

## **Supporting Information**

for

# Selenophene-containing heterotriacenes by a C–Se coupling/ cyclization reaction

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## Additional spectral and crystallographic data

# <sup>1</sup>H and <sup>13</sup>C NMR spectra of the target heterotriacenes 1–4

Dithieno[3,2-b:2',3'-d]thiophene (1, DTT)



Figure S1: <sup>1</sup>H (top) and <sup>13</sup>C NMR (bottom) spectrum of heterotriacene 1 in CDCl<sub>3</sub>. \*= residual solvent signals

## Selenolo[3,2-*b*:4,5-*b*']dithiophene (**2**, DTS).



**Figure S2:** <sup>1</sup>H (top) and <sup>13</sup>C NMR (bottom) spectrum of heterotriacene **2** in CDCl<sub>3</sub>. \*= residual solvent signals

## Bisselenolo[3,2-b:2',3'-d]thiophene (3, DST)



## Bisselenolo[3,2-b:2',3'-d]selenophene (4, DSS)



## Single crystal X-ray structure analysis

Identification code	DTS <b>2</b>	CCDC 1897412
Empirical formula	$C_{36}H_{18}S_9Se_{4.5}$	
Formula weight	1094.36	
Temperature/K	293.15	
Crystal system	monoclinic	
Space group	P21/c	
a/Å	5.978(3)	
b/Å	29.005(11)	
c/Å	21.173(8)	
α/°	90	
β/°	91.903(19)	
γ/°	90	
Volume/ų	3669(3)	
Z	4	
$\rho_{calc}g/cm^3$	1.981	
µ/mm⁻¹	5.037	
F(000)	2124.0	
Crystal size/mm <sup>3</sup>	0.164 × 0.064 ×	0.064
Radiation	ΜοΚα (λ = 0.710	073)
20 range for data collection/	' 4.098 to 61.022	
Index ranges	-8 ≤ h ≤ 8, -41 ≤	$k \le 41, -30 \le l \le 30$
Reflections collected	125755	
Independent reflections	11219 [R <sub>int</sub> = 0.0	)445, R <sub>sigma</sub> = 0.0221]
Data/restraints/parameters	11219/935/706	
Goodness-of-fit on F <sup>2</sup>	1.276	
Final R indexes [I>=2σ (I)]	R <sub>1</sub> = 0.0557, wR	<sub>2</sub> = 0.0977
Final R indexes [all data]	R <sub>1</sub> = 0.0632, wR	<sub>2</sub> = 0.0998
Largest diff. peak/hole / e Å <sup>-3</sup>	0.72/-0.76	

 Table S1: X-ray structure analysis data of heterotriacene DTS 2.



**Figure S5:** Single-crystal X-ray structure analysis of selenolotriacene DTS **2**, (a) individual molecule and atom numbering (top view); (b) side view. (c) Herringbone-type packing structure of the molecules in the unit cell.



**Figure S6:** Single-crystal X-ray structure analysis of selenolotriacene DTS **2**: (a) partial overlap of two stacked and displaced molecules leading to  $\pi$ - $\pi$  interactions with distances between 3.27 and 3.40 Å (side view); top view of  $\pi$ - $\pi$  antiparallel (43% molecular overlap) (b) and parallel (53% molecular overlap) (c) interacting molecules. (d) Intermolecular interactions between heteroatoms and hydrogen-heteroatoms (labelled cyan and blue respectively) for one of the two non-disordered non-equivalent molecules in the reduced unit cell.

