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FULL PAPER

Symmetric Mixed Sulfur-Selenium Fused Ring Systems as Potential Materials for Organic Field-Effect Transistors

Brigitte Holzer,*[a] Barbara Dellago,[a] Ann-Katrin Thamm,[b] Thomas Mathis,[b] Berthold Stöger,[c] Ernst Horkel,[a] Christian Hametner,[a] Bertram Batlogg,[b] Johannes Fröhlich[a] and Daniel Lumpi*[a]

Abstract: A reliable synthetic protocol toward a series of fused chalcogenopheno[1]benzochalcogenophene (CBC) building blocks was developed based on a Fiesselmann reaction. The obtained CBC units were applied in McMurry and Stille coupling reactions toward symmetric regioisomeric ene-linked dimers. These π-conjugated compounds were characterized regarding their photophysical and electrochemical properties and proved to be materials with reduced HOMO-LUMO gaps compared to their sulfur-based analogues. Single-crystal X-ray diffraction experiments revealed strong intermolecular selenium-selenium and selenium-carbon interactions depending on the position and number of incorporated selenium atoms. Good field-effect transistor performance with charge carrier mobilities up to $4 \cdot 10^{-3}$ cm^2 V^{-1} s^{-1} and high on/off ratios could be observed.

Introduction

Organic field-effect transistors (OFETs) have attracted attention owing to their potential advantages of flexibility, large-area fabrication and low weight.[1] Accordingly, OFETs are being considered for applications in electronic paper,[2] organic light emitting displays and sensor devices,[3] such as electronic noses (e-nose),[4] electronic skin (e-skin),[5] medical diagnostics,[6] environmental monitoring[7] but also in everyday technology like radio frequency identification tags (RFIDs).[8]

Since the first OFETs emerged,[9] many efforts have been dedicated to improving their performance by adopting new organic semiconductors (OSC) or optimizing the device configuration.[10] Despite the broad fields of promising applications of organic semiconductors, there is still a need for further research to synthesize stable materials bearing high charge carrier mobility for fast electrical switching, low operating voltages and large on/off ratios.[11]

Both the film morphology and the molecular arrangement in organic semiconducting layers play a significant role to achieve good OFET performance.[12] The molecular packing and consequently charge carrier mobility are essentially determined by intermolecular coupling between the π-electron clouds of aromatic molecules, which is maximized when molecules adopt a face-to-face orientation.[10,13,14] Intermolecular π···π and C-H··· π interactions are predominant in acenes and their thiophene analogues. The incorporation of sulfur in acenes may induce an effective overlap between the HOMOs of neighbouring molecules in the solid state due to the large electron densities on the heteroatoms.[15] Consequently, the molecular packing in sulfur-rich thienoacenes is strongly influenced by the combination of intermolecular multiple S···S, S···C, and CH··· π interactions, which in turn can be correlated to high charge carrier mobility.[16,17] Another benefit of replacing benzene rings with heteroaromatic groups is an increase of the molecular oxidation stability.[1]

Recently, we have published on the electrical properties of OFET materials based on thieno[2,3-*b*][1]benzothiophene building blocks connected by different π-spacers (e.g. ethylene spacer, **BTTE**; Figure 1, left) exhibiting both high stability and charge carrier mobility.[18] Also, its regioisomer **DTBTE** (Figure 1, right), was reported to possess strong intermolecular interactions with S···S contacts being shorter than the double van der Waals radius of sulfur.[19]

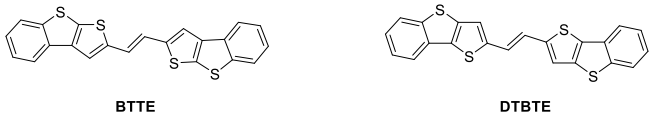

Figure 1. Thieno[1]benzothiophene-based materials **BTTE** (left) and **DTBTE** (right) exhibiting mobilities up to 3.3 x 10^{-3} cm^2 V^{-1} s^{-1} and 0.5 cm^2 V^{-1} s^{-1}, respectively.

Further enhancement of intermolecular overlap may be achieved by molecular modification of thienoacenes: the substitution of sulfur by selenium atoms may increase interactions in organic compounds due to the larger atomic radius and therefore higher polarizability of selenium atoms,[20] possibly enhancing device performance by improvement of intermolecular overlap in the solid state and consequently also the charge carrier mobility. Thus, selenophene-fused aromatics constitute attractive candidates for electronic applications. However, owing to a lack of available starting materials, up to now the development of reliable synthetic pathways toward selenium-based materials is matter of ongoing research.[21–23]

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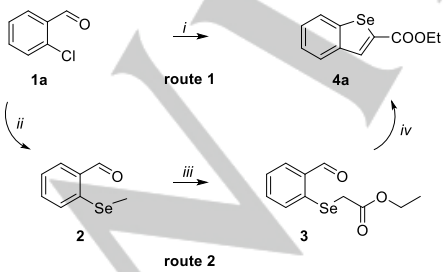
Herein, we report on the design and synthesis of regioisomeric chalcogenopheno[1]benzochalcogenophene (CBC) building blocks. These selenium-based moieties were applied in a series of symmetrical ene-linked π-conjugated organic semiconductors, which were characterized by NMR, UV-Vis absorption spectroscopy, cyclic voltammetry and X-ray diffraction (XRD). In particular, the effect of the selenium position and the annelation side of the CBC subunits on the properties of these materials was matter of interest. Furthermore, these compounds were tested as semiconductors in organic field effect transistors.

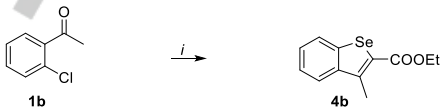
Results and Discussion

The synthesis toward ene-bridging target molecules was planned by linkage of chalcogenopheno[1]benzo-chalcogenophene (CBC) building blocks. However, the synthetic pathways toward benzo[*b*]selenophenes described in literature often consist of tedious multi-step reactions. In order to ensure good accessibility and avoid the need of isolating intermediates the synthesis of benzo[*b*]selenophene derivatives was planned based on a Fiesselmann type reaction (Scheme 1). The synthetic sequence was first probed by a stepwise approach yielding **4a** (route 2). Introduction of selenium in commercially available **1a** was achieved by nucleophilic aromatic substitution applying *in situ* generated lithium methyl selenide, giving rise to methyl selenide **2** in 42% yield. The applied method inspired by Tiecco *et al*.[24] introduces selenium as organo-selenide, while earlier reports on the synthesis toward phenyl selenides are based on lithiation of the phenyl ring and subsequent conversion with elemental selenium requiring protective groups for carbonyl substituents.[25] Thus the need for derivatization of the carbonyl functionality and the tedious preparation of unstable Na_2Se or NaHSe frequently used to prepare phenyl selenides are avoided by the applied synthetic protocol.[26,27] Further conversion toward **3** was realized by refluxing **2** with ethyl bromoacetate following a similar procedure reported by Renson *et al*.[28] This step was proposed to proceed by the addition of ethyl bromoacetate to the aryl methyl selenide forming an intermediate selenonium bromide.[29] Thermal decomposition of this salt gave rise to arylselenoacetic ester **3** in 73% yield. Finally ring closure toward benzo[*b*]selenophene carboxylate **4a** was achieved by applying a base-induced condensation reaction in 96% yield.



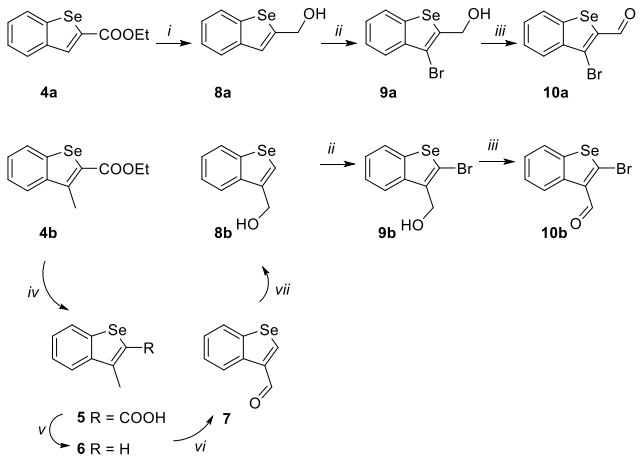
Scheme 1. One-pot (route 1): *i*: grey selenium, n-BuLi, THF, r.t. 40 min / DMF, ethyl bromoacetate, reflux / K_2CO_3, 120 °C; and stepwise synthesis procedure (route 2): *ii*: grey selenium, MeLi THF, r.t. 40 min; *iii:* ethyl bromoacetate, reflux; *iv:* DMF, K_2CO_3, 120 °C.

Based on the obtained results a one-pot approach toward **4a** avoiding the necessity of isolating **2** and **3** was pursued. Since the decomposition of the *in situ* generated triorgano-selenonium bromide generates toxic bromomethane as side product, the first step of the synthetic pathway was altered: instead of lithium methyl selenide its butyl analog, generated *in situ* from elementary selenium and n-butyllithium, was applied. The reaction progress was monitored by GC-MS analysis and clean conversion toward the respective aryl butyl selenide could be observed. Subsequently the solvent was distilled off under vacuum and replaced by DMF in order to achieve the high reaction temperatures necessary for the decomposition of the selenonium salt. Ethyl bromoacetate was added, the reaction mixture was refluxed and after an appropriate reaction time base was added. The desired compound **4a** was obtained in 74% yield, however GC-MS analysis revealed butyl benzo[*b*]selenophene-2-carboxylate as side product. The formation of the latter can be attributed to trans-esterification of **4a** with butanol, which originates from the hydrolysis of butyl bromide generated during the decomposition of the selenonium bromide. The developed procedure was also applied to o-chloroacetophenone (Scheme 2) giving rise to **4b** in 57% yield.



Scheme 2. Synthesis of **4b**. Reaction conditions: *i*: grey selenium, n-BuLi, THF, r.t., 40 min / DMF, ethyl bromoacetate, reflux / K_2CO_3, 120 °C.

Since benzo[*b*]selenophenes substituted in the 2- and 3-position bearing a carbonyl group and a halogenide constitute essential building blocks providing valuable strategic linking points for further transformation, an efficient and reliable synthetic methodology was probed toward both isomers **10a** and **10b** (Scheme 3). Derivatization of ester **4a** was achieved by reduction applying $LiAlH_4$ in 97% yield.



Scheme 3. Synthesis of substituted benzo[*b*]selenophenes **10a** and **10b**. Reaction conditions: *i*: $LiAlH_4$, THF; *ii*: NBS, $CHCl_3$ or THF; *iii*: MnO_2, $CHCl_3$ or ethyl acetate; *iv*: NaOH, H_2O / MeOH, reflux; *v*: Cu, quinoline, 160 °C; *vi*: SeO_2, 1,4-dioxane, reflux; *vii*: $NaBH_4$, EtOH.

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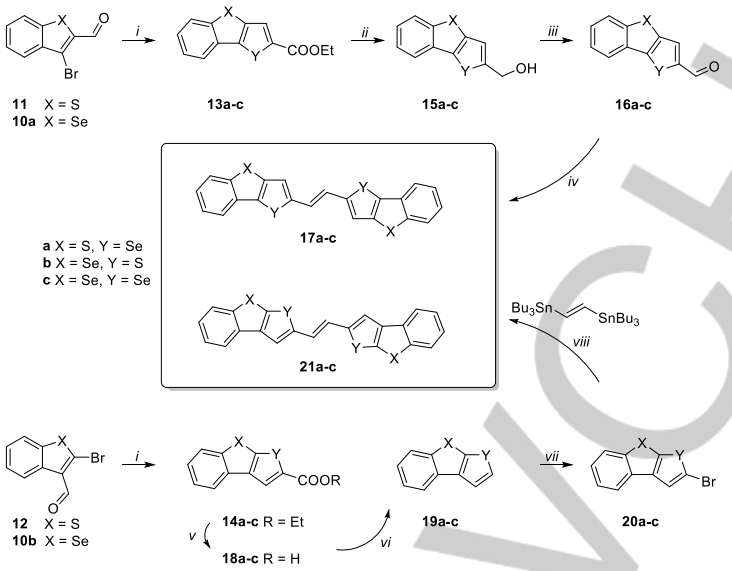

Scheme 4. Synthetic strategy toward target molecules **17a-c** and **21a-c**: i: NaHSe, ethyl bromoacetate or triethylamine, ethyl thioglycolate, ii: $LiAlH_4$, THF, iii: MnO_2, iv: Zn, $TiCl_4$, pyridine, THF, v: NaOH, H_2O / MeOH, vi: Cu, quinoline, 160 °C, vii: NBS, THF, viii: $Pd(PPh_3)_4$, toluene, reflux.

