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From Thia- to Selenadiazoles: Changing Interaction Priority

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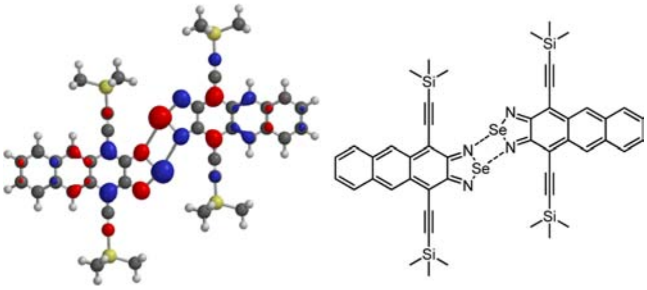
ABSTRACT



The synthesis, optical, and electrochemical properties as well as solid-state structures of a series of alkynylated, benzannulated selenadiazoles are reported. This set of compounds is compared to the lighter homologue series, the thiadiazoles. The selenadiazoles show head-to-head dimerization in the solid state, while packing of the thiadiazoles was dominated by the steric bulk of the side groups. The Se–N interaction is a supramolecular motif that should drive the effective self-assembly and modulate charge transport when these compounds are used as thin films in devices.

There is a general interest in stabilized acenes as potentially useful charge transporting materials,[1,2] particularly those with electron poor aromatic cores.[3] Trialkylsilylethynylation (e.g., TIPSA: triisopropylsilylacetylene) dramatically stabilizes acenes and heteroacenes and at the same time renders their solid state structure predictable.[4,5] Mutagenesis of the molecular structure of electron-poor acenes is critical for rational development of novel materials with desirable molecular and solid-state properties.

Extended aceno[2,1,3]thiadiazoles[6] as potential representatives show different packing arrangements depending on both the bulk of the trialkylsilyl side chains and the size of the heteroaromatic core. Moreover, some acenothiadiazole cores dimerize pairwise head-to-head in the solid state enabled by N–S dipole interactions.[6,7] This leads to increased intermolecular overlap in the crystal and might be favorable for charge-carrier mobility. One way to further exploit this phenomenon, while keeping the general structure intact, is the introduction of a more electropositive chalcogen atom, i.e. selenium or tellurium.[8,9] This should lead to an increase of dipole–dipole interactions and foster increased head-to-head dimerization.[10] Herein we report the synthesis and the solid-state properties of Se-containing (aza)diazoles. We demonstrate that Se–N interactions enforce compulsory head-to-head packing in

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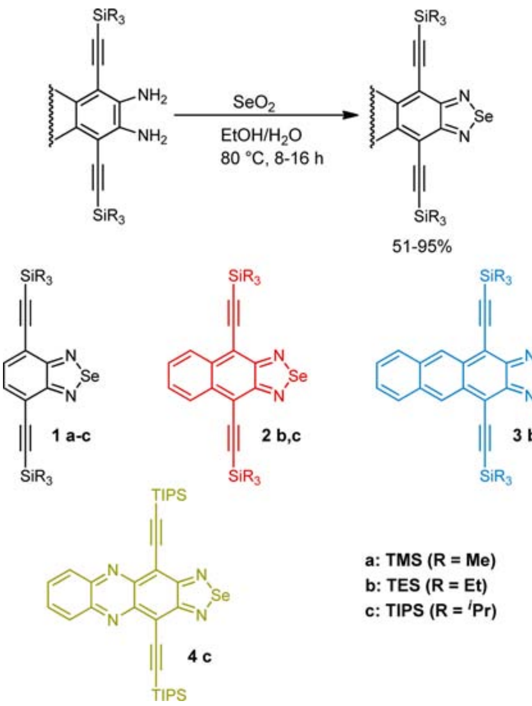
selenadiazoles, while TIPS-alkyne groups in these compounds lead to a brick wall motif packing of the aromatic cores.

Scheme 1. General Scheme Describing Preparation of Trialkylsilyl-Substituted Materials **1**−**4**



The synthesis of **1**−**4** was carried out from the respective known aromatic diamines.[2,6,8,11−13] By condensation with SeO$_2$ based on a procedure from Miyashi et al.,[14] compounds **1**−**4** could be obtained in yields up to 95% (Scheme 1). Attempts to apply this procedure to TeO$_2$ or TeCl$_4$ failed due to the apparent instability of the heterocyclic products. As an increasing number of electronegative heteroatoms within the aromatic core should stabilize the corresponding radical anion against oxidation,[15] we also prepared and included phenazino-selenadiazole **4c** in this study.

