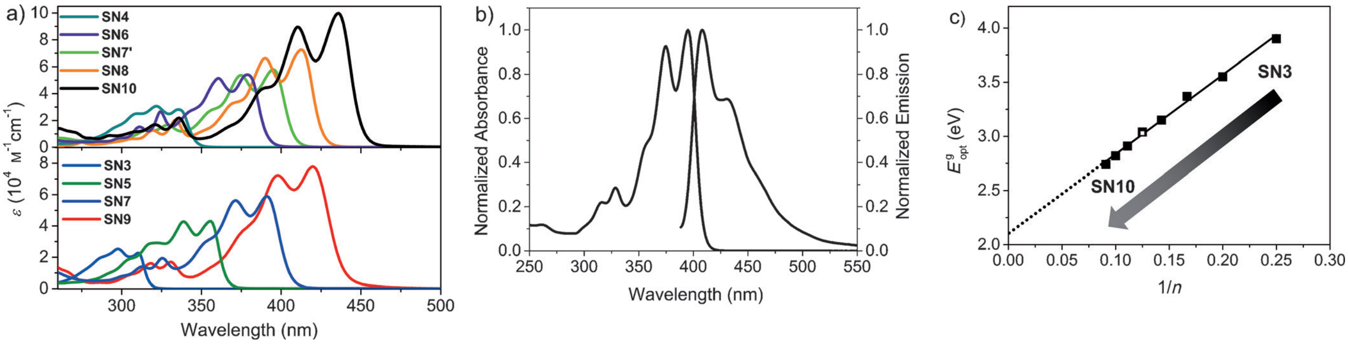


***Figure 3.*** a) UV/Vis absorption spectra of S,N-heteroacenes in THF; b) normalized absorption and emission spectra shown for **SN7′**; c) optical gap of **SN3** to **SN10** in correlation with the reciprocal number of conjugated double bonds (correlation coefficient: 0.995), **SN7′** (□).

oxidation wave characteristic of the formation of reactive radical cations that arise because of the free terminal α-positions available for subsequent coupling reactions. Hexafused **SN6** showed two quasi-reversible oxidation waves whereas the longer systems with seven or more fused rings exhibited two reversible ones which indicate the formation of stable radical cations and dications. The first oxidation potential decreased as expected with increasing conjugation length of the heteroacenes and reached a very low value of −0.26 V for decamer **SN10**. Besides the length of the conjugated backbone, the redox potentials also depend on the number of electron-rich pyrrole rings. This effect becomes clearly visible when heteroheptacene **SN7′** containing two pyrrole rings is compared to **SN7** with three pyrrole rings in the conjugated backbone. The first and second oxidation potential for **SN7** are shifted by 0.20 V and 0.29 V to more negative potentials compared to those of **SN7′**. The same trend applies correspondingly to the HOMO energies (Figure 4b). This effect is also noticeable in comparison to TIPS-protected thienoacenes,[6] which are consistently more difficult to oxidize by 0.3–0.6 V.

Herein, we presented the synthesis and extension of the S,N-heteroacene series consisting only of five-membered heterocycles up to a very long, stable, and still readily soluble

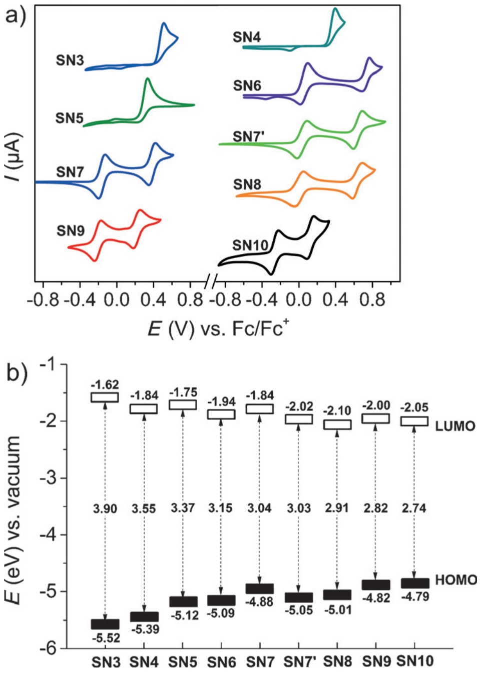


***Figure 4.*** a) Cyclic voltammograms of the S,N-heteroacenene series **SN3**–**SN10**; b) HOMO and LUMO energies and energetic gaps of all S,N-heteroacenes.

heterodecacene **SN10**. The characterization of the structural features showed nearly complete bond-length equalization towards the cyanine limit in the inner part of the conjugated π system. As a result of S–S and S–π dipolar interactions a herringbone packing motif is observed in the solid state which is quite unusual for functionalized acenes. The optoelectronic properties are in accordance with the structural features and provide valuable structure–property relationships. Overall, a new class of π-conjugated polycyclic hydrocarbons with potential application in organic electronic devices is now available. We are now interested, in comparison to oligoacenes, to find how far the practical synthesis of even longer and still stable derivatives can be pushed.

**Keywords:** amination · heteroacenes · nitrogen–sulfur heterocycles · structure–property relationships · X-ray structure analysis

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