Subsequent bromination of alcohol **8a** gave **9a** in 86% yield, further oxidation with MnO_2 led to aldehyde **10a** in 75% yield. The synthetic pathway toward isomer **10b** (Scheme 3) was performed *via* alcohol **8b** including two additional steps to remove the carboxylate functionality. Saponification of **4b** in 91% yield, decarboxylation of the obtained acid **5** in 94% yield, and oxidation of **6** using SeO_2 gave aldehyde **7** (90% yield). Further reduction applying $NaBH_4$ led to alcohol **8b** in 92% yield. Bromination of **8b** with *N*-bromosuccinimide led to **9b** in 45% yield, which gave rise to **10b** in 98% yield after oxidation.

Starting from properly substituted benzo[*b*]thiophenes **11** and **12** and benzo[*b*]selenophenes **10a** and **10b**, the key step toward fused CBC moieties **13** as well as **14** is based on an optimized one-pot Fiesselmann reaction adapted from Machara *et al.*[30] Nucleophilic aromatic substitutions of aldehydes with *in situ* generated sodium hydrogenselenide and subsequent addition of ethyl bromoacetate or application of ethyl thioglycolate in triethylamine gave access to annelated ring systems **13a-c** as well as **14a-c** in good to excellent yields (Scheme 4). Although the one-pot route developed for **4a** (based on an aromatic substitution and a subsequent Fiesselman reaction) is also feasible towards **13a,c** and **14a,c**, first synthetic experiments indicated low yields; therefore, this approach was not followed.

Based on previously reported approaches toward ene-bridged substrates[19,31] derivatization of the obtained CBCs for McMurry reactions was the basis of further synthetic efforts. Functionalization of CBCs as aldehydes was realized by reduction of **13a-c** with $LiAlH_4$ and subsequent re-oxidation of the obtained alcohols **15a-c** to yield aldehydes **16a-c**. Finally, regioisomers **17a-c** (Scheme 4, Table 1) were selectively accessible as *E*-isomers in good yields applying reductive McMurry reaction conditions toward **DTBTE** systems (X, Y = S) according to literature. For regioisomers **21a-c** an alternative synthetic pathway was chosen since the reduction of **14a-c** yielded the respective alcohols only in low yield. Therefore, hydrolysis of CBC esters **14a-c** and subsequent decarboxylation of the acquired acids **18a-c** led to CBC cores **19a-c** (Scheme 1). Further bromination of the latter applying NBS gave the respective CBC bromides **20a-c** in good to excellent yields. The synthesis toward **21a-c** was realized applying brominated CBC cores **20a-c** in a Stille coupling reaction with trans-1,2-bis(tri-n-butylstannyl)ethylene according to literature.[31] The obtained solid materials **17a-c** and **21a-c** appear yellow to orange in color and are slightly soluble in chlorinated organic solvents. The characterization of all compounds was performed by ^1H / ^{13}C / ^{77}Se NMR spectroscopy, HR-MS analysis, and single-crystal XRD. The data are consistent with the proposed structural formulations.

Optical and Electrochemical Properties. Photophysical properties of **17a-c** and **21a-c** were determined in 5 µM CH_2Cl_2 solution by UV-Vis spectroscopy (Figure 2a, Table 1 and supporting information; due to solubility issues of the target compounds, a numerical determination of the extinction coefficients was omitted and normalized spectra are given only) and compared to the sulfur-based compounds **BTTE** and **DTBTE.** The UV-Vis absorption spectra of the compounds are strongly affected by the heteroatoms incorporated. Three absorption maxima were observed for each substance: the maxima for all selenium containing compounds are shifted to higher wavelengths, which can be attributed to the higher electron density induced by the selenium heteroatom. The heterocycle next to the ene-bridge of **17a-c** plays an important role and strongly correlates with the position of the absorption maximum: while for the thiophene ene-conjugated moieties **17b** and **21b** only a slight bathochromic shift can be observed, its selenophene analogues **17c** and **21c** exhibit red shifts compared to **DTBTE** and **BTTE**, respectively. The HOMO-LUMO gaps were determined from the onset of the UV-Vis absorption (Table 1).

In the series **17a-c**, the shape of the absorption edge remains as sharp as in the reference **DTBTE**, the value of the optical gap shifts to lower

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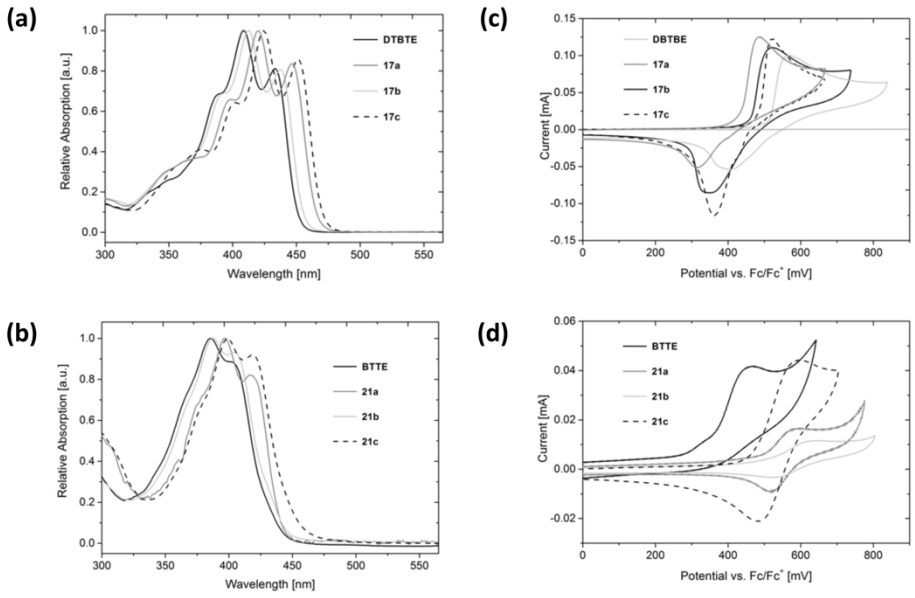

Figure 2. Absorption spectra of **17a-c** as well as **DTBTE** (a) and **21a-c** as well as **BTTE** (b). Cyclic voltammograms of **17a-c** as well as **DTBTE** (c) and **21a-c** as well as **BTTE** (d) in DCM solution.

Table 1. Experimental data, physical characterization and computational data of compounds **17a-c** and **21a-c**.

Comp.	Yield	λ_{max}[a]	HOMO-LUMO gap[b]	HOMO[c]	LUMO[d]	HOMO-LUMO gap[e]	HOMO[e]	LUMO[e]
	%	[nm]	[nm, eV]	[eV]	[eV]	[eV]	[eV]	[eV]
DTBTE	-	433, 409, 388	452, 2.74	-5.31	-2.57	2.99	-5.39	-2.40
17a	68	447, 420, 398	467, 2.65	-5.23	-2.58	2.91	-5.37	-2.40
17b	55	438, 412, 392	456, 2.72	-5.26	-2.54	2.97	-5.39	-2.48
17c	63	451, 424, 400	470, 2.64	-5.28	-2.64	2.89	-5.37	-2.48
BTTE	-	402, 385	433, 2.87	-5.16	-2.29	3.28	-5.32	-2.04
21a	23	417, 397	443, 2.80	-5.30	-2.50	3.18	-5.32	-2.14
21b	30	405, 387	436, 2.84	-5.30	-2.46	3.26	-5.29	-2.03
21c	28	419, 398	450, 2.76	-5.27	-2.51	3.16	-5.29	-2.13

[a] Absorption maxima measured in DCM solutions. [b] Optical energy gaps were determined from the onsets of the absorption in DCM solutions. [c] HOMO levels determined by cyclic voltammetric measurements. All E_{ox} data are reported relative to ferrocene (Fc/Fc^+, E_{ox} = 446 mV). The concentration of the compounds used in this experiment was 5 µM in DCM; the scan rate was 50 mV s^{-1}. [d] LUMO levels were determined from the optical band gap and the HOMO energy level according to the following equation: $E_{LUMO} = E_{HOMO} + E_{energy\ gap}$. [e] Calculated HOMO-LUMO gaps and HOMO/LUMO levels (B3LYP / 6-311+G(d)).

energy just as the overall curves do, i.e. by approximately 0.11 eV. The same trend is observed in the **BTTE** related series, except for **21a**, where the lower part of the absorption curve is somewhat steeper than in the three related materials, with the pronounced "foot" near threshold absorption. In general, the optical energy gap of regioisomers **21a-c** are higher than for **17a-c**. Overall, the modification of the optical spectra upon selenium substitution is quantitatively remarkable similar in the two series **17a-c** and **21a-c**. Compared to the respective reference spectra, **17a** and **21a** shift by 0.088 eV, **17b** and **21b** by 0.023 eV and **17c** and **21c** by 0.115 eV towards lower energy. These findings are further supported by DFT calculations using the Gaussian 09 package at B3LYP / 6-311+G(d) showing good accordance with the experimental data for all target compounds (Table 1). Comparing the HOMO-LUMO gaps obtained by computational chemistry with those determined from the absorption onset, similar shifts could be observed for **17a** and **21a** (0.09 eV), **17b** and **21b** (0.02 eV) as well as **17c** and **21c** (0.10 eV) towards lower energy with respect to the references **DTBTE** and **BTTE**.

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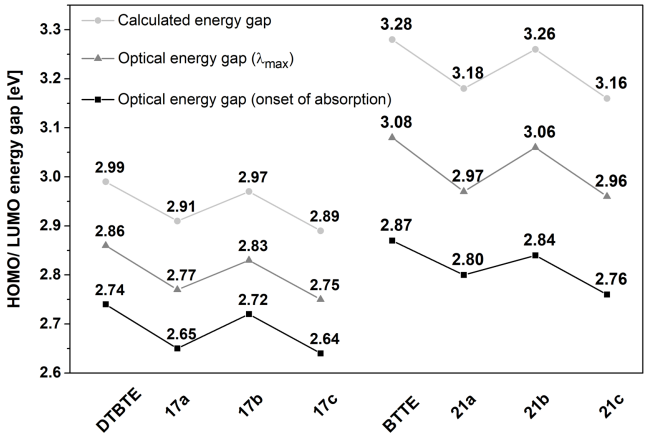

Figure 3. Comparison of calculated energy gaps using Gaussian (B3LYP / 6-311+G(d)) and the optical energy gaps determined either from the absorption maximum of the lowest energy transition or the onset of absorption for all target compounds.

Table 2. Short intermolecular distances (less than the sum of the van-der-Waal radii) in **DTBTE, 17a-c, 21a** and **21c**.

Comp.	S···C [Å]	CH··· π [Å]	S···S [Å]	Se···Se [Å]	Se···C [Å]	S···Se [Å]
DTBTE	3.323, 3.364, 3.497	2.816	3.507	-	-	-
17a	3.403, 3.431, 3.438	-	-	-	3.496, 3.585	3.579
17b	-	2.813	-	-	3.341, 3.349	3.622
17c	-	2.831, 2.857, 2.860, 2.872, 2.876	-	-	3.342, 3.468, 3.512	-
21a		-	-	-	3.590	-
21c	-	2.845	-	3.547, 3.702	3.557	-

For all compounds the correlation between the calculated energy gap and the energy gap either obtained from the aborption maximum of the lowest energy transition or the onset of aborption shows good agreement (Figure 3).