The UV−vis absorption and fluorescence spectra of **2**−**4** are displayed in Figure 1. As expected, benzannulation leads to a bathochromically shifted absorption and emission with negligible influence of the alkyl substituent in the silylalkynyl group. The spectral features of the selenium compounds are significantly shifted to longer wavelengths relative to those of the sulfur congeners, up to 80 nm, depending on the chalcogenadiazole core size (see Supporting Information (SI)). This is consistent with the calculated frontier molecular orbital (FMO) energies,[16] which also explain the blue-shifted absorption of **4c** compared to **3c** (see SI).

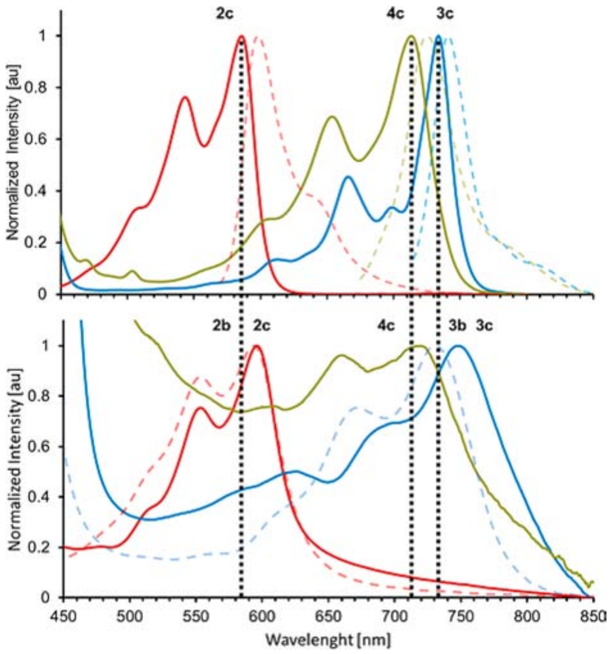


Figure 1. Absorption (solid) and emission (dashed) spectra of **2c**−**4c** in hexane (top); thin film absorption spectra (bottom) of TIPS- (**2c**−**4c**; solid) and TES-substituted **2b** and **3b** (dashed). Vertical lines illustrate the red shift of **2c**−**4c** in the solid state. Spectra of **1** omitted for clarity (see SI).

The thin film absorption spectra (Figure 1, bottom) show a pronounced red shift of the absorption edge and broadened fine structure, which points to coplanar $\pi-\pi$ aggregation in the solid state. While there is little difference between **2b** and **2c**, the stronger red shift of **3c** compared to TES-alkynylated **3b** points to optimized packing for the bulkier side chain as has been discussed for pentacenes.[4]

Emission profiles are narrow with shoulders on the red-edge of the larger compounds' main emission peaks. Shifts in the emission maxima mirror the pattern observed in the absorption profiles with small Stokes shifts, due to the rigidity of aromatic systems.

Fluorescence quantum yields were measured for materials **1c** and **2c**, with the larger system displaying a higher value (Table 1). The emission spectra of the anthraceno- and phenazino-systems (**3c** and **4c**) display significant noise, suggesting these materials would exhibit low quantum yields, but consistent data could not be recorded.

Cyclic voltammetry measurements were compared to quantum chemical calculations to examine the electronic properties of **1c**−**4c**. The first reduction potentials correlate to the calculated LUMO levels and can be compared to a correlation established for azaacenes (see SI).[2] Absolute

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(16) FMOs were calculated using Spartan'10 (B3LYP, 6-311+G**).