Identification code	DST <b>3</b>	CCDC 1025419
Empirical formula	$C_8H_4SSe_2$	
Formula weight	290.09	
Temperature/K	150.00(10)	
Crystal system	monoclinic	
Space group	P21/n	
a/Å	6.02748(19)	
b/Å	10.6662(3)	
c/Å	12.9279(4)	
α/°	90	
β/°	96.747(3)	
γ/°	90	
Volume/ų	825.38(4)	
Z	4	
$\rho_{calc}g/cm^3$	2.334	
µ/mm <sup>-1</sup>	9.133	
F(000)	544.0	
Crystal size/mm <sup>3</sup>	0.237 × 0.142 × 0	0.114
Radiation	ΜοΚα (λ = 0.710	73)
20 range for data collection/	6.346 to 58.688	
Index ranges	-8 ≤ h ≤ 6, -14 ≤	k ≤ 14, -14 ≤ l ≤ 17
Reflections collected	6191	
Independent reflections	2037 [R <sub>int</sub> = 0.04	54, R <sub>sigma</sub> = 0.0517]
Data/restraints/parameters	2037/0/101	
Goodness-of-fit on F <sup>2</sup>	1.056	
Final R indexes [I>=2σ (I)]	$R_1 = 0.0312, wR_2$	= 0.0568
Final R indexes [all data]	$R_1 = 0.0436, wR_2$	= 0.0632
Largest diff. peak/hole / e Å <sup>-3</sup>	0.61/-0.55	

Identification code	DSS <b>4</b>	CCDC 1898450
Empirical formula	$C_{36}H_{18}Se_{13.5}$	
Formula weight	1516.27	
Temperature/K	293.15	
Crystal system	monoclinic	
Space group	P21/c	
a/Å	6.108(3)	
b/Å	29.049(17)	
c/Å	21.949(11)	
α/°	90	
β/°	91.815(12)	
γ/°	90	
Volume/ų	3892(3)	
Z	4	
$ ho_{calc}g/cm^3$	2.588	
µ/mm <sup>-1</sup>	12.681	
F(000)	2772.0	
Crystal size/mm <sup>3</sup>	$0.221 \times 0.085 \times 0$	0.044
Radiation	ΜοΚα (λ = 0.710	73)
20 range for data collection/°	' 4.598 to 52.778	
Index ranges	-7 ≤ h ≤ 7, -36 ≤ l	k ≤ 36, -26 ≤ l ≤ 27
Reflections collected	74466	
Independent reflections	7962 [R <sub>int</sub> = 0.07	83, R <sub>sigma</sub> = 0.0388]
Data/restraints/parameters	7962/1704/713	
Goodness-of-fit on F <sup>2</sup>	1.233	
Final R indexes [I>=2σ (I)]	$R_1 = 0.0663, wR_2$	= 0.1254
Final R indexes [all data]	R <sub>1</sub> = 0.0758, wR <sub>2</sub>	= 0.1288
Largest diff. peak/hole / e Å <sup>-3</sup>	2.52/-1.63	



**Figure S7:** Single-crystal X-ray structure analysis of selenolotriacene DSS **4**, (a) individual molecule and atom numbering (top view); (b) side view. (c) Herringbone-type packing structure of the molecules in the unit cell.



**Figure S8**: Single-crystal X-ray structure analysis of selenolotriacene DSS **4**: (a) partial overlap of two stacked and displaced molecules leading to  $\pi - \pi$  interactions with distances between 3.34 and 3.38 Å (side view); top view of  $\pi - \pi$  antiparallel (45% molecular overlap) (b) and parallel (52% molecular overlap) (c) interacting molecules. (d) Intermolecular interactions between heteroatoms and hydrogen-heteroatoms (labelled cyan and blue respectively) for one of the two non-disordered non-equivalent molecules in the reduced unit cell.

Table S4: Short contacts f	or one molecule in the as	ymmetric unit of DST <b>3</b> (a	a) and DTT <b>1</b> (	b) from ref. [1,2].
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DST 3					H	b)				
Atom1	Atom2	Distance	Mol. 1	Mol. 2		DTT <b>1</b>				
Se2	S3	3,645	x,y,z	-1+x,y,z		Atom1	Atom2	Distance	Mol. 1	Mol. 2
Se1	H5	3,028	x,y,z	1/2-x,-1/2+y,1/2-z		S2	S1	3,566	x,y,z	1-x,-1/2+y,1/2-z
H8	S3	2,819	x,y,z	-1/2+x,1.5-y,1/2+z		S2	S2	3,537	x,y,z	1-x,-1/2+y,1/2-z

 Table S5: Short contacts for one molecule in the asymmetric unit of DTS 2.

