Electronic Supplementary Material (ESI) for Materials Advances. This journal is © The Royal Society of Chemistry 2021

Supporting Information

π -Conjugated Stannole Copolymers Synthesised by a Tin-Selective Stille Cross-Coupling Reaction⁺

Isabel-Maria Ramirez y Medina,^{a,b} Markus Rohdenburg,^{c,d} Pascal Rusch,^{e,f} Daniel Duvinage,^{g,b} Nadja C. Bigall,^{e,f} Anne Staubitz ^{*a,b}

^a University of Bremen, Institute for Organic and Analytical Chemistry, Leobener Str. 7, 28359 Bremen, Germany

^b University of Bremen, MAPEX Center for Materials and Processes, Bibliothekstr. 1, 28359 Bremen, Germany

^c University of Bremen, Institute for Applied and Physical Chemistry, Leobener Str. 5, 28359 Bremen, Germany

^d University of Leipzig, Wilhelm-Ostwald-Institute for Physical and Theoretical Chemistry, Linnéstr. 2, 04103 Leipzig, Germany

^e Leibniz University Hannover, Institute of Physical Chemistry and Electrochemistry, Schneiderberg
39, 30167 Hannover, Germany

^f Cluster of Excellence PhoenixD (Photonics, Optics, and Engineering – Innovation Across Disciplines), Hannover, Germany

^g University of Bremen, Institute of Inorganic Chemistry and Crystallography, Leobener Str. 7, 28359 Bremen, Germany

*E-Mail: staubitz@uni-bremen.de

⁺ This article was submitted on the occasion of the 85th birthday of Ei-ichi Negishi, the creator of the Negishi coupling and Negishi's Zirconocene.

Table of Contents

1	Gen	eral Considerations				
	1.1	Abbreviations				
	1.2	Chemicals and Solvents				
	1.3	Analytical Instruments				
	1.4	Crystallography6				
2	Synt	heses7				
3	Crys	tallography24				
4	Opt	cal Properties				
	4.1	Monomer St1				
	4.2	Monomer St2				
	4.3	Monomer St3				
	4.4	Monomer St4				
	4.5	Polymers				
5	The	pretical Calculations				
7	GPC	and MALDI64				
8	TGA	Measurements				
9	NM	R Spectra				
Li	Literature					

1 General Considerations

1.1 Abbreviations

calcd.	calculated
DFT	density functional theory
DCM	dichloromethane
Ср	cyclopentadienyl
EI	electron impact
GB	glove box
НОМО	highest occupied molecular orbital
IR	infrared spectroscopy
LUMO	lowest unoccupied molecular orbital
MeOH	methanol
NMR	nuclear magnetic resonance
PFK	perfluorokerosene
ppm	parts per million
R	resolution (for mass spectrometry)
sat. soln.	saturated solution
SPS	solvent purification system
TEA	triethylamine
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	tetramethylsilane

1.2 Chemicals and Solvents

All reactions were carried out using standard Schlenk techniques under a dry, inert nitrogen or argon atmosphere unless noted otherwise. Some reactions were performed inside a nitrogen filled glovebox from Inert, Innovative Technology, Inc. Company (< 0.1 ppm O₂ and < 0.1 ppm H₂O). All anhydrous solvents were taken from the solvent purification system (SPS), degassed by freeze-pump-thaw cycles and stored under a nitrogen atmosphere unless noted otherwise. All chemicals were commercially available and were used without further purification unless noted otherwise.

Reagent	Supplier	Purity	Comments	
3,5-Bis(trifluoromethyl)-	abcr	99%		
bromo-benzene				
1-Bromohexane	Sigma-Aldrich	98%		
4-Bromophenol	Sigma-Aldrich	99%		
1-Bromo-4-(trifluoromethyl)-	abcr	99%		
benzene				
Copper(I)chloride	Alfa Aesar	99.999%	stored in a GB	
<i>n</i> -Butyllithium	Acros Organics	n. a.	2.5 M in hexanes	
<i>t</i> -Butyllithium	Merck	n. a.	1.7 M in <i>n</i> -pentane	
1,4-Dibromobenzene	Alfa Aesar	98%		
1-Iodohexane	Acros Organics	98%	stored in a GB	
Magnesium sulfate	Sigma-Aldrich	> 99%		
[Pd(<i>t</i> -Bu ₃ P) ₂]	Sigma-Aldrich	99%	stored in a freezer	
			in a GB	
[Pd(PPh ₃) ₄]	TCI	> 97%	stored in a freezer	
			in a GB	
Potassium carbonate	Sigma-Aldrich	> 99%		
Sodium sulfate	Sigma-Aldrich	> 99%		
Tin tetrachloride	Acros Organics	99%	Stored in a J.	
			Young's tube under	
			a N ₂ atmosphere	

Table S1. List of supplier and purity of chemicals used.