Electrochemical characteristics of compounds **17a-c** and **21a-c** were investigated by cyclic voltammetric (CV) methods and compared to those of **DTBTE** and **BTTE**, respectively (Figure 2b). The HOMO energy levels were determined from the onset of the oxidation potential assuming the ferrocene/ferrocenium reference to be 4.8 eV[32] below the vacuum level. All compounds **17a-c** undergo reversible oxidation indicating the formation of stable cation radicals. The HOMO levels of selenium-based compounds are slightly increased (ranging from -5.28 eV to -5.23 eV) compared to **DTBTE** (-5.31 eV). When comparing the regioisomers **21a-c** with **BTTE**, however, a significant reduction of the HOMO level can be observed, which indicates good stability. The LUMO energy levels were determined from the optical energy gaps and the HOMO levels obtained from CV data and vary in the range from -2.58 to -2.64 eV.

Single Crystal Structures. The effect of molecular conformation and packing properties in single crystals on charge carrier transport is a fundamental issue for organic semiconducting materials. Single crystals of **17a-c** were grown by slow evaporation from DCM (Figure 4), **21a** and **21c** from chlorobenzene (Figure 5); all crystals were structurally characterized. Compound **17b** is isostructural with **DTBTE**,[19] the remaining molecules crystallize in unique structure types. **21b** was only obtained as the pyridine solvate (molecular structure confirmed; no proper refinement owing to disorder and weak diffraction intensities). All CBC subunits are essentially planar and adopt an anti-conformation of the two fused chalcogenophenes, which may be favorable for charge carrier transport.[33] Generally, the molecules are located on centers of inversion, hence the two CBC units are ideally coplanar. Only compound **17c** is located on a general position allowing for twisting [angle between least squares planes (LS) of the CBC units: 8.72(4)°].

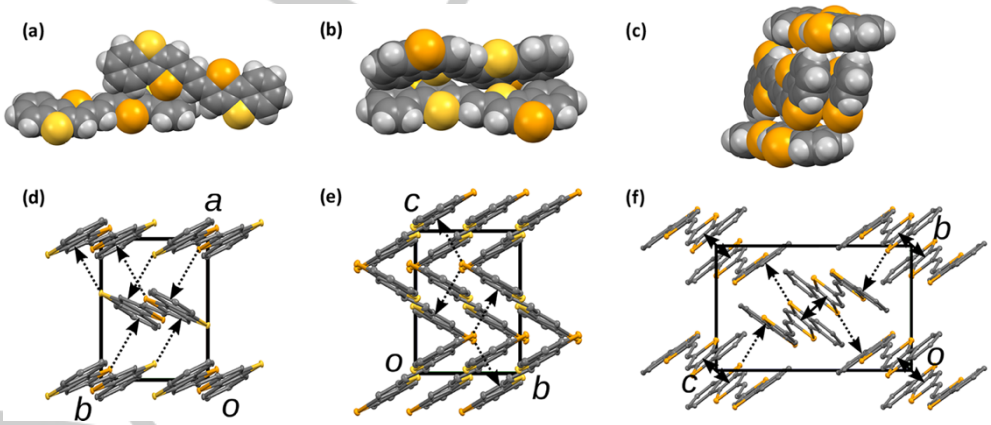

Figure 4. Packing plots of **17a** (a), **17b** (b) and **17c** (c) and neighboring interactions of **17a** (d), **17b** (e) and **17c** (f). Chalcogen-π and π-π interactions are represented by dotted and continuous arrows, respectively.

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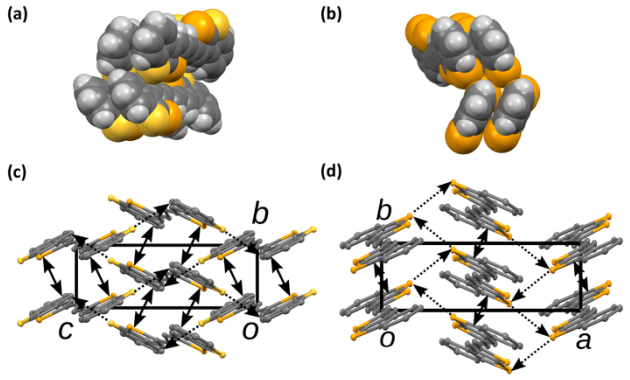

Figure 5. Packing plots of **21a** (a) and **21c** (b) and neighbouring interactions of **21a** (c) and **21c** (d). Chalcogen-π and π-π interactions are represented by dotted and continuous arrows, respectively.

With the exception of **21c**, all structures feature pronounced chalcogen-π interactions (in **17c** only one CBC subunit being involved). In **21c**, on the other hand, Se – Se contacts can be observed. Generally, the LS planes of the such contacted molecules are twisted by 53-55°, only **17c** features a larger twist angle of 82.1°. π- π interactions are not observed in **DTBTE, 17a** or **17b** owing to a distinct inclination of adjacent molecules. In **17c**, π-π interactions form pairs of molecules, in **21a** and **21b** infinite rods. All these short interactions may be beneficial to obtaining a high charge transport performance.

OFET device performance. The OFET device performance was determined in the top contact geometry; transfer and output characteristics were measured with an Agilent 4155 A semiconductor analyzer in vacuum. Typical transfer curves of **17a** on the amorphous fluoropolymer Cytop^{TM} (red, solid line) and on SiO_2 (blue, dashed line) are shown in Figure 6a, a typical output characteristic of **17a** on Cytop^{TM} is shown in Figure 6b.

Table 3. OFET performance parameters of **17a** and **DTBTE** prepared by vacuum deposition (μ_{Sat}: saturated mobility, I_{on}:I_{off}: on/off current ratio, V_T: threshold voltage).

	T	Dielectric	μ_{sat} [$cm^2\,V^{-1}\,s^{-1}$]	I_{on}:I_{off}	V_T [V]
17a	RT	SiO_2	0.0015	$5.6\cdot10^5$	-31
	70°C	SiO_2	0.00004	$1.7\cdot10^3$	-54
	RT	Cytop^{TM}	0.004	$1.2\cdot10^6$	-47
	70°C	Cytop^{TM}	0.0006	$2.3\cdot10^4$	-52
DTBTE	RT	SiO_2	0.0009	$9.8\cdot10^4$	-48
	RT	Cytop^{TM}	-	-	-
	RT	OTS	-	-	-

The measured device characteristics are summarized in Table 3 (for details on transfer characteristics refer to Figure S125). The devices made with **17a** showed a better OFET performance: on silicon the mobility was $1.5\cdot10^{-3}$ $cm^2\,V^{-1}\,s^{-1}$ and the on/off current ratio $5.6\cdot10^5$ when evaporated at room temperature. Using a Cytop film on SiO_2, the device performance could be improved with an increased charge carrier mobility of $4\cdot10^{-3}$ $cm^2\,V^{-1}\,s^{-1}$ and an on/off current ratio of $1.2\cdot10^6$. Additionally, the transfer curve measured on Cytop^{TM} showed a much smaller hysteresis than the one measured on SiO_2. When the substrate was heated to 70°C during the evaporation of **17a** (see Table 3) the OFET performance fell off compared to the ones kept at room temperature during the evaporation: the mobilities on silicon and on Cytop^{TM} both decreased (to $4\cdot10^{-5}$ $cm^2\,V^{-1}\,s^{-1}$ on Cytop^{TM} and $6\cdot10^{-4}$ $cm^2\,V^{-1}\,s^{-1}$ on pure SiO_2) just as the on/off current ratio ($2.3\cdot10^4$ on Cytop^{TM} and $1.7\cdot10^3$ on SiO_2). In comparison, the **DTBTE** semiconductor showed only a field effect performance on SiO_2 with a mobility of 0.001 $cm^2\,V^{-1}\,s^{-1}$ and an on/off current ratio of $9.8\cdot10^{-4}$.

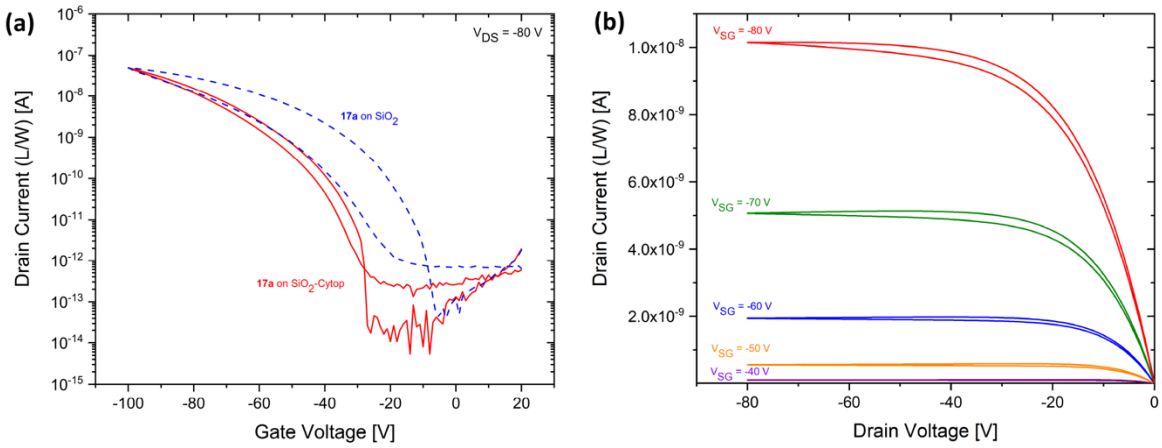

Figure 6. (a) Transfer characteristics for transistors (L=50 µm, W=560 µm) made with **17a** on Cytop (red, solid line) and on SiO_2 (blue, dashed line). The source-drain current, which is normalized by the transistor dimensions is plotted against the gate voltage. The drain-source voltage was -80 V in these measurements. (b) Output characteristics for **17a** on Cytop: the drain current is plotted against the drain voltage for different gate voltages: -80 V (red curve), -70 V (green curve), -60 V (blue curve), -50 V (yellow curve), -40 V (purple curve). For gate voltages over -40 V the measured drain current was at least one order of magnitude below.

However, neither on Cytop™ nor on octadecyltrichlorosilane (OTS) modified SiO_2 any device performance could be observed in contrast to earlier reports by Chen *et al*.[19] Devices based on compound **17a** on SiO_2 showed a high on/off current ratio and a higher charge carrier mobility compared to the sulfur-based compound **DTBTE** studied under the same processing conditions. The threshold voltages for **17a** were relatively low: -31 V for **17a** on pure SiO_2 and -47 V on Cytop™ (at RT).

Conclusions

This contribution outlines optimized synthetic pathways toward functionalized building blocks of chalcogenopheno[1]benzo-chalcogenophene (CBC) regioisomers. These CBC units were applied in McMurry and Stille coupling reactions yielding selenium-based potential semiconductors linked by ene-spacers. Photophysical measurements and crystallographic data reveal that the properties and molecular packing of all target molecules are strongly influenced by the position and number of incorporated selenium atoms. Both 3,2-*b*-fused ene-bridged materials **17a-c** as well as 2,3-*b*-fused regioisomers **21a-c** exhibit lower optical energy gaps and slightly increased HOMO levels compared to the respective sulfur-based analogues **DTBTE** and **BTTE**. These data are supported by quantum chemical calculations showing excellent agreement of the calculated energy gap and the energy gap obtained from optical measurements. Furthermore, analysis of single crystals confirmed the planarity of all CBC subunits; the molecular structure and packing of the materials indicate strong intermolecular interaction for all ene-based compounds, which may be beneficial for charge carrier transport. This set of regioisomeric sulfur-selenium based materials proves to be a promising new material class with good charge carrier mobilities and high on/off ratios in organic thin film transistors.