Table 1. Photophysical (recorded in hexanes) and Electrochemical (in DCM) Properties Recorded for Compounds **1**−**4**

compd	abs λ_{max}/ nm	emsn λ_{max}/ nm	ε/ mol^{-1} dm^3	Stokes shift/ cm^{-1}	PLQY $\Phi_f \pm 0.1$	observed $S_1 \leftarrow S_0$ cm^{-1}	calculated $S_1 \leftarrow S_0$ cm^{-1a}	$E_{1/2}{}^{red}$/ V^b
1c	412	480	19 900	3440	0.04	24 270	24 650	−1.58
2c	586	597	21 400	310	0.13	17 060	17 800	−1.26
3c	734	739	30 700	90	–	13 620	13 620	−1.12
4c	711	724	9 780	250	–	14 060	14 100	−0.77/−1.33

[a] Spartan10/TDDFT/B3LYP/6-311+G**. [b] Half-wave reduction potential from cyclic voltammetry experiments (vs Fc/Fc^+). For details, see SI.

values however show an ~0.4 eV offset between theoretically (gas phase) and experimentally (DCM solution) determined LUMO levels.[17]

Almost all of the prepared alkynylated selenadiazoles show a strong tendency to crystallize,[18] and single crystals suitable for X-ray analysis were obtained for **1a** and **2b**, as well as for the TIPSA compound series **1c**−**4c** (**3c** and **4c** shown in Figure 2). As envisaged, all crystal structures showed pronounced head-to-head dimerization in the solid state with remarkably short intermolecular Se−N distances of 2.87 (**1c**), 2.87 (**2c**), 2.82 (**3c**), and 2.95 Å (**4c**), respectively, compared to the sum of van der Waals radii (Se−N, 3.45 Å). It is worth noting that **3c** shows an even shorter chalcogen−N distance than the consanguine anthracenothiadiazole (S−N, 2.96 Å).

The selenadiazoles **1**−**2** form planar head-to-head dimers. In the case of **3c** the molecules π-stack in the solid state with an offset of 0.06 Å within the dimer and distances of 3.36 and 3.42 Å between the different layers. The dimers of **4c** show an offset of 1.20 Å (Figure 2, bottom, left), apparently a solid state effect of the π-stacking, which shows an intermolecular distance of 3.38 and 4.57 Å (a shorter π−π distance and larger offset).

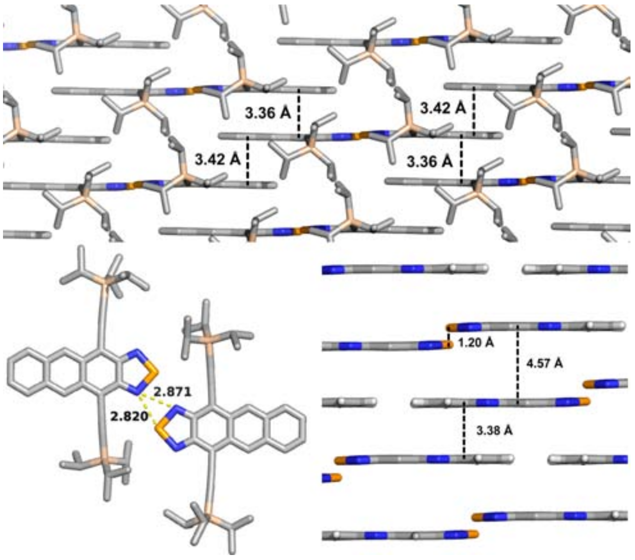

Figure 2. Crystal structure of the brickwall motif of **3c** (top) and coplanar N−Se and N−N short contacts of **3c** dimer (bottom, left). Planar offset for the dimers of **4c** (bottom, right). For clarity hydrogens and some side chains were omitted.

These solid state π-interactions are consistent with the above-mentioned red-shifted thin film absorption spectra for **3** and **4**. For the anthracenothiadiazoles, the TMS-alkynylated compound exhibited a packing structure with no head-to-head dimerization and coplanar packing only, while TES-alkynylation led to weak head-to-head dimerization with a large offset.[6] This indicates competing interaction effects arising from the bulky silylated side chains, the stacking of the aromatic cores, and the intermolecular N−chalcogen interactions. Comparison of TIPSA-anthracenothiadiazole with **3c** shows that the latter effect became much more pronounced with the introduction of selenium. This is in line with recently published data on D-A-copolymers featuring chalcogendiazole homologues.[19]

The Se−N interaction was further investigated by gas phase quantum chemical calculations of the monomer compared to a planar head-to-head dimer (Figure 3). A geometry optimization starting from a linear coplanar arrangement of the thiadiazole dimers (B3LYP, 6-311+G**) yielded structures with increasing angles for the larger aromatic cores, while the selenadiazoles (**1a**, **2a**, **3a**) *formed strictly coplanar dimers* (Figure 3). In agreement with the crystal structure, the calculated intermolecular Se−N distances are shorter than the S−N distances (see SI).