DTS <b>2</b>				
Atom1	Atom2	Distance	Mol. 1	Mol. 2
Se1	S6	3,544	x,y,z	-1+x,y,z
Se1	S8	3,605	x,y,z	-1+x,y,z
H28	S9	2,956	x,y,z	-2+x,y,z
H9	C21	2,824	x,y,z	-1+x,y,z
S6	Se3	3,498	x,y,z	x,y,z
S6	H6	2,974	x,y,z	x,y,z
Se1	S13	3,413	x,y,z	-1+x,1.5-y,-1/2+z
H23	C27	2,854	x,y,z	x,y,z
S6	S11	3,547	x,y,z	1+x,y,z
Se1	C3AA	3,348	x,y,z	-1-x,1-y,-z
Se1	H3AA	2,92	x,y,z	-1-x,1-y,-z
Se2	S7	3,641	x,y,z	-1+x,y,z
C16	C16	3,267	x,y,z	2-x,2-y,-z
C16	C21	3,399	x,y,z	2-x,2-y,-z
H32	C30	2,863	x,y,z	-x,1/2+y,1/2-z
H32	C33	2,794	x,y,z	-x,1/2+y,1/2-z

 Table S6: Short contacts for one molecule in the asymmetric unit of DSS 4.

DSS 4				
Atom1	Atom2	Distance	Mol. 1	Mol. 2
Se6	Se1	3,657	x,y,z	-1+x,y,z
C4	C4	3,348	x,y,z	-x,-y,2-z
C8	C14	3,395	x,y,z	-x,-y,2-z
Se9	H19	3,038	x,y,z	x,1/2-y,1/2+z
Se6	Se8	3,765	x,y,z	1+x,1/2-y,1/2+z
C8	H9	2,8	x,y,z	1+x,1/2-y,1/2+z
C13	Se8	3,578	x,y,z	1+x,1/2-y,1/2+z
HOAA	C17	2,857	x,y,z	-x,-1/2+y,1.5-z
Se9	C22	3,457	x,y,z	x,1/2-y,1/2+z
H14	Se5	3,092	x,y,z	x,1/2-y,1/2+z
Se6	C16	3,569	x,y,z	x,y,z
Se4	Se2	3,65	x,y,z	-1+x,y,z
Se8	Se2	3,667	x,y,z	-1+x,y,z
Se2	Se1A	3,52	x,y,z	x,y,z
H19	Se1A	3,064	x,y,z	x,y,z
Se4	Se11	3,546	x,y,z	-1+x,1/2-y,-1/2+z
Se4	H1	3,017	x,y,z	-1+x,1/2-y,-1/2+z
C2	H1AA	2,88	x,y,z	-1+x,y,z
Se2	C3AA	3,417	x,y,z	x,y,z
Se2	H3AA	3,03	x,y,z	x,y,z
Se10	Se2A	3,564	x,y,z	x,y,z
Se1A	H3AA	3,089	x,y,z	x,y,z

#### **XRD** measurements



**Figure S9:** XRD plots of heterotriacenes **1–4**. Insets: magnification of the region  $2\Theta = 5-40^{\circ}$ .



**Figure S10:** XRD plot and X-Ray powder pattern of DTT **1** (a), including missing reflexions (red encircled). Table with  $d_{hkl}$  and relative intensity of X-Ray and XRD reflexions for selected Miller indices.



)	XRD	
Miller indices	d <sub>hlk</sub> [Å] (Peak Intensity)	d <sub>hlk</sub> [Å] (Peak Intensity)
<0 1 2>	9.93 (40%)	9.92 (18%)
<0 3 1>	8.80 (11%)	8.75 (10%)
<0 4 0>	7.23 (100%)	7.22 (100%)
<0 1 3>	6.48 (35%)	6.87 (29%)
<1 1 0>	5.83 (22%)	5.88 (13%)
<0 3 3>	5.70 (11%)	5.71 (12%)
<1 1 1>	5.59 (50%)	5.59 (61%)
<0 1 4>	5.20 (26%)	5.22 (26%)
<0 4 3>	5.05 (33%)	5.07 (32%)
<1 2 -2>	4.96 (16%)	4.99 (18%)
<0 6 0>	4.82 (18%)	4.83 (8%)
<0 5 3>	4.47 (27%)	4.50 (16%)
<0 4 4>	4.27 (11%)	4.30 (9%)
<1 3 3>	4.07 (18%)	4.02 (31%)
<0 6 3>	3.99 (64%)	3.92 (44%)
<1 5 -2>	3.90 (46%)	3.79 (28%)
<1 6 0>	3.76 (54%)	3.70 (39%)
<1 6 1>	3.69 (63%)	3.64 (9%)
<1 3 4>	3.61 (14%)	3.58 (12%)
<1 6 2>	3.51 (38%)	3.54 (21%)
<0.2.6>	3.43 (61%)	3.43 (72%)
<1 0 5>	3.40 (70%)	3.36 (26%)
<1 6 -3>	3.35 (36%)	2.22 (5.10)
<1 3 5>	3.30 (61%)	3.23 (51%)