Experimental Section

Substances purchased from commercial sources were used as received. Anhydrous *N,N*-dimethylformamide (DMF), methyllithium (1.6 M solution in diethyl ether), n-butyllithium solution (2.5 M solution in hexanes), o-chlorobenzaldehyde, o-chloroacetophenone, *trans*-1,2-bis(tri-n-butylstannyl)ethylene and titanium tetrachloride were purchased from ACROS Co, *N*-bromosuccinimide from Apollo Scientific Ltd. and grey selenium from Aldrich Chemical Co. 3-Bromobenzo[*b*]thiophene-2-carbaldehyde (CAS 10135-00-9)[34] and 2-bromobenzo[*b*]thiophene-3-carbaldehyde (CAS 39856-98-9)[35] were synthesized according to literature. Anhydrous tetrahydrofuran (THF), dioxane, diethyl ether, and dichloromethane (DCM) were prepared immediately prior to use by a *PURESOLV*-plant (*it-innovative technology inc.*). Technical grade solvents were distilled prior to use. Analytical TLC was performed on Merck silica gel 60 F254 plates. Chromatographic separations at preparative scale were carried out on silica gel (Merck silica gel 60, 40 - 63 µm). Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker Avance III HD 600 MHz with cryo probe or Avance III HD 400 MHz fourier transform spectrometer operating at the following frequencies: Avance III HD 600 MHz: 600.2 MHz (^{1}H), 150.9 MHz (^{13}C) and 114.5 MHz (^{77}Se); Avance III HD 400 MHz: 400.1 MHz (^{1}H), 100.6 MHz (^{13}C) and 76.5 MHz (^{77}Se). The ^{1}H and ^{13}C chemical shifts are reported in δ units, parts per million (ppm) downfield from tetramethylsilane using residual solvent signals for calibration. ^{77}Se chemical shifts are given in ppm relative to dimethylselenide, using selenophene (δ = 605 ppm)[36] as an external secondary standard. Coupling constants are reported in Hertz; multiplicity of signals is indicated by using following abbreviations: s=singlet, d=doublet, t=triplet, q=quartet, quin=quintet. The multiplicity of ^{13}C signals was obtained by measuring JMOD spectra. GC-MS measurements were conducted on a GC-MS hyphenation from Thermo Finnigan: focus GC with a BGB5 column (*l* = 30 m, Ø = 0.25 mm, 0.25 mm film); DSQ II Quadrupole (EI^+ mode). High-resolution mass spectra (HRMS) were acquired using a Thermo Scientific LTQ Orbitrap XL hybrid FTMS (Fourier Transform Mass Spectrometer) equipped with Thermo Fischer Exactive Plus Orbitrap (LC-ESI+) and a Shimadzu IT-TOF Mass Spectrometer.

UV-Vis absorption spectra were recorded in DCM solutions (5 µM) with a Perkin Elmer Lambda 750 spectrometer. Samples were filtered using a 0.2 µm PTFE syringe filter prior to measurement. Cyclic voltammetry was performed using a three electrode configuration consisting of a Pt working electrode, a Pt counter electrode and an Ag/AgCl reference electrode and a PGSTAT128N, ADC164, DAC164, External, DI048 potentiostat provided by Metrohm Autolab B. V. Measurements were carried out in a 0.5 mM solution in anhydrous DCM (oxidation scan) with Bu_4NBF_4 (0.1 M) as the supporting electrolyte. Samples were filtered using a 0.2 µm PTFE syringe filter prior to measurement. The solutions were purged with nitrogen for 15 minutes prior to measurement. HOMO energy levels were calculated from the onset of oxidation. The onset potential was determined by the intersection of two tangents drawn at the background and the rising of oxidation peaks.

All DFT computations were performed using the Gaussian 09 package, revision A.02.[37] For the calculation of HOMO/LUMO levels of compounds **17a-c** and **21a-c** ground state (S_0) geometries were optimized in gas phase within C3 symmetry using the Becke three parameters hybrid functional with Lee–Yang–Perdew correlation (B3LYP)[38,39] in combination with Pople basis set 6-311+G*.[40]

Diffraction intensities of single crystals of **17a-c, 21a** and **21c** (CCDC 1881248-1881252) were collected on a Bruker Kappa Apex II diffractometer system equipped with a CCD detector using MoKα radiation from a sealed tube monochromatized with graphite. Data were reduced to intensity values using SAINT and absorption correction applied with a semi-empirical approach implemented in SADAB (Bruker computer programs: APEX2, SAINT and SADABS (Bruker AXS Inc., Madison, WI, 2018)). The structures were solved with SHELXT[41] and refined against F2 with Jana2006.[42] Molecular graphics were generated with the program MERCURY.[43]

2-(Methylseleno)benzaldehyde (**2**). Grey selenium (1.58 g, 20 mmol, 1 eq.) was suspended in 40 mL anhydrous degassed THF under argon atmosphere. The suspension was cooled to 0 °C and MeLi (1.45 mL, 22 mmol, 1.1 eq.) was added dropwise. The resulting white suspension was stirred for 40 minutes. o-Chlorobenzaldehyde **1a** (2.80 g, 20 mmol, 1 eq.) was added dropwise giving a clear orange solution, which was stirred overnight at room temperature, quenched with water and extracted repeatedly with ethyl acetate. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and the solution was concentrated in vacuo. **2** was purified by column chromatography (40 g silica gel, light petroleum : ethyl acetate 20:1) and isolated in 42% yield as a yellow oil (1.70 g). TLC (silica gel, light petroleum : ethyl acetate 7:1): R_f = 0.45. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.15 (s, 1 H), 7.81 (dd, J = 7.6, 1.5 Hz, 1 H), 7.51 - 7.49 (m, 1 H), 7.46 - 7.45 (m, 1 H), 7.35 (td, J = 7.3, 1.1 Hz, 1 H), 2.30 (s, 3 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.4 (d), 138.7 (s), 135.5 (d), 134.2 (s), 133.8 (d), 127.8 (d), 124.8 (d), 5.77 (q) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$):

δ = 248 ppm. HR-ESI-FTMS $[M+H]^+$ m/z calcd. 200.9813 for $C_8H_9OSe^+$, found 200.9811.

Ethyl 2-[(2-formylphenyl)seleno]acetate (**3**). **2** (1.70 g, 8.5 mmol, 1 eq.) and ethyl bromoacetate (1.40 g, 8.5 mmol, 1 eq.) were heated to reflux. Conversion was monitored by TLC. After 12 hours the resulting red liquid was dissolved in dichloromethane and directly concentrated on 6 g silica gel and purified by column chromatography (40 g silica gel, light petroleum : ethyl acetate 10:1). **3** was isolated in 73% yield (1.68 g) as a yellow solid. TLC (silica gel, light petroleum : ethyl acetate 7:1): R_f = 0.52. mp = 34.2 – 36.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.15 (s, 1 H), 7.85 (dd, J = 7.6, 1.5 Hz, 1 H), 7.76 (m, 1 H), 7.53 (m, 1 H), 7.40 (m, 1 H), 4.17 (q, J = 7.2 Hz, 2 H), 3.58 (s, 2 H), 1.24 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.6 (d), 170.9 (s), 136.9 (s), 135.2 (d), 134.5 (s), 134.1 (d), 129.3 (d), 125.8 (d), 61.4 (t), 25.3 (t), 14.1 (q) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$): δ = 367 ppm. HR-ESI-FTMS $[M+H]^+$ m/z calcd. 273.0024 for $C_{11}H_{13}O_3Se^+$, found 273.0058.

Ethyl benzo[*b*]selenophene-2-carboxylate (**4a**). **3** (1.68 g, 6.2 mmol, 1 eq.) was dissolved in 20 mL anhydrous DMF, K_2CO_3 (1.71 g, 12.4 mmol, 2 eq.) was added and the reaction mixture was heated to 120 °C for two hours. The solution was quenched with water and extracted repeatedly with ethyl acetate. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. **4a** was purified by column chromatography (40 g silica gel, light petroleum : ethyl acetate 20:1) and isolated in 96% yield as a yellow oil (1.50 g). TLC (silica gel, light petroleum : ethyl acetate 9:1): R_f = 0.59. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (s, 1 H), 7.94 - 7.87 (m, 2 H), 7.43 - 7.36 (m, 2 H), 4.39 (q, J = 7.3 Hz, 2 H), 1.41 (t, J = 7.3 Hz, 3 H) ppm. The obtained NMR data are in accordance with literature.[44] HR-ESI-FTMS $[M+H]^+$ m/z calcd. 254.9919 for $C_{11}H_{11}O_2Se^+$, found 254.9916.

General Procedure for the one-pot synthesis of **4a** and **4b**: Grey selenium (1 eq.) was suspended in anhydrous degassed THF under argon atmosphere. The suspension was cooled to 0 °C and n-BuLi (1.1 eq.) was added dropwise. The resulting white suspension was stirred for 40 minutes. **1a** or **1b** (1 eq.) dissolved in 20 mL anhydrous DMF was added dropwise giving a clear orange solution. The resulting solution was stirred overnight at room temperature. Full conversion of starting material was confirmed by GC-MS analysis. THF and hexanes were distilled off under reduced pressure and 100 mL anhydrous DMF was added. Ethyl bromoacetate (2 eq.) was added and the resulting solution was refluxed overnight. Potassium carbonate (2 eq.) was added and the reaction mixture was refluxed for four hours. The reaction mixture was cooled to room temperature, 100 mL 2N NaOH was added and the product was extracted repeatedly with ethyl acetate. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo.

Ethyl benzo[*b*]selenophene-2-carboxylate (**4a**). Starting from n-BuLi (44 mL, 110 mmol) in 160 mL THF, freshly distilled o-chlorobenzaldehyde (14.06 g, 100 mmol), ethyl bromoacetate (33.6 g, 200 mmol) and potassium carbonate (27.6 g, 200 mmol) **4a** was synthesized according to the general procedure. **4a** was purified by distillation (0.15 mbar, 120 °C) and isolated in 74% yield (18.81 g) as a yellow oil. The obtained NMR and HRMS data were consistent with those acquired from the multistep procedure.

Ethyl 3-methylbenzo[*b*]selenophene-2-carboxylate (**4b**). Starting from from n-BuLi (26.4 mL, 66 mmol) in 100 mL THF, o-chloroacetophenone (9.30 g, 60 mmol), ethyl bromoacetate (20.04 g, 120 mmol) and potassium carbonate (16.58 g, 120 mmol) **4b** was synthesized according to the general procedure. **4b** was purified by column chromatography (light petroleum: ethyl acetate 9:1) and isolated in 57% yield (9.10 g) as a yellow solid. TLC (180 g silica gel, light petroleum : ethyl acetate 7:1): R_f = 0.61. mp = 42.3 - 43.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 - 7.81 (m, 2 H), 7.45 - 7.38 (m, 2 H), 4.38 (q, J = 7.3 Hz, 2 H), 2.73 (s, 3 H), 1.41 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.5 (s), 143.9 (s), 142.7 (s), 141.7 (s), 129.1 (s), 127.0 (d), 125.6 (d), 125.5 (d), 124.6 (d), 61.1 (t), 14.3 (q), 14.4 (q) ppm. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 521 ppm. HR-ESI-FTMS $[M+H]^+$ m/z calcd. 269.0075 for $C_{12}H_{13}O_2Se^+$, found 269.0075.

3-Methylbenzo[*b*]selenophene-2-carboxylic acid (**5**). **4b** (5.44 g, 20 mmol, 1 eq.) and sodium hydroxide (1.60 g, 40 mmol, 2 eq.) were refluxed in 60 mL solvent (methanol : H_2O 2:3) for four hours. Conversion was monitored by TLC (dichloromethane : methanol 9:1). The reaction mixture was cooled to room temperature and 2 N HCl was added. The precipitate was filtrated and dried in vacuo. **5** was isolated in 91% yield (4.34 g) as a colourless solid. TLC (silica gel, dichloromethane : methanol 9:1): R_f = 0.38. mp = 189.2 - 191.4 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 13.32 (bs, 1 H), 8.08 - 8.07 (m, 1 H), 7.94 - 7.92 (m, 1 H), 7.50 - 7.45 (m, 2 H), 2.66 (s, 3 H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 165.5 (s), 142.6 (s), 142.6 (s), 140.9 (s), 130.6 (s), 127.3 (d), 126.1 (d), 125.8 (d), 125.0 (d), 14.1 (q) ppm. ^{77}Se NMR (114 MHz, DMSO-d_6): δ = 516 ppm. MS (EI): m/z 240 (M^+, 28%), 194 (16), 115 (100).

3-Methylbenzo[*b*]selenophene (**6**). **5** (4.07 g, 17 mmol, 1 eq.) and copper (486 mg, 7.7 mmol, 0.45 eq.) were refluxed in 40 mL quinoline for three hours. The reaction mixture was cooled to room temperature and 2 N HCl was added. The aqueous layer was extracted repeatedly with diethyl ether. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. **6** was purified by column chromatography (90 g silica gel, light petroleum) and isolated in 94% yield (3.12 g) as a yellow liquid. TLC (silica gel, light petroleum): R_f = 0.63. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 - 8.10 (m, 1 H), 7.90 - 7.88 (m, 1 H), 7.71 (d, J = 1.3 Hz, 1 H), 7.61 (ddd, J = 8.1, 7.0, 1.1 Hz, 1 H), 7.50 (ddd, J = 8.3, 7.0, 1.2 Hz, 1 H), 2.57 (d, J = 1.3 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.8 (s), 141.4 (s), 134.9 (s), 125.8 (d), 124.1 (d), 124.1 (d), 123.4 (d), 123.2 (d), 15.8 (q) ppm. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 479 ppm. HR-ESI-FTMS $[M+H]^+$ m/z calcd. 196.9864 for $C_9H_9Se^+$, found 196.9882.