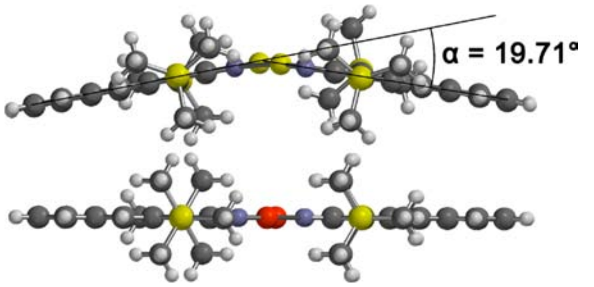

Figure 3. Side view of the calculated dimers of **3a** (bottom) and the corresponding thiadiazole (top).

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(18) For compound **2b**, a ca. 1 × 1 × 0.5 cm^3 single crystal was obtained; see SI for a photograph.

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As a measure for electronic coupling, the FMO splitting was analyzed (Figure 4).[20] For the **3a** dimer, the HOMO splitting is neglibly small ($\Delta E_{\mathrm{HOMO/HOMO\text{-}1}} = 0.02$ eV) while the LUMO and LUMO+1 differ by $\Delta E_{\mathrm{LUMO/LUMO+1}} = 0.17$ eV (cf. SI). This will translate into large transfer integrals for electron transport. The splitting for the anthracenothiadiazole was lower ($\Delta E_{\mathrm{LUMO/LUMO+1}} = 0.09$ eV) which is a consequence of the increased distance and the tilted arrangement.

To quantify the stabilization of the dimers the zero-point energies (ZPE) were calculated based on their ground state energies. A stabilization (SCF + ZPE) of 4.6, 4.8, and 5.2 kcal/mol compared to twice the monomer energy was obtained for **1a**, **2a**, and **3a**, respectively. For the thiadiazoles, the dimer stabilization was only 2–3 kcal/mol. The dimer of **2a** was 2.3 kcal/mol more stabilized than its thiadiazole congener, pointing to strong electrostatic dipole–dipole interactions as a driving force for the observed solid-state structure.

The development of new semiconducting materials for organic electronics raises a need for advanced design principles for (molecular) electronic properties and a concomitant predictability in the short-range ordering of thin films. The strong tendency of the analyzed selenadiazoles to aggregate in a head-to-head fashion highlights a rational method using coplanar alignment for the molecular engineering of small molecule semiconductors. In fact, the dimers of **3c** may be regarded as and compared to an octacene in the solid state. The offset of the **4c** dimer raises the question which modifications to the structure will lead to planar dimerization or might also increase the step height.

The well-understood influence of selenium on FMOs and the ease of preparation of these compounds further rationalizes the use of these materials as the active layer in organic thin film transistors, and work along these lines is currently being done in our laboratories.

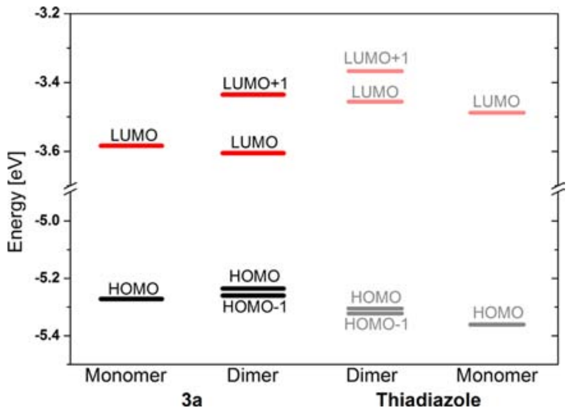

Figure 4. Graphic representation of the frontier orbitals of monomer and dimer of **3a** compared to the thiadiazole.

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Supporting Information Available. Detailed synthetic procedures, spectra, crystal data, and calculation results. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.