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Electron-Transporting Phenazinothiadiazoles With Engineered Microstructure$^{\perp}$

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$^{\perp}$Electronic supplementary information (ESI) available: Experimental procedures and analytical data for all prepared compounds; crystallographic data; details on thin-film transistor fabrication and computational studies.

ABSTRACT

Novel triisopropylsilyl-(TIPS)-alkynylated phenazinothiadiazoles were prepared by condensation of *ortho*-quinones and an alkynylated 5,6-diamino-2,1,3-benzothiadiazole. The targets show head-to-head dimerisation in the solid state, which, according to calculated transfer integrals should favor charge transport. The compounds form polycrystalline thin films when spin cast from solution. Two derivatives are attractive electron transporting materials with an average electron mobility μ_e in thin film transistors (TFT) of 0.07 cm²/Vs.

1. Introduction

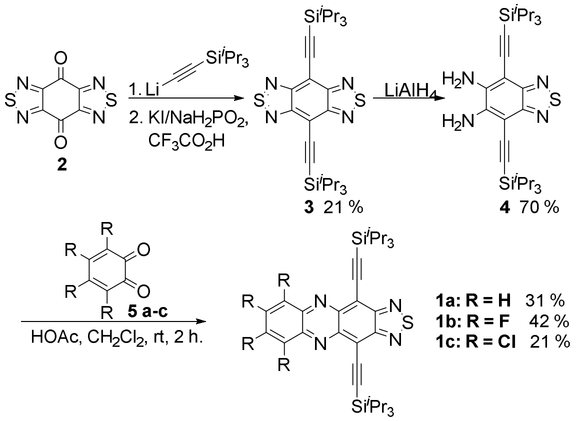
Small molecule[1] and polymeric[2] organic semiconductors featuring electrons as majority charge carrier and air-stability in TFTs remain challenging to procure. Due to increasing rationalisation of structural concepts for efficient charge transport in molecular solids, the number of high-mobility compounds is growing. Herein we show a new structural motif giving rise to a predictable intermolecular order in solid state, producing efficient electron-transporting thin films.

Motivated by our work on alkynylated phenazines and chalkogenodiazoles,[3] we became interested in merging these two structural features. As linear, benzannulated thiadiazoles and selenodiazoles show head-to-head dimerisation in the solid state with electronic coupling across the dimer, the same was expected to be true for phenazine thiadiazoles. Herein we describe the synthesis of phenazinothiadiazoles and investigate their chemical, electronic and electrical properties.

2. Results and Discussion

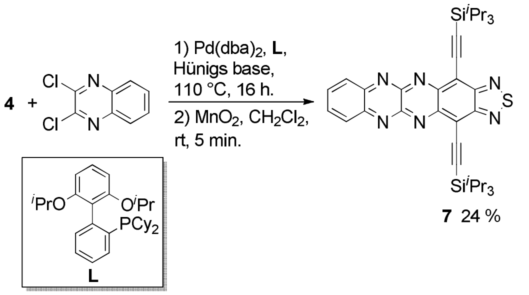
2.1. Synthesis

The synthesis of the alkynylated phenazinothiadiazoles **1a-c** is depicted in Scheme 1, starting from benzo[1,2-c:4,5-c']bis([1,2,5]thiadiazole)-4,8-dione **2**.[4] Alkynylation, and reductive deoxygenation gives **3**. Mono-desulfurization yields diaminobenzothiadiazole **4** which was condensed with *ortho*-quinones **5a-c** to give the phenazinothiadiazoles **1a-c**.[5]



Scheme 1: Synthetic route towards substituted phenazinothiadiazoles 1a-c.

To further extend the size of the aromatic core and incorporate more electronegative moieties, we chose to prepare the hetero-tetracenothiadiazole **7** by a cross coupling-oxidation sequence (Scheme 2).[6] However heteroacene **7** proved to be not stable enough for device application, as the compound already starts to decompose to the dihydro-compund **7-H$_2$** during purification (see ESI).



Scheme 2: Synthesis of hetero-tetracenothiadiazole 7.