Benzo[*b*]selenophene-3-carbaldehyde (**7**). **6** (1.07 g, 5.5 mmol, 1 eq.) and SeO_2 (732 mg, 6.6 mmol, 1.2 eq.) were refluxed in 10 mL anhydrous 1,4-dioxane for six hours. The reaction mixture was cooled to room temperature, grey selenium was filtered over celite and the obtained solution was concentrated in vacuo. The crude product was purified by column chromatography (90 g silica gel, light petroleum : ethyl acetate 8:1) and isolated in 90% yield (1.04 g) as a colourless solid. TLC (silica gel, light petroleum : ethyl acetate 9:1): R_f = 0.42. mp = 87.8 - 88.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.08 (s, 1 H), 9.00 (s, 1 H), 8.78 - 8.77 (m, 1 H), 7.93 - 7.91 (m, 1 H), 7.52 - 7.49 (m, 1 H), 7.42 - 7.40 (m, 1 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 186.1 (d), 149.3 (d), 142.4 (s), 140.0 (s), 137.0 (s), 126.6 (d), 126.3 (d), 126.0 (d), 125.3 (d) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$): δ = 537 ppm. HR-ESI-FTMS $[M+H]^+$ m/z calcd. 210.9657 for $C_9H_7OSe^+$, found 210.9659.

Benzo[*b*]selenophene-2-methanol (**8a**). **4a** (10.13 g, 40 mmol, 1 eq.) was dissolved in 100 mL anhydrous THF. The solution was cooled to 0 °C and $LiAlH_4$ (1.52 g, 40 mmol, 1 eq.) was added in portions. The reaction mixture was stirred at room temperature for one hour and hydrolysed with 2 N NaOH. The aqueous layer was extracted repeatedly with diethyl ether. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. **8a** was isolated in 97% yield (8.20 g) as a colourless solid. TLC (silica gel, light petroleum : ethyl acetate 3:1): R_f = 0.49. mp = 107.7 - 108.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 - 7.86 (m, 1 H), 7.73 - 7.71 (m, 1 H), 7.37 - 7.33 (m, 2 H), 7.27 - 7.23 (m, 1 H), 4.95 (d, J = 1.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.2 (s), 141.9 (s), 141.3 (s), 125.6 (d), 125.2 (d), 124.6 (d), 124.4 (d), 124.4 (d),

62.9 (t) ppm. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 513 ppm. MS (EI): m/z 212 (M^+, 69%), 195 (24), 183 (100).

Benzo[*b*]selenophene-3-methanol (**8b**). **7** (1.34 g, 6.4 mmol, 1 eq.) was dissolved in 20 mL anhydrous ethanol. The solution was cooled to 0 °C and $NaBH_4$ (242 mg, 6.4 mmol, 1 eq.) was added in portions. The reaction mixture was stirred at room temperature for three hours and hydrolysed with water. The aqueous layer was extracted repeatedly with diethyl ether. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. **8b** was isolated in 92% yield (1.24 g) as a yellow oil. TLC (silica gel, light petroleum : ethyl acetate 3:1): R_f = 0.46. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.93 - 7.92 (m, 1 H), 7.91 (s, 1 H), 7.86 - 7.84 (m, 1 H), 7.41 (ddd, J = 8.1, 7.1, 1.1 Hz, 1 H), 7.33 (ddd, J = 8.5, 6.9, 1.2 Hz, 1 H), 4.87 (d, J = 0.9 Hz, 2 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.1 (s), 139.8 (s), 139.0 (s), 126.1 (d), 126.0 (d), 124.8 (d), 124.5 (d), 123.7 (d), 61.3 (t) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$): δ = 491 ppm. MS (EI): m/z 212 (M^+, 69%), 195 (24), 183 (100).

3-Bromobenzo[*b*]selenophene-2-methanol (**9a**). **8a** (7.39 g, 35 mmol, 1 eq.) was dissolved in 150 mL chloroform. The solution was cooled to 0 °C and *N*-bromosuccinimide (6.22 g, 35 mmol, 1 eq.) was added in portions. The reaction mixture was stirred at room temperature for one hour and hydrolysed with 50 mL 2 N NaOH. The aqueous layer was extracted repeatedly with chloroform. The organic layer was dried over anhydrous Na_2SO_4 and **9a** was isolated in 86% yield (8.68 g). TLC (silica gel, light petroleum : ethyl acetate 3:1): R_f = 0.62. mp = 103.2 - 104.9 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.91 (dd, J = 8.3, 0.8 Hz, 1 H), 7.78 (dd, J = 8.2, 0.9 Hz, 1 H), 7.39 (ddd, J = 8.3, 7.0, 1.3 Hz, 1 H), 7.31 (ddd, J = 8.2, 6.8, 1.3 Hz, 1 H), 4.87 (s, 2 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 141.7 (s), 139.8 (s), 137.7 (s), 125.3 (d), 125.2 (d), 125.1 (d), 124.0 (d), 116.4 (s), 58.7 (t) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$): δ = 581 ppm. HR-ESI-FTMS $[M+H]^+$ m/z calcd. 290.8918 for $C_9H_8BrOSe^+$, found 290.8915.

2-Bromobenzo[*b*]selenophene-3-methanol (**9b**). **8b** (2.01 g, 9.5 mmol, 1 eq.) was dissolved in 10 mL anhydrous chloroform. The solution was cooled to 0 °C and *N*-bromosuccinimide (1.69 g, 9.5 mmol, 1 eq.) was added in portions. The reaction mixture was stirred at room temperature for one hour and hydrolysed with 50 mL 2 N NaOH. The aqueous layer was extracted repeatedly with diethyl ether. The organic layer was dried over anhydrous Na_2SO_4, the crude product was purified by column chromatography (50 g silica gel, light petroleum : ethyl acetate 9:1). **9b** was isolated as yellow oil in 45% yield (1.23 g). TLC (silica gel, light petroleum : ethyl acetate 3:1): R_f = 0.60. mp = 139.6 - 142.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.91 - 7.90 (m, 1 H), 7.79 - 7.77 (m, 1 H), 7.39 (ddd, J = 8.2, 6.9, 1.3 Hz, 1 H), 7.31 (ddd, J = 8.2, 6.9, 1.3 Hz, 1 H), 4.87 (s, 2 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 141.7 (s), 139.9 (s), 137.7 (s), 125.3 (d), 125.2 (d), 125.1 (d), 124.0 (d), 116.5 (s), 58.8 (t) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$): δ = 581 ppm. HR-ESI-FTMS $[M+H]^+$ m/z calcd. 290.8918 for $C_9H_8BrOSe^+$, found 290.8913.

3-Bromobenzo[*b*]selenophene-2-carbaldehyde (**10a**). **9a** (8.70 g, 30 mmol, 1 eq.) was dissolved in 150 mL ethyl acetate. MnO_2 (15.65 g, 180 mmol, 6 eq.) was added and the reaction mixture was stirred at room temperature overnight. The reaction mixture was filtered over celite, concentrated, dissolved in dichloromethane and stirred with active charcoal for one hour. The charcoal was filtered over celite and **10a** was isolated in 75% yield (6.50 g) as a colourless solid. TLC (silica gel, light petroleum : ethyl acetate 15:1): R_f = 0.54. mp = 99.7 - 102.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.20 (s, 1 H), 8.12 - 8.10 (m, 1 H), 7.93 - 7.92 (m, 1 H), 7.54 - 7.49 (m, 2 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 186.2 (d), 141.2 (s), 140.1 (s), 139.5 (s), 129.2 (d), 127.2 (d), 126.3 (d), 126.1 (d), 120.4 (s) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$): δ = 536 ppm. HR-ESI-FTMS $[M+H]^+$ m/z calcd. 288.8762 for $C_9H_6BrOSe^+$, found 288.8758.

2-Bromobenzo[*b*]selenophene-3-carbaldehyde (**10b**). **9b** (1.62 g, 5.6 mmol, 1 eq.) was dissolved in 150 mL ethyl acetate. MnO_2 (2.92 g, 33.6 mmol, 6 eq.) was added and the reaction mixture refluxed for 30 hours. The reaction mixture was filtered over celite, concentrated and **10b** was isolated in 98% yield (1.58 g) as a colourless solid. TLC (silica gel, light petroleum : ethyl acetate 7:1): R_f = 0.60. mp = 140.8 - 143.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.21 (s, 1 H), 8.79 (dd, J = 8.1, 1.4 Hz, 1 H), 7.76 (dd, J = 8.1, 1.0 Hz, 1 H), 7.46 - 7.36 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.3 (d), 140.7 (s), 137.4 (s), 137.1 (s), 134.5 (s), 126.4 (d), 126.3 (d), 125.6 (d), 124.3 (d) ppm. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 618 ppm. HR-ESI-FTMS $[M+H]^+$ m/z calcd. 288.8762 for $C_9H_6BrOSe^+$, found 288.8756.

General procedure toward **13a**, **13c**, **14a** and **14c**. Grey selenium (1.1 eq.) was suspended in anhydrous ethanol under argon atmosphere and cooled to 0 °C. Sodium borohydride (1.43 eq.) was added in portions and stirred for 40 minutes. Sodium hydride was added as dispersion (60%, 0.98 eq.). After 30 minutes a solution of **4a**, **4b**, **11** or **12** (1 eq.) in anhydrous THF was added and the obtained solution was stirred for two hours at room temperature. Subsequently, ethyl bromoacetate (2.16 eq.) was added dropwise resulting in a suspension. After one hour sodium ethanolate (2 eq.) was added and the reaction mixture was stirred for further 12 hours at room temperature. The reaction mixture was quenched with water, the aqueous phase was extracted repeatedly with ethyl acetate, the obtained organic layers were washed with water and 10% NH_4Cl solution, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The obtained crude product was purified by column chromatography.

Ethyl selenolo[3,2-*b*][1]benzothiophene-2-carboxylate (**13a**). According to the general procedure **13a** was synthesized applying grey selenium (533 mg, 6.7 mmol) suspended in 30 mL anhydrous ethanol, sodium borohydride (332 mg, 8.8 mmol), sodium hydride (240 mg, 6 mmol), a solution of **11** (1.48 g, 6.1 mmol) in 40 mL anhydrous THF, ethyl bromoacetate (2.38 g, 13.3 mmol) and sodium ethanolate (12.2 mmol). After work-up the crude product was purified by column chromatography (light petrol / ethyl acetate 5%, 90 g silica gel) and **13a** was obtained as yellow solid in 72% yield (1.37 g). R_f = 0.74 (light petrol / ethyl acetate 6:1). mp = 108.3 - 109.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.27 (s, 1 H), 7.89 - 7.81 (m, 2 H), 7.45 - 7.42 (m, 2 H), 4.40 (q, J = 7.2 Hz, 2 H), 1.41 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.3 (s), 143.0 (s), 141.2 (s), 139.4 (s), 138.4 (s), 134.8 (s), 129.0 (d), 125.9 (d), 125.0 (d), 123.8 (d), 122.5 (d), 61.6 (t), 14.3 (q) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$): δ = 542.2 ppm. HR-ESI-FTMS $[M+H]^+$ m/z calcd. 310.9639 for $C_{13}H_{11}O_2SSe^+$, found 310.9634.