Table S2. List of suppliers and purity of solvents used.

Solvent	Comments			
Acetone	VWR Chemicals; ACS, Reag. Ph. Eur.			
Chloroform	VWR Chemicals; ACS, Reag. Ph. Eur.			
Dichloromethane	VWR Chemicals; ACS, Reag. Ph. Eur.			
Diethyl ether	VWR Chemicals; ACS, Reag. Ph. Eur.			
Dimethylformamide	Acros Organics, 99.8%, SuperDry, with molecular			
	sieves, Acrosealed			
Ethyl acetate	VWR Chemicals; ACS, Reag. Ph. Eur.			
<i>n</i> -Hexane	VWR Chemicals; ACS, Reag. Ph. Eur.			
Methanol	VWR Chemicals; ACS, Reag. Ph. Eur.			
<i>n</i> -Pentane	VWR Chemicals; for HPLC; anhydrous from the			
	SPS and degassed			
<i>n</i> -Pentane	VWR Chemicals; ACS, Reag. Ph. Eur.			
<i>t</i> -Butanol	VWR Chemicals, ACS, Reag. Ph. Eur.			
Tetrahydrofuran	VWR Chemicals; for HPLC; anhydrous from the			
	SPS and degassed			
Toluene	VWR Chemicals; for HPLC; anhydrous from the			
	SPS and degassed			

1.3 Analytical Instruments

¹H, ¹³C{¹H}, ¹⁹F, and ¹¹⁹Sn{¹H} NMR spectra were recorded on a Bruker Avance Neo 600 or Bruker DRX 500 at 23 °C. All ¹H NMR and ¹³C{¹H} NMR spectra were referenced against the solvent residual proton signals (¹H), or the solvent itself (¹³C). The reference for the ¹⁹F and ¹¹⁹Sn{¹H} NMR spectra were calculated based on the ¹H NMR spectrum of TMS. All chemical δ shifts are given in parts per million (ppm) and all coupling constants *J* in Hz. The following abbreviations are used to describe splitting patterns: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, td = triplet of doublets, m = multiplet.

Electron Impact (EI) ionization mass spectra were obtained on the double focusing mass spectrometer MAT 95XL. Samples were measured by direct inlet or indirect inlet method with a source temperature of 200° C. The ionization energy of the electron impact ionization was 70 eV. All signals were reported with the quotient from mass to charge m/z. High resolution (HR) El mass spectra were recorded on the double focusing mass spectrometer MAT 95XL from FINNIGAN MAT. Precision weights were

determined via the peak-matching method. The reference substance was perfluorokerosene (PFK). The resolution (R) of the peak-matching performance was 10000. The calculated isotopic distribution for each ion agreed with experimental values. HR-APCI mass spectra were recorded on a Bruker Impact II. MALDI mass spectra were recorded on a AutoflexMax from Bruker Daltonik, Bremen using DCTB (20 mg mL⁻¹) as the matrix. Sample preparation: 50 μ L matrix solution premixed with 20 μ L sample solution, both dissolved in chloroform. A 355 nm laser with 4x2000 laser shots accumulated for one spectrum was used.

Gel permeation chromatography (GPC) was performed on a GPC-PSS/Agilent SECurity 1260 System. The columns were heated at 35 °C with a column thermostat SECurity TCC6000. Conventional calibration using polystyrene standards (PS) was conducted to calibrate the system. Chloroform (HPLC grade without stabiliser) was used as an eluent.

IR spectra were recorded on a Nicolet Thermo IS10 SCIENTIFIC spectrometer with a diamond ATR unit. The resolution was 4 cm⁻¹. Relative intensities of the IR bands were described by s = strong (0 - 33% T), m = medium (34 - 66% T) or w = weak (67 - 100% T).

All melting points were measured with a Büchi Melting Point M-560 apparatus.

Thin layer chromatography (TLC) was carried out on aluminium plates coated with silica gel 60 F₂₅₄ with a layer thickness of 0.2 mm from Macherey-Nagel. All bands were detected by using UV light (254 nm and 366 nm). Column chromatography was carried out by using the column machine PuriFlash 4250 from Interchim. Silica gel columns of the type PF-15SiHP-F0025, PF-50SiHP-JP-F0080, PF-50SiHP-JP-F0120, and PF-50SiHP-JP-F0220 were used. The injection of the sample was made via dry load. The column material of the dry load was Celite 503 from Macherey-Nagel.