2.2. Material characterisation and solid state structure

The optical properties of **1a**-**c** were determined from their solution absorption and emission spectra (Figure 1, Table 1, see ESI for emission spectra and optical spectra of **7-H$_2$** and **7**). All compounds show similar absorption profiles, resembling the all-carbon parent structure anthracenothiadiazole **6**, which indicates an equal influence of the nitrogen substitution concerning the HOMO and LUMO levels. Halogen-substitution of the outer benzannulated ring however, reduces the optical gap due to higher LUMO coefficients in this ring. Emission profiles show a small Stokes' shift, which is in line with a rigid molecular frame and hints towards a low reorganisation energy.

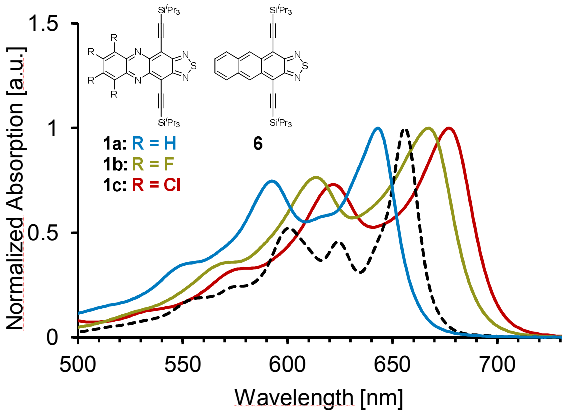


Figure 1: Optical absorption spectra of **1a**-**c** (solid lines) and the all-carbon congener anthracenothiadiazole **6** (dashed line).

Reduction potentials for the new compounds were determined by cyclic voltammetry in THF and compared to density functional theory (DFT) gas-phase calculations (Table 1). Compounds **1a**-**c** show reduced first (and second) reduction potentials in the sequence H→Cl→F which is in line with theoretical prediction and the electronegativity. However, the difference between **1b** (F) and **1c** (Cl) is within the experimental error margin of this determination method as well as the simplifications of the calculation.[7] The correlation of experimentally determined LUMO levels to DFT-calculated values is qualitatively correct, but shows an average 0.33 eV offset.[3g]

To gain further insight into the potential semiconducting properties we examined the single crystal structures of **1a**-**c** and **6** obtained from X-ray analysis (Figure 2 and ESI).

Table 1: Optical and electrochemical properties of phenazinothiadiazoles **1a**-**c** compared with anthracenothiadiazole **6** and data of tetracenothiadiazole **7**.

Compound	**$\lambda_{max/Abs}$ [nm]**	**$\lambda_{max/Em}$ [nm]**	**ε [$mol^{-1}dm^{3}$ cm^{-1}]**	**Stokes shift [cm^{-1}]**	**$E^{0/-1}$ [V]** [a)]	**$E^{-1/-2}$ [V]** [a)]	**$E_{LUMO, Exp}$ [eV]** [b)]	**$E_{LUMO, DFT}$ [eV]**[c)]
1a	643	651	17 201	191	-0.83	-1.47	-4.27	-3.85
1b	667	679	25 851	265	-0.57	-1.29	-4.53	-4.23
1c	677	687	19 892	215	-0.62	-1.22	-4.48	-4.20
6	656	662	22 636	138	-1.15	-1.80	-3.95	-3.40
7	795	---	---	---	-0,43	-0,93	-4,67	-4.31

a) reduction potentials measured with gold working electrode in THF vs. Fc/Fc$^+$ as reference redox system; b) $E_{LUMO,\ Exp}$ = - ($E^{0/-1}$ + 5.1 eV);[7] c) gas-phase energy calculated for trimethylsilylalkynyl groups using Spartan´10: DFT, B3LYP, 6-311+G**.

All of the solid state structures feature head-to-head dimerisation of the thiadiazole moieties with S-N distances shorter than the combined van der Waals *radii*. The vertical offset (0.27 Å for **1b**; 0.35 Å for **1c**) within the dimer might be a consequence of the proximity of the two pairs of triisopropylsilyl groups.