Ethyl selenolo[3,2-*b*][1]benzoselenophene-2-carboxylate (**13c**). According to the general procedure **13c** was synthesized applying grey selenium (869 mg, 11 mmol) suspended in 50 mL anhydrous ethanol, sodium borohydride (541 mg, 14.3 mmol), sodium hydride (376 mg, 9.8 mmol), a solution of **4a** (2.88 g, 10 mmol) in 20 mL anhydrous THF, ethyl bromoacetate (3.89 g, 21.6 mmol) and sodium ethanolate (20 mmol). After work-up the crude product was purified by column chromatography (light petrol / ethyl acetate 5%, 90 g silica gel) and **13c** was obtained as yellow solid in 95% yield (3.38 g). R_f = 0.69 (light petrol / ethyl acetate 6:1). mp = 90.1 - 90.9 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.27 (s, 1 H), 7.93 - 7.92 (m, 1 H), 7.85 (dd, J = 7.7, 1.0 Hz, 1 H), 7.44 (ddd, J = 8.1, 7.1, 1.2 Hz, 1 H), 7.35 (ddd, J = 8.2, 7.1, 1.2 Hz, 1 H), 4.39 (q, J = 7.2 Hz, 2 H), 1.41 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.2 (s), 144.4 (s), 143.2 (s), 138.8 (s), 137.0 (s), 135.7 (s), 131.8 (d), 126.9 (d), 126.0 (d), 125.5 (d), 124.1 (d), 61.6 (t), 14.4 (q) ppm. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 569.7, 494.0 ppm. HR-ESI-FTMS $[M+H]^+$ m/z calcd. 358.9084 for $C_{13}H_{11}O_2Se_2^+$, found 358.9081.

Ethyl selenolo[2,3-*b*][1]benzothiophene-2-carboxylate (**14a**). According to the general procedure **14a** was synthesized applying grey selenium (1.30 g, 16.5 mmol) suspended in 30 mL anhydrous ethanol, sodium borohydride (811 mg, 21.45 mmol), sodium hydride (546 mg, 14.7 mmol), a solution of **12** (3.62 g, 15 mmol) in 20 mL THF, ethyl bromoacetate (5.83 g, 32.4 mmol) and sodium ethanolate (30 mmol). After work-up the crude product was purified by column chromatography (light petrol / DCM 40%, 90 g silica gel) and **14a** was obtained as yellow solid in 91% yield (4.24 g). R_f = 0.68 (light petrol / ethyl acetate 6:1). mp = 89.7 - 92.2 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.47 (s, 1 H), 7.95 - 7.93 (m, 1 H), 7.83 - 7.82 (m, 1 H), 7.43 (ddd, J = 8.7, 6.8, 1.1 Hz, 1 H), 7.35 (ddd, J = 8.9, 6.6, 1.1 Hz, 1 H), 4.40 (q, J = 7.2 Hz, 2 H), 1.42 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.2 (s), 144.8 (s), 144.1 (s), 143.0 (s), 139.3 (s), 133.9 (s), 127.7 (d), 124.9 (d), 124.6 (d), 122.8 (d), 121.6 (d), 61.5 (t), 14.4 (q) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$): δ = 571.1 ppm. HR-ESI-FTMS $[M+H]^+$ m/z calcd. 310.9695 for $C_{13}H_{11}O_2SSe^+$, found 310.9633.

Ethyl selenolo[2,3-*b*][1]benzoselenophene-2-carboxylate (**14c**). According to the general procedure **14c** was synthesized applying grey selenium (304 mg, 3.85 mmol) suspended in 10 mL anhydrous ethanol, sodium borohydride (189 mg, 5 mmol), sodium hydride (82 mg, 3.4 mmol), a solution of **4b** (1.01 g, 3.5 mmol) in 3 mL THF, ethyl bromoacetate (1.36 g, 7.6 mmol) and sodium ethanolate (7 mmol). After work-up the crude product was purified by column chromatography (light petrol / ethyl acetate 5%, 90 g silica gel) and **14c** was obtained as colorless solid in 68% yield (851 mg). R_f = 0.66 (light petrol / ethyl acetate 6:1). mp = 100.4 - 102.5 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.47 (s, 1 H), 7.95 (dd, J = 8.0, 1.0 Hz, 1 H), 7.86 - 7.85 (m, 1 H), 7.42 (ddd, J = 8.2, 6.6, 1.1 Hz, 1 H), 7.30 (ddd, J = 8.3, 6.6, 1.3 Hz, 1H), 4.40 (q, J = 7.1 Hz, 2 H), 1.42 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.1 (s), 145.9 (s), 144.4 (s), 142.6 (s), 140.6 (s), 136.1 (s), 128.9 (d), 125.9 (d), 125.3 (d), 124.9 (d), 123.1 (d), 61.5 (t), 14.4 (q) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$): δ = 601.5, 512.0 ppm. MS (EI): m/z 358 (M^+, 100%), 330 (49), 313 (55), 285 (42), 193 (23).

General procedure toward **13b** and **14b**. The properly substituted aldehyde **4a** or **4b** (1 eq.), ethyl mercaptoacetate (1.17 eq.) and K_2CO_3 (2 eq.) were suspended in anhydrous DMF and stirred at room temperature for 48 hours. The reaction mixture was quenched with water and the aqueous phase was extracted repeatedly with DCM. The obtained organic phases were washed with a saturated NH_4Cl solution, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The obtained crude product was purified by column chromatography.

Ethyl [1]benzoselenopheno[3,2-*b*]thiophene-2-carboxylate (**13b**). **4a** (500 mg, 1.7 mmol), ethyl mercaptoacetate (240 mg, 2 mmol) and K_2CO_3 (484 mg, 3.5 mmol) were suspended in 3.5 mL DMF. After work-up the crude product was purified by column chromatography (light petrol / ethyl acetate 5%, 90 g silica gel) and **13b** was isolated as yellow solid in 48% yield (253 mg). R_f = 0.68 (light petrol / ethyl acetate 6:1). mp = 94.4 - 95.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.03 (s, 1 H), 7.91 - 7.88 (m, 2 H), 7.44 (ddd, J = 8.3, 6.7, 1.1 Hz, 1 H), 7.35 (ddd, J = 8.3, 6.7, 1.1 Hz, 1 H), 4.41 (q, J = 7.1 Hz, 2 H), 1.41 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 162.1 (s), 143.7 (s), 142.8 (s), 134.8 (s), 134.4 (s), 134.2 (s), 129.3 (d), 127.0 (d), 126.1 (d), 125.5 (d), 123.2 (d), 61.5 (t), 14.4 (q) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$): δ = 462.3 ppm. HR-ESI-FTMS $[M+H]^+$ m/z calcd. 310.9695 for $C_{13}H_{11}O_2SSe^+$, found 310.9637.

Ethyl [1]benzoselenopheno[2,3-*b*]thiophene-2-carboxylate (**14b**). **4b** (1.01 g, 3.5 mmol), ethyl mercaptoacetate (492 mg, 4.1 mmol) and K_2CO_3 (967 mg, 7 mmol) were suspended in 7 mL DMF. After work-up the crude product was purified by column chromatography (light petrol / ethyl acetate 5%, 90 g silica gel) and **14b** was isolated as yellow solid in 92% yield (995 mg). R_f = 0.67 (light petrol / ethyl acetate 6:1). mp = 94.3 - 95.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.21 (s, 1 H), 7.94 (dd, J = 7.9, 1.0 Hz, 1 H), 7.85 (m, 1 H), 7.44 (ddd, J = 8.3, 6.7, 1.2 Hz, 1 H), 7.32 (ddd, J = 8.2, 6.7, 1.2 Hz, 1 H), 4.41 (q, J = 7.2 Hz, 2 H), 1.42 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.9 (s), 144.4 (s), 143.6 (s), 141.2 (s), 137.1 (s), 134.7 (s), 126.2 (d), 126.2 (d), 125.4 (d), 125.4 (d), 123.1 (d), 61.4 (t), 14.4 (q) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$): δ = 484.8 ppm. HR-ESI-FTMS $[M+H]^+$ m/z calcd. 310.9640 for $C_{13}H_{11}O_2SSe^+$, found 310.9637. MS (EI): m/z 310 (M^+, 100%), 281 (64), 265 (52), 237 (35), 193 (30).

General procedure toward **15a-c**. $LiAlH_4$ (1 eq.) was suspended in anhydrous THF and cooled to 0 °C. The appropriate ester **13a-c** (1 eq.) was added as a THF solution. The reaction mixture was stirred at room temperature and conversion was monitored by TLC (light petrol / ethyl acetate 7:1). The reaction mixture was quenched drop wise with 2 N NaOH and the aqueous phase was extracted with DCM. The organic layer was washed with water, dried over anhydrous sodium sulfate and concentrated under reduced pressure.

Selenolo[3,2-*b*][1]benzothiophene-2-methanol (**15a**). According to the general procedure **13a** (1.24 g, 4.00 mmol) was dissolved in 10 mL anhydrous THF and added to a suspension of $LiAlH_4$ (152 mg, 4.00 mmol) in 20 mL anhydrous THF. After work-up the crude product was purified by column chromatography (light petrol / ethyl acetate 10%, 90 g silica gel) and **15a** was isolated as yellow solid in 80% yield (858 mg). R_f = 0.23 (light petrol / ethyl acetate 4:1). mp = 130.3 - 132.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 - 7.85 (m, 1 H), 7.78 - 7.76 (m, 1 H), 7.43 - 7.32 (m, 3 H), 4.97 (d, J = 5.3 Hz, 2 H), 2.06 (t, J = 5.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.1 (s), 141.5 (s), 138.1 (s), 135.5 (s), 135.0 (s), 124.7 (d), 124.4 (d), 123.7 (d), 121.6 (d), 120.0 (d), 62.9 (t) ppm. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 521.2 ppm. HR-ESI-FTMS $[M+H]^+$ m/z calcd. 268.9534 for $C_{11}H_9OSSe^+$, found 268.9531.

[1]Benzoselenopheno[3,2-*b*]thiophene-2-methanol (**15b**). According to the general procedure **13b** (2.78 g, 9.00 mmol) was dissolved in 10 mL anhydrous THF and added to a suspension of $LiAlH_4$ (342 mg, 9.00 mmol) in 30 mL anhydrous THF. After work-up the crude product was purified by column chromatography (light petrol / ethyl acetate 10%, 90 g silica gel) and **15b** was isolated as yellow solid in 67% yield (1.61 g). R_f = 0.24 (light petrol / ethyl acetate 4:1). mp = 128.2 - 130.0 °C. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 7.88 - 7.87 (m, 1 H), 7.79 - 7.78 (m, 1 H), 7.43 - 7.34 (m, 3 H), 4.95 (d, J = 5.4 Hz, 2 H), 2.24 (t, J = 5.4 Hz, 1 H) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 154.5 (s), 142.0 (s), 138.7 (s), 136.0 (s), 135.2 (s), 125.3 (d), 124.9 (d), 124.2 (d), 122.0 (d), 120.2 (d), 63.2 (t) ppm. ^{77}Se NMR (114 MHz, CD_2Cl_2): δ = 517.4 ppm. HR-ESI-FTMS $[M+H]^+$ m/z calcd. 268.9534 for $C_{11}H_9OSSe^+$, found 268.9533.

Selenolo[3,2-*b*][1]benzoselenophene-2-methanol (**15c**). According to the general procedure **13c** (3.21 g, 9.00 mmol) was dissolved in 10 mL anhydrous THF and added to a suspension of $LiAlH_4$ (342 mg, 9.00 mmol) in 10 mL anhydrous THF. After work-up the crude product was purified by column chromatography (light petrol / ethyl acetate 10%, 90 g silica gel) and **15c** was isolated as yellow solid in 66% yield (1.85 g). R_f = 0.23 (light petrol / ethyl acetate 4:1). mp = 104.4 -105.8 °C. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 7.93 - 7.91 (m, 1 H), 7.77 - 7.76 (m, 1 H), 7.43 - 7.40 (m, 2 H), 7.28 (ddd, J = 8.3, 6.6, 1.2 Hz, 1 H), 4.95 (dd, J = 6.1, 1.1 Hz, 2H), 2.19 (t, J = 6.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 153.8 (s), 142.2 (s), 138.1 (s), 138.0 (s), 136.0 (s), 127.3 (d), 125.8 (d), 125.1 (d), 123.6 (d), 123.0 (d), 63.1 (t) ppm. ^{77}Se NMR (114 MHz, CD_2Cl_2): δ = 541.3, 483.6 ppm. HR-ESI-FTMS $[M+H]^+$ m/z calcd. 316.8978 for $C_{11}H_9OSe_2^+$, found 316.8912.