UV-Vis spectra were recorded with a resolution of 0.1 nm on a UV-2700 spectrometer from Shimadzu.

Emission spectra were recorded on an Edinburgh Instruments FLS 1000 photoluminescence spectrometer. Absolute quantum yields were measured with an Edinburgh Instruments integrating sphere. TCSPC measurements were performed using a fast response MCP-PMT detector and a 376 nm Edinburgh Instruments EPL Laser as excitation source with 10 - 20 MHz repetition rate and 80 ps pulse width. Temperature dependent-fluorescence measurements were carried out using an Oxford Instruments Optistat-CF cryostat cooled with liquid nitrogen. CIE 1931chromaticity coordinates were

generated from the respective photoluminescence spectra using the Edinburgh Instruments software Fluoracle. All emission spectra are corrected spectra.

Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA instrument using aluminium crucibles under N_2 at a flow rate of 20 mL/min and a heating rate of 10 K/min.

1.4 Crystallography

Crystallography. Intensity data of **ST2** and **ST3** were collected on a Bruker Venture D8 diffractometer at 100 K with Mo-Kα (0.7107 Å) radiation. All structures were solved by direct methods and refined based on F² by use of the SHELX¹ program package as implemented in OLex2 1.2.² All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model. Crystal and refinement data are collected in Tables S3. Figures were created using DIAMOND (Diamond - Crystal and Molecular Structure Visualization; Crystal Impact - Dr. H. Putz & Dr. K. Brandenburg GbR, Kreuzherrenstr. 102, 53227 Bonn, Germany; <u>http://www.crystalimpact.com/diamond</u>).

Crystallographic data for the structural analyses have been deposited with in Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

2 Syntheses

The precursor molecules for the stannoles, 1,8-bis(5-iodo-thiophen-2-yl)octa-1,7-diyne (**10**), 1,8-bis(5-iodo-4-hexylthiophen-2-yl)octa-1,7-diyne (**12**), and Rosenthal's zirconocene **13** were reproduced according to the published procedures.³ 2,5-Bis-(trimethylstannyl)-thiophene was reproduced according to the published procedure.⁴

1-Bromo-4-hexylbenzene (1)^{3d, 5}



To a solution of 1,4-dibromobenzene (20.0 g, 84.8 mmol) in THF (160 mL), n-BuLi (2.50 M in hexanes, 33.4 mL, 84.8 mmol) was added dropwise over the course of 8 min at -78 °C. The yellow reaction mixture was stirred for further 30 min. Then, 1-iodohexane (17.97 g, 84.78 mmol) was added dropwise over the course of 7 min at -78 °C. The reaction was stirred for 2 h and was then allowed to warm to 22 °C by removing the cooling bath. The mixture was washed with a sat. soln. of NaCl (1 x 100 mL). The organic phase was dried over MgSO₄, filtered, and concentrated *in vacuo*. Fractionated distillation (1st fraction: 1-iodohexane, 35-40 °C, 5·10⁻² mbar; 2nd fraction: 1-bromo-4-hexylbenzene, 85-90 °C, 5·10⁻² ² mbar) gave the product as a colourless oil (11.7 g, 57%). IR (ATR): v 3024 (w), 2955 (w), 2925 (m), 2855 (w), 1892 (w), 1591 (w), 1488 (m), 1465 (w), 1403 (w), 1378 (w), 1201 (w), 1113 (w), 1072 (m), 1011 (m), 840 (w), 825 (w), 799 (m), 780 (w), 751 (w), 724 (w), 710 (w) cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ 7.39 (d, ³J_{HH} = 8.4 Hz, 2H, H-2), 7.05 (d, ³J_{HH} = 8.4 Hz, 2H, H-3), 2.56 (t, ³J_{HH} = 8.4 Hz, 2H, H-5), 1.62 -1.56 (m, 2H, H-6), 1.36 – 1.26 (m, 6H, H-7, 8, 9), 0.89 (t, ${}^{3}J_{HH}$ = 7.0 Hz, 3H, H-10) ppm; ${}^{13}C{}^{1}H$ NMR (151 MHz, CDCl₃): δ 142.0 (C-4), 131.4 (C-2), 130.3 (C-3), 119.4 (C-1), 35.5 (C-5), 31.8 (C-8), 31.4 (C-6), 29.0 (C-7), 22.7 (C-9), 14.2 (C-10) ppm; HR-MS (C₁₂H₁₇Br): calcd. 240.0508, found 240.05125 (R = 10,000); MS (EI, 70 eV, indirect inlet, 200 °C): *m/z* (% relative intensity) = 240 (2) [M]^{+,}, 169 (100) [M-C₅H₁₁]⁺.