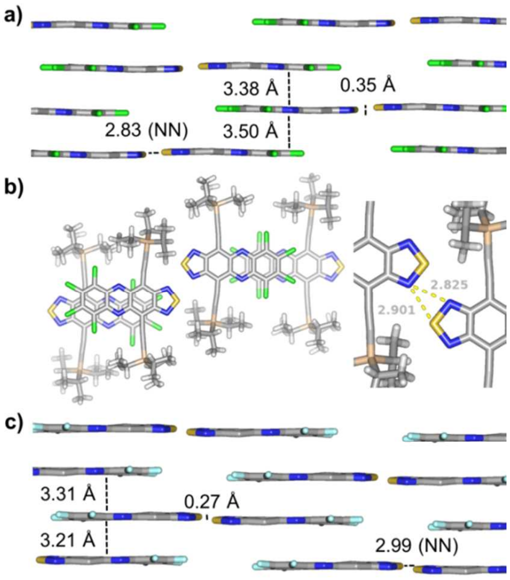


Figure 2: Side view a) and top view b) of the crystal structures of **1c** and side view c) of **1b** illustrating the intermolecular distances in the solid state structure.

The dimers form a brick wall type packing motif with almost symmetrical π-stacking distance from one phenazine core to the adjacent aromatic moieties (3.31 and 3.21 Å, respectively). To assess the implication of the dimerization on charge transfer according to Marcus theory, we calculated the transfer integrals for dimers of **1a**-**c** in all different π-π-overlaps and the head-to-head arrangement based on the crystal structures. We used the projective method developed by Kirkpatrick *et al.* at the B3LYP/6-311G** level,[8,9] and found that almost all transfer integrals for the LUMOs are between 40-80 meV. The HOMO values are invariably smaller than the corresponding LUMO values. The highest value of 128 meV was found to be a LUMO-π-π-overlap of **1b** which is shown in Figure 3, the corresponding head-to-head value being 43 meV. The transfer integrals underline the strong electronic coupling over the head-to-head contacts. For a complete list of values and arrangements see ESI.

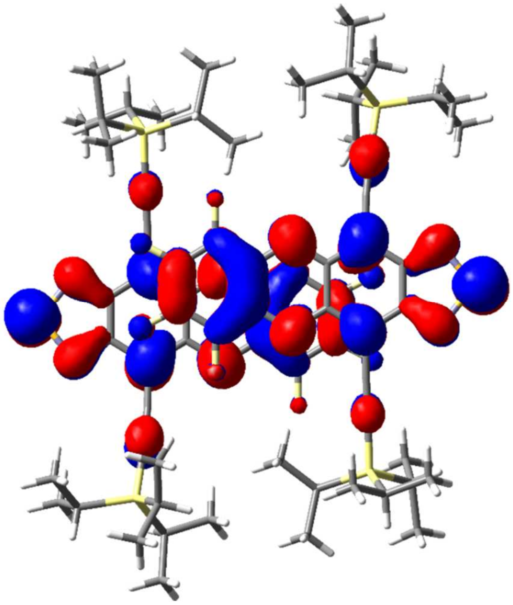


Figure 3: Top view of the dimer of **1b** extracted from the crystal structure and the calculated Frontier molecular orbitals. The presented arrangement shows the dimer with the highest overlap of the LUMOs.

2.3. Device Fabrication

This solid state structure and the promising transfer integrals derived from it prompted us to continue with our investigation on the semiconducting properties of **1a**-**c** and we consequentially fabricated thin film field effect transistors. We investigated the performance of **1b** and **1c** as n-channel semiconductors in bottom-contact/ top-gate TFTs based on the architecture described by Sakanoue *et al.*.[10] Polycrystalline films of **1b** and **1c** were obtained by spincoating from chlorobenzene on pre-patterned gold contacts on glass/polyimide substrates.