General procedure toward **16a-c**. The appropriate alcohol **15a-c** (1 eq.) and MnO_2 (6 eq.) were stirred in ethyl acetate for 12 hours. The reaction progress was monitored by TLC (light petrol / ethyl acetate 5:1). The

reaction mixture was filtrated over celite and the obtained solution was concentrated under reduced pressure.

Selenolo[3,2-*b*][1]benzothiophene-2-carbaldehyde (**16a**). To a solution of **15a** (3.47 g, 13 mmol) in 50 mL ethyl acetate MnO_2 (6.64 g, 76 mmol) was added. After work-up according to the general procedure the crude product was purified by column chromatography (light petrol / ethyl acetate 50%, 90 g silica gel) and **16a** was isolated as yellow solid in 75% yield (2.60 g). R_f = 0.50 (light petrol / ethyl acetate 4:1). mp = 98.9 - 100.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.86 (s, 1 H), 8.20 (s, 1 H), 7.91 - 7.88 (m, 2 H), 7.48 - 7.43 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.1 (d), 150.1 (s), 143.8 (s), 143.0 (s), 138.8 (s), 134.6 (s), 132.7 (d), 126.6 (d), 125.3 (d), 123.8 (d), 123.2 (d) ppm. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 519.0 ppm. HR-ESI-FTMS $[M+H]^+$ m/z calcd. 266.9377 for $C_{11}H_7OSSe^+$, found 266.9374.

[1]Benzoselenopheno[3,2-*b*]thiophene-2-carbaldehyde (**16b**). To a solution of **15b** (1.34 g, 5 mmol) in 25 mL ethyl acetate MnO_2 (2.61 g, 30 mmol) was added. After work-up according to the general procedure the crude product was purified by column chromatography (light petrol / ethyl acetate 50%, 90 g silica gel) and **16b** was isolated as yellow solid in 87% yield (1.15 g). R_f = 0.49 (light petrol / ethyl acetate 4:1). mp = 112.1 - 115.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.87 (s, 1 H), 8.22 (s, 1 H), 7.92 - 7.89 (m, 2 H), 7.48 - 7.45 (m, 2 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 184.2 (d), 150.1 (s), 143.8 (s), 143.0 (s), 138.8 (s), 134.6 (s), 132.7 (d), 126.7 (d), 125.3 (d), 123.9 (d), 123.2 (d) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$): δ = 517.0 ppm. HR-ESI-FTMS $[M+H]^+$ m/z calcd. 266.9377 for $C_{11}H_7OSSe^+$, found 266.9377.

Selenolo[3,2-*b*][1]benzoselenophene-2-carbaldehyde (**16c**). To a solution of **15c** (1.57 g, 5 mmol) in 25 mL ethyl acetate MnO_2 (2.61 g, 30 mmol) was added. After work-up according to the general procedure the crude product was purified by column chromatography (light petrol / ethyl acetate 50%, 90 g silica gel) and **16c** was isolated as yellow solid in 86% yield (1.34 g). R_f = 0.49 (light petrol / ethyl acetate 4:1). mp = 110.3 - 112.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.85 (s, 1 H), 8.20 (s, 1 H), 7.93 - 7.92 (m, 1 H), 7.89 (dd, J = 7.8, 0.9 Hz, 1 H), 7.45 (ddd, J = 8.4, 6.6, 0.9 Hz, 1 H), 7.38 (ddd, J = 8.6, 6.6, 1.2 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 184.0 (d), 149.4 (s), 146.3 (s), 143.9 (s), 136.7 (s), 136.0 (s), 135.6 (d), 126.9 (d), 126.7 (d), 125.7 (d), 124.7 (d) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$): δ = 542.2, 494.2 ppm. HR-ESI-FTMS $[M+H]^+$ m/z calcd. 314.8822 for $C_{11}H_7OSe_2^+$, found 314.8820.

General procedure toward **18a-c**. The obtained esters **14a-c** and (1 eq.) and sodium hydroxide (2 eq.) were refluxed in a mixture of methanol and water (2:3). The conversion was monitored by TLC (DCM / MeOH 10:1). The reaction mixture was cooled to room temperature and the respective acid was precipitated by addition a sufficient amount of 2 N HCl. The precipitate was filtered, washed with water and dried in vacuo.

Selenolo[2,3-*b*][1]benzothiophene-2-carboxylic acid (**18a**). A mixture of **14a** (760 mg, 2.5 mmol) and sodium hydroxide (200 mg, 5 mmol) was refluxed in 15 mL solvent for 6 hours. After work-up according to the general procedure **18a** was isolated as yellow solid in 90% yield (623 mg). R_f = 0.24 (DCM / MeOH 10:1). mp = 240.5 - 243.6 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 13.18 (bs, 1 H), 8.66 (s, 1 H), 8.23 - 8.22 (m, 1 H), 8.04 - 8.03 (m, 1 H), 7.46 - 7.37 (m, 2 H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 164.4 (s), 145.0 (s), 143.7 (s), 142.4 (s), 140.9 (s), 133.8 (s), 128.1 (d), 124.9 (d), 124.6 (d), 123.1 (d), 121.9 (d) ppm. ^{77}Se NMR (114 MHz, DMSO-d_6): δ = 582.0 ppm.

[1]Benzoselenopheno[2,3-*b*]thiophene-2-carboxylic acid (**18b**). A mixture of **14b** (989 mg, 3.2 mmol) and sodium hydroxide (255 mg, 6.4 mmol) was refluxed in 15 mL solvent for 6 hours. After work-up according to the general procedure **18b** was isolated as yellow solid in 74% yield (663 mg). R_f = 0.21 (DCM / MeOH 10:1). mp = 234.0 - 237.6 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 13.19 (bs, 1 H), 8.41 (s, 1 H), 8.19 - 8.18 (m, 1 H), 8.11 - 8.09 (m, 1 H), 7.44 - 7.43 (m, 1 H), 7.35 - 7.33 (m, 1 H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 162.9 (s), 143.9 (s), 143.7 (s), 142.3 (s), 137.8 (s), 134.6 (s), 126.7 (d), 126.6 (d), 125.2 (d), 125.1 (d), 123.3 (d) ppm. ^{77}Se NMR (114 MHz, DMSO-d_6): δ = 498.7 ppm.

Selenolo[2,3-*b*][1]benzoselenophene-2-carboxylic acid (**18c**). A mixture of **14c** (854 mg, 2.4 mmol) and sodium hydroxide (192 mg, 4.8 mmol) was refluxed in 15 mL solvent for 6 hours. After work-up according to the general procedure **18c** was isolated as yellow solid in 81% yield (640 mg). R_f = 0.20 (DCM / MeOH 10:1). mp = 233.5 - 235.3 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 13.09 (bs, 1 H), 8.62 (s, 1 H), 8.19 - 8.18 (m, 1 H), 8.09 - 8.08 (m, 1 H), 7.43 - 7.40 (m, 1 H), 7.32 - 7.29 (m, 1 H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 164.4 (s), 144.8 (s), 144.6 (s), 144.4 (s), 141.8 (s), 136.3 (s), 129.7 (d), 126.8 (d), 125.5 (d), 125.1 (d), 123.6 (d) ppm. ^{77}Se NMR (114 MHz, DMSO-d_6): δ = 611.0, 526.1 ppm.

General procedure toward **19a-c**. Decarboxylation of carboxylic acids was achieved by refluxing **18a-c** and copper (0.45 eq.) in quinoline. The conversion was monitored by TLC (DCM / MeOH 10:1). The reaction mixture was cooled to room temperature and repeatedly extracted with chloroform after addition of 2 N HCl. The obtained organic phases were washed with water, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The obtained crude product was purified by column chromatography (light petrol, 90 g silica gel).

Selenolo[2,3-*b*][1]benzothiophene (**19a**). **18a** (815 mg, 2.9 mmol) and copper (83 mg, 1.3 mmol) were refluxed in 40 mL quinoline for four hours. After work-up according to the general procedure **19a** was isolated as yellow solid in 58% yield (403 mg). R_f = 0.45 (light petrol). mp = 81.6 - 82.4 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.01 (d, J = 5.5 Hz, 1 H), 7.95 - 7.94 (m, 1 H), 7.85 - 7.83 (m, 1 H), 7.80 (d, J = 5.5 Hz, 1 H), 7.42 - 7.40 (m, 1 H), 7.34 - 7.31 (m, 1 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.8 (s), 143.6 (s), 138.0 (s), 134.0 (s), 131.2 (d), 124.4 (d), 123.8 (d), 122.9 (d), 121.8 (d), 121.5 (d) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$): δ = 551.7 ppm. MS (EI): m/z 238 (M^+, 100%), 193 (3), 158 (80).

[1]Benzoselenopheno[2,3-*b*]thiophene (**19b**). **18b** (647 mg, 2.3 mmol) and copper (66 mg, 1 mmol) were refluxed in 40 mL quinoline for four hours. After work-up according to the general procedure **19b** was isolated as yellow solid in 43% yield (237 mg). R_f = 0.37 (light petrol). mp = 50.7 - 51.6 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.93 - 7.92 (m, 1 H), 7.86 - 7.85 (m, 1 H), 7.57 (d, J = 5.2 Hz, 1 H), 7.50 (d, J = 5.2 Hz, 1 H), 7.43 - 7.41 (m, 1 H), 7.29 - 7.28 (m, 1 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.5 (s), 144.1 (s), 135.1 (s), 133.7 (s), 128.9 (d), 126.3 (d), 125.0 (d), 124.6 (d), 123.0 (d), 120.5 (d) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$): δ = 471.3 ppm. MS (EI): m/z 238 (M^+, 100%), 193 (8), 158 (81).

Selenolo[2,3-*b*][1]benzoselenophene (**19c**). **18c** (623 mg, 1.9 mmol) and copper (54 mg, 0.86 mmol) were refluxed in 40 mL quinoline for four hours. After work-up according to the general procedure **19c** was isolated as yellow solid in 77% yield (413 mg). R_f = 0.42 (light petrol). mp = 61.9 - 62.3 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.10 (d, J = 5.6 Hz, 1 H), 7.95 - 7.93 (m, 1 H), 7.88 - 7.87 (m, 1 H), 7.81 (d, J = 5.6 Hz, 1 H), 7.41 (ddd, J = 8.2, 6.9, 1.1 Hz, 1 H), 7.27 (ddd, J = 8.2, 6.9, 1.1 Hz, 1 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 146.2 (s), 144.9 (s), 136.3 (s), 134.6 (s), 132.5 (d), 126.1 (d), 124.9 (d), 124.2 (d), 123.2 (d), 123.1 (d) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$): δ = 580.4, 496.4 ppm. MS (EI): m/z 284 (M^+, 58%), 206 (57), 126 (100).

General procedure toward **20a-c**. Bromination of **19a-c** was achieved by addition of NBS (1.0 eq.) to a cooled solution of **19a-c** in THF. The reaction progress was monitored by TLC (light petrol). After full conversion the reaction mixture was quenched with 2 N sodium hydroxide solution and repeatedly extracted with chloroform. The obtained organic phase was washed with water, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The obtained crude product was purified by column chromatography (light petrol, 90 g silica gel).

2-Bromoselenolo[2,3-*b*][1]benzothiophene (**20a**). **19a** (403 mg, 1.7 mmol) was dissolved in 20 mL THF and cooled to 0 °C. NBS (302 mg, 1.7 mmol) was added in portions. After work-up according to the general procedure **20a** was isolated as yellow solid in 98% yield (528 mg). R_f = 0.58 (light petrol). mp = 95.8 - 98.0 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.86 - 7.85 (m, 1 H), 7.83 - 7.82 (m, 1 H), 7.77 (s, 1 H), 7.41 (ddd, J = 8.3, 6.8, 1.1 Hz, 1 H), 7.33 (ddd, J = 8.0, 6.8, 1.1 Hz, 1 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.4 (s), 141.9 (s), 137.9 (s), 133.3 (s), 125.3 (d), 124.7 (d), 124.1 (d), 122.8 (d), 121.4 (d), 114.4 (s) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$): δ = 625.9 ppm. MS (EI): m/z 316 (M^+, 100%), 237 (48), 193 (27).