**Figure S11:** XRD plot and X-Ray powder pattern of DTS **2** (a). Table with d<sub>hkl</sub> and relative intensity of X-ray and XRD reflexions for selected Miller indices.



**Figure S12:** XRD plot and X-ray powder pattern of DST **3** (a). Table with d<sub>hkl</sub> and relative intensity of X-ray and XRD reflexions for selected Miller indices.

#### Electrochemical characterization of heterotriacenes 1–4



**Figure S13:** Cyclic voltammograms (acetonitrile / TBAPF<sub>6</sub> ( $10^{-3}$  M) scan rate = 100 mV s<sup>-1</sup>) of DTT **1** (in black), DTS **2** (in red), DST **3** (in blue), and DSS **4** (in green).

### Electrochemical polymerization of heterotriacenes DTT 1, DST 3, and DSS 4 and characterization of corresponding polymers P1, P3, and P4



**Figure S14:** Multisweep voltammograms for the electrochemical polymerization of monomeric heterotriacenes DTT **1**, DST **3**, and DSS **4** in DCM/TBAPF<sub>6</sub> (0.1 M) at a scan rate of 100 mV s<sup>-1</sup> (left) and electrochemical characterization of the corresponding polymers **P1**, **P3**, and **P4** in monomer-free electrolyte DCM/TBAPF<sub>6</sub> (0.1 M) at different scan rates (10–500 mV s<sup>-1</sup>) (right).



Multisweep voltammograms and cycling stability for poly(heterotriacenes) P1–P4

**Figure S15:** Multisweep voltammogram (30 scans) for the electrochemical cycling stability of polymer **P1** (i), **P2** (ii), **P3** (iii), and **P4** (iv) in DCM/TBAPF<sub>6</sub> (0.1 M) at a scan rate of 100 mV s<sup>-1</sup>.

#### Spectroelectrochemistry of poly(heterotriacenes) P1-P4



**Figure S16:** UV–vis–NIR spectra obtained from spectroelectrochemical measurements of polymer **P1** (i), **P2** (ii), **P3** (iii), and **P4** (iv). Applied voltages are stated vs. Ag/AgCl. Artefacts are marked with \* in the spectra. Black arrows show the changes starting at low potentials, blue arrows show the further changes at high potentials.

**Table S1**: Optical properties of poly(heterotriacenes) **P1–P4**. The values of  $\lambda_{max}$ ,  $\lambda_{onset}$ , and the energy gap  $E_g$  were obtained from UV–vis–NIR spectra of neutral polymer films measured in a spectroelectrochemical setup. The maxima  $\lambda_{max, ox}$  of the oxidized films were obtained from spectroelectrochemical measurements. The LUMO energy levels were calculated from the HOMO energy level (Table 3) and  $E_g$ , respectively.

Polymer	λ <sub>max</sub> [nm]	λ <sub>onset</sub> [nm]	E <sub>g</sub> [eV]	LUMO [eV]	λ <sub>max, ox</sub> [eV]
<b>P1</b> (PDTT)	532	692	1.79	-3.13	763 (br)
<b>P2</b> (PDTS)	532 (369)	744	1.67	-3.28	1090 (497, 629 (sh))
<b>P3</b> (PDST)	509	748	1.66	-3.27	773 (br)
<b>P4</b> (PDSS)	478 (395)	744	1.67	-3.31	1090 (493, 703 (sh))
<b>PDTP</b> (S NH S) [3]	524	665	1.86	-2.70	1079 (br)

#### References

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