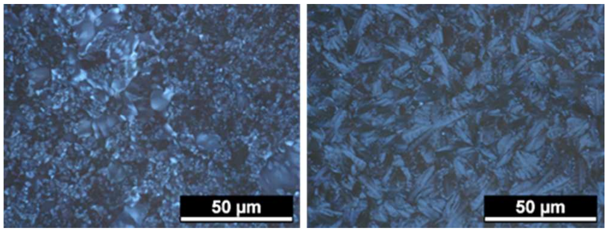


Figure 4: Cross polarised microscopy images of **1c** (left) and **1b** (right). The films were spincoated from chlorobenzene onto polyimide-covered glass substrates.

The morphology was investigated by polarising microscopy. The average domain size of the crystallites is in the range of 2 to 20 µm for both materials (Figure 4). The fluorinated compound **1b** exhibits a slightly larger grain size compared to **1c** and films look more uniform.

We used fluorinated Cytop polymer as gate dielectric followed by a thermally evaporated gate electrode. The output characteristics show good injection of electrons from gold into the materials and in both cases nearly no hysteresis is observed (Figure 4 for **1b**, for **1c** see ESI).

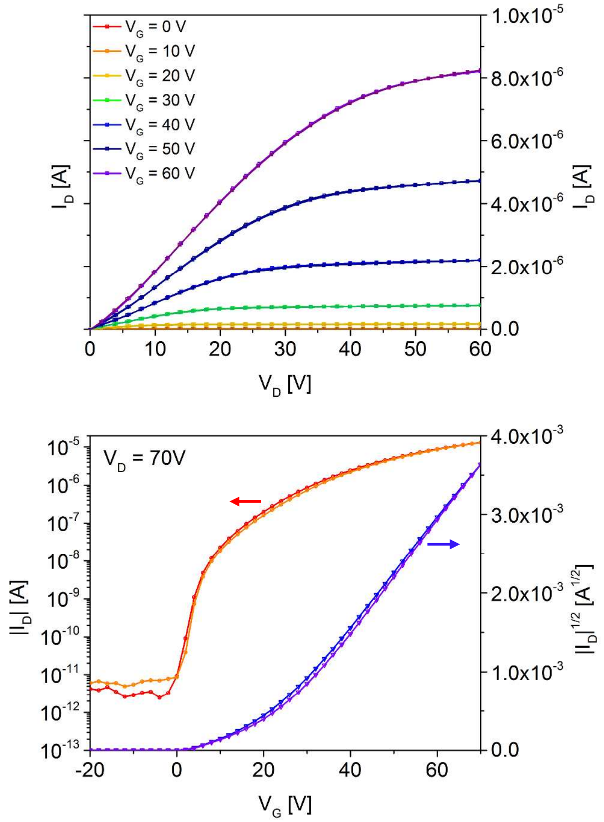


Figure 5 Output and transfer characteristic of a representative TFT (W/L = 1000 µm / 20µm) with **1b** as active layer.

The average device parameters are summarised in Table 2. Both **1b** and **1c** show good on/off ratios and, despite their polycrystalline nature and the small domain size, the observed electron mobilities are always over 10^{-2} cm^2/Vs. Transistors fabricated from **1b** exhibit slightly higher average electron mobility μ_{sat} compared to **1c**.

Table 2: Thin film transistor parameters.

Compound	**$\mu_{e,sat}$ [cm^2/Vs]**	**V_{th} [V]**	**On/off ratio**[a)]
1b	0.07 ± 0.02	26 ± 8	10^4 - 10^5
1c	0.04 ± 0.01	10 ± 5	10^4 - 10^5

a) on/off ratios were calculated as $I_{on}(V_G = V_{th}+10V) / I_{off}(V_G = 0V)$.

3. Conclusion

In conclusion, we have prepared three different phenazinothiadiazoles with excellent electron affinities. The solid state structure shows a predictable intermolecular interaction priority, which enables these compounds to show efficient charge transport. The halogenated representatives **1b** and **1c** are attractive electron transport materials with average μ_e up to 0.07 cm^2/Vs. Further modification of this interesting structural motif will yield additional attractive materials with increased mobility, while further work on the processing conditions, like e.g. solvent vapour treatments, for this current set of compounds may lead to an improved morphology and TFT performance and work along these lines is ongoing in our laboratories.

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