2-Bromo[1]benzoselenopheno[2,3-*b*]thiophene (**20b**). **19b** (237 mg, 1 mmol) was dissolved in 20 mL THF and cooled to 0 °C. NBS (178 mg, 1 mmol) was added in portions. After work-up according to the general procedure **20b** was isolated as yellow solid in 67% yield (212 mg). R_f = 0.50 (light petrol). mp = 95.8 - 100.3 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.85 - 7.84 (m, 2 H), 7.54 (s, 1 H), 7.42 (ddd, J = 8.1, 6.9, 1.1 Hz, 1 H), 7.29 (ddd, J = 8.1, 6.9, 1.1 Hz, 1 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.6 (s), 143.1 (s), 134.5 (s), 132.9 (s), 126.2 (d), 125.2 (d), 124.8 (d), 123.6 (d), 122.9 (d), 113.1 (s) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$): δ = 491.7 ppm. MS (EI): m/z 316 (M^+, 100%), 237 (32), 193 (38).

2-Bromoselenolo[2,3-*b*][1]benzoselenophene (**20c**). **19c** (398 mg, 1.4 mmol) was dissolved in 20 mL THF and cooled to 0 °C. NBS (249 mg, 1.4 mmol) was added in portions. After work-up according to the general procedure **20c** was isolated as yellow solid in 95% yield (484 mg). R_f = 0.51 (light petrol). mp = 93.7 - 96.1 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.87 - 7.84 (m, 2 H), 7.76 (s, 1 H), 7.42 - 7.39 (m, 1 H), 7.29 - 7.26 (m, 1 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.7 (s), 143.9 (s), 135.7 (s), 134.7 (s), 126.7 (d), 126.0 (d), 125.1 (d), 124.5 (d), 123.1 (d), 115.1 (s) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$): δ = 652.6, 512.4 ppm. MS (EI): m/z 364 (M^+, 100%), 285 (30), 202 (5), 193 (17).

General procedure toward **17a-c**. To a suspension of zinc powder (10 eq.) in THF was slowly added titanium tetrachloride (5 eq.) at 0 °C, and then the mixture was refluxed for 3 h under an argon atmosphere. A solution of compound **16a-c** (1 eq.) and pyridine (11 eq.) in 30 mL THF was slowly added to the mixture, and then the mixture was refluxed for another 6 h. After cooling to room temperature, the mixture was diluted with 50 mL saturated sodium bicarbonate and stirred for 30 min. The solid was filtered and washed with diluted hydrochloric acid, water, and acetone and then dried in vacuo.

(*E*)-2,2'-(1,2-Ethenediyl)bis[selenolo[3,2-*b*][1]benzothiophene] (**17a**). The synthesis of **17a** was carried out according to the general procedure starting from **16a** (1.59 g, 6 mmol), zinc powder (3.92 g, 60 mmol) and titanium tetrachloride (5.69 g, 30 mmol). The crude product was sublimated twice to give a bright yellow solid (1.02 g, 68%). R_f = 0.30 (light petrol : DCM 4:1). ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 7.89 - 7.87 (m, 2 H), 7.80 - 7.79 (m, 2 H), 7.49 (s, 2 H), 7.43 (ddd, J = 8.0, 6.9, 1.0 Hz, 2 H), 7.37 (ddd, J = 8.0, 6.9, 1.0 Hz, 2 H), 7.17 (s, 2 H) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 149.7, 142.5, 140.0, 135.7, 133.9, 126.0, 125.5, 125.3, 124.2, 122.9, 122.2 ppm. ^{77}Se NMR (114 MHz, CD_2Cl_2): δ = 495.6 ppm. HR-APCI-FTMS $[M+H]^+$ m/z calcd. 500.8784 for $C_{11}H_9OSe_2^+$, found 500.8784.

(*E*)-2,2'-(1,2-Ethenediyl)bis[[1]benzoselenopheno[3,2-*b*]thiophene] (**17b**). The synthesis of **17b** was carried out according to the general procedure starting from **16b** (1.06 g, 4 mmol), zinc powder (2.62 g, 40 mmol) and titanium tetrachloride (3.79 g, 20 mmol). The crude product was sublimated twice to give a bright yellow solid (548 mg, 55%). R_f = 0.27 (light petrol : DCM 4:1). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.92 - 7.90 (m, 2 H), 7.83 - 7.81 (m, 2 H), 7.44 (ddd, J = 8.0, 6.9, 1.0 Hz, 2 H), 7.36 (s, 2 H), 7.29 (ddd, J = 8.0, 6.9, 1.0 Hz, 2 H), 7.24 (s, 2 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.2 (s), 142.6 (s), 136.0 (s), 135.4 (s), 134.8 (s), 126.9 (d), 125.3 (d), 124.8 (d), 122.5 (d), 122.4 (d), 122.1 (d) ppm. ^{77}Se NMR (114 MHz, CD_2Cl_2): δ = 457.5 ppm. HR-APCI-FTMS $[M+H]^+$ m/z calcd. 500.8784 for $C_{11}H_9OSe_2^+$, found 500.8786.

(*E*)-2,2'-(1,2-Ethenediyl)bis[selenolo[3,2-*b*][1]benzoselenophene] (**17c**). The synthesis of **17c** was carried out according to the general procedure starting from **16c** (1.87 g, 6 mmol), zinc powder (3.92 g, 60 mmol) and titanium tetrachloride (5.69 g, 30 mmol). The crude product was purified by column chromatography (90 g activated basic aluminum oxide, Brockmann 1, light petrol / DCM 0 → 100%) to give a bright yellow solid (1.12 g, 63%). R_f = 0.24 (light petrol : DCM 4:1). ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 7.93 - 7.92 (m, 2 H), 7.79 - 7.77 (m, 2 H), 7.50 (s, 2 H), 7.43 (ddd, J = 8.3, 6.8, 0.9 Hz, 2 H), 7.30 (ddd, J = 8.3, 6.9, 1.2 Hz, 2 H), 7.16 (s, 2 H) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 149.2 (s), 142.8 (s), 137.9 (s), 137.4 (s), 136.8 (s), 127.3 (d), 126.0 (d), 125.9 (d), 125.9 (d), 125.4 (d), 123.8 (d) ppm. ^{77}Se NMR (114 MHz, CD_2Cl_2): δ = 518.5, 486.1 ppm. HR-APCI-FTMS $[M+H]^+$ m/z calcd. 596.7673 for $C_{11}H_9OSe_2^+$, found 596.7675.

General procedure toward **21a-c**. Bromide **20a-c** (2.5 eq.) and (*E*)-1,2-bis(tri-n-butylstannyl)ethylene (1 eq.) were dissolved in anhydrous toluene. The mixture was bubbled with argon for 30 min. $Pd(PPh_3)_4$ (0.03 eq.) was added and the mixture was heated to 90 °C for 48 hours under an argon atmosphere. The reaction mixture was cooled to room temperature, the obtained precipitate filtered, washed with methanol as well as acetone and dried in vacuo.

(*E*)-2,2'-(1,2-Ethenediyl)bis[selenolo[2,3-*b*][1]benzothiophene] (**21a**). **21a** was synthesized according to the general procedure starting from **20a** (506 mg, 1.6 mmol), (*E*)-1,2-bis(tri-n-butylstannyl)ethylene (388 mg, 0.64 mmol) and $Pd(PPh_3)_4$ (22 mg, 0.02 mmol). The crude product was sublimated twice to give a bright yellow solid (73 mg, 23%). R_f = 0.34 (light petrol : DCM 4:1). ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 7.94 - 7.93 (m, 2 H), 7.87 - 7.86 (m, 2 H), 7.69 (s, 2 H), 7.44 (ddd, J = 8.1, 7.0, 1.2 Hz, 2 H), 7.35 (ddd, J = 8.0, 7.0, 1.2 Hz, 2 H), 7.10 (s, 2 H) ppm. HR-APCI-FTMS $[M+H]^+$ m/z calcd. 500.8784 for $C_{11}H_9OSe_2^+$, found 500.8784.

(*E*)-2,2'-(1,2-Ethenediyl)bis[[1]benzoselenopheno[2,3-*b*]thiophene] (**21b**). **21b** was synthesized according to the general procedure starting from **20b** (190 mg, 0.6 mmol), (*E*)-1,2-bis(tri-n-butylstannyl)ethylene (120 mg, 0.2 mmol) and $Pd(PPh_3)_4$ (2 mg, 0.002 mmol). The crude product was sublimated twice to give a bright yellow solid (36 mg, 30%). R_f = 0.31 (light petrol : DCM 4:1). ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 7.96 – 7.91 (m, 2 H), 7.91 - 7.86 (m, 2 H), 7.53 (s, 2 H), 7.47 - 7.43 (m, 2 H), 7.33 - 7.29 (m, 2 H), 7.18 (s, 2 H) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 146.7 (s), 145.4 (s), 144.2 (s), 135.5 (s), 134.2 (s), 126.8 (d), 125.8 (d), 125.3 (d), 123.5 (d), 122.1 (d), 119.9 (d) ppm. HR-APCI-FTMS $[M+H]^+$ m/z calcd. 500.8784 for $C_{11}H_9OSe_2^+$, found 500.8782.

(*E*)-2,2'-(1,2-Ethenediyl)bis[selenolo[2,3-*b*][1]benzoselenophene] (**21c**). **21c** was synthesized according to the general procedure starting from **20c** (474 mg, 1.5 mmol), (*E*)-1,2-bis(tri-n-butylstannyl)ethylene (303 mg, 0.5 mmol) and $Pd(PPh_3)_4$ (17 mg, 0.02 mmol). The crude product was purified by column chromatography (90 g activated basic aluminum oxide, Brockmann 1, light petrol / DCM 0 → 100%) as brownish solid (83 mg,

28%). R_f = 0.29 (light petrol / DCM 4:1). ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 7.95 - 7.86 (m, 4 H), 7.69 (s, 2 H), 7.47 - 7.40 (m, 2 H), 7.33 - 7.26 (m, 2 H), 7.10 (s, 2 H) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 150.8 (s), 146.7 (s), 145.0 (s), 136.8 (s), 125.7 (d), 125.4 (d), 125.0 (d), 123.6 (d), 122.7 (d) ppm. HR-APCI-FTMS $[M+H]^+$ m/z calcd. 596.7673 for $C_{11}H_9OSe_2^+$, found 596.7676.

OFETs were fabricated in a top-contact configuration. The used wafers were made of 500 µm highly doped silicon with 260 nm polished SiO_2 grown on top. They were cleaned in an ultrasonic bath first with acetone and then isopropanol. The wafers were used as purchased or were modified with a thin dielectric layer of spin coated Cytop™ (30 nm) or a self-assembled monolayer of octadecyltrichlorosilane (OTS). Cytop is a fluoropolymer which is highly hydrophobic and has a smooth surface,[45,46] the self-assembled monolayer of OTS results in a surface where the evaporated thin film of the organic semiconductor has fewer impurities. For the coating with Cytop, the SiO_2 wafers were cleaned with an N_2 stream to remove dust particles. A solution of Cytop CTL-809M and the solvent CT-180 in a ratio of 1:10 was spin coated at a rotation speed of 500 rpm for 10 s followed by 1000 rpm for 30 s with an acceleration of max 500 rpm/s. The samples were annealed on a plate for 30 min at 90° followed by 1 h at 130°. The organic semiconductors were thermally evaporated through a shadow mask at 10^{-6} mbar on top of the dielectric: the layer thickness of the used **17a** devices was 30 nm, the one of the **DTBTE** devices was 15 nm. The substrate was kept at room temperature or was heated to 70°C during the evaporation (see Table 3). To form a bottom gate top electrode device the gold electrodes for source and drain were evaporated onto the semiconductor (thickness of ~ 25 nm) in high vacuum.

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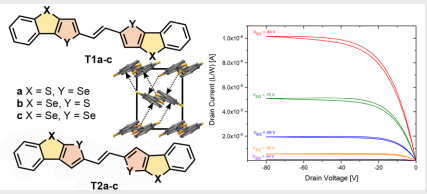

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Symmetric Mixed Sulfur-Selenium Fused Ring Systems as Potential Materials for Organic Field-Effect Transistors

This study introduces a series of regioisomeric symmetric sulfur-selenium fused materials for organic field effect transistors (OFETs). These π-conjugated materials show strong intermolecular interactions beneficial for charge carrier transport.