The analytical data are in agreement with the literature.^{3d, 5}

1-Bromo-4-hexyloxybenzene (2)⁶



A mixture of 4-bromophenol (15.0 g, 86.7 mmol) in acetone (200 mL) and K₂CO₃ (24.0 g, 173 mmol) was stirred at 20 °C for 15 min. A solution of 1-bromohexane (15.7 g, 95.4 mmol) in acetone (50 mL) was added dropwise over the course of 5 min to the reaction. Then, the reaction mixture was heated to reflux temperature for 16 h. The mixture was filtered and the filtrate was concentrated in vacuo. The residue was dissolved in Et₂O (1 x 50 mL), washed with a sat. soln. of NaCl (1 x 50 mL) and H₂O (1 x 50 mL). The organic layer was dried over MgSO₄ and filtered. The crude product was filtered through a plug of silica (n-hexane, 10 x 5 cm). The excess of 1-bromohexane was removed by distillation (90-100 °C, 7 mbar). The product (20.6 g, 92%) was obtained as colourless oil without further purification. ¹H NMR (500 MHz, CDCl₃): δ 7.36 (d, ³J_{HH} = 9.0 Hz, 2H, H-2), 6.77 (d, ³J_{HH} = 9.0 Hz, 2H, H-3), 3.91 (t, ³J_{HH} = 6.6 Hz, 2H, H-6), 1.80 – 1.73 (m, 2H, H-7), 1.48 – 1.42 (m, 2H, H-8), 1.37 – 1.31 (m, 4H, H-9, 10), 0.91 (t, ³*J*_{HH} = 7.1 Hz, 3H, H-11) ppm; ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 158.4 (C-4), 132.3 (C-2), 116.5 (C-3), 112.7 (C-1), 68.4 (C-6), 31.7 (C-9), 29.3 (C-7), 25.8 (C-8), 22.7 (C-10), 14.2 (C-11) ppm; IR (ATR): v 2953 (w), 2928 (w), 2858 (w), 1591 (w), 1577 (w), 1488 (s), 1468 (m), 1389 (w), 1285 (m), 1240 (s), 1170 (m), 1114 (w), 1101 (w), 1072 (m), 1047 (w), 1027 (w), 1001 (m), 936 (w), 899 (w), 819 (s), 799 (w), 725 (w), 696 (w) cm⁻¹; HR-MS (C₁₂H₁₇BrO): calcd. 256.0457, found 256.04619 (R = 10,000); MS (EI, 70 eV, indirect inlet, 200 °C): m/z (% relative intensity) = 256 (19) [M]⁺, 172 (100) [M-C₆H₁₂]⁺.

The analytical data are in agreement with the literature.⁶

Tetrakis(p-hexylphenyl)stannane (5)^{3d, 7}



A solution of 1-bromo-4-hexylbenzene (4.00 g, 16.6 mmol) in THF (48 mL) was cooled to -78 °C. Then, t-BuLi (1.7 м in *n*-pentane, 19.5 mL, 33.2 mmol) was added dropwise over the course of 40 min and the reaction mixture was stirred at this temperature for 5 min. Tin(IV)chloride (440 µL, 3.74 mmol) was added slowly over the course of 2 min and the reaction was stirred at -78 °C for 40 min. The mixture was allowed to warm up to 20 °C by removing the cooling bath and stirred for an additional 16 h. Then, it was quenched with t-BuOH and the solvent was removed in vacuo. The residue was treated with nhexane (1 x 60 mL) and washed with H₂O (1 x 60 mL). The organic phase was dried over MgSO₄ and filtered. The solvent was removed in vacuo and the excess of 1-bromo-4-hexylbenzene was removed by distillation (85-90 °C, $5 \cdot 10^{-2}$ mbar). The product was obtained as a colourless oil (2.49 g, 87%). IR (ATR): v 3059 (w), 3029 (w), 3006 (w), 2954 (w), 2924 (m), 2854 (m), 1907 (w), 1804 (w), 1592 (w), 1554 (w), 1494 (w), 1456 (w), 1394 (w), 1377 (w), 1268 (w), 1188 (w), 1113 (w), 1072 (m), 1017 (w), 964 (w), 945 (w), 847 (w), 824 (w), 799 (m), 723 (w) cm⁻¹; ¹H NMR¹ (600 MHz, CDCl₃): δ 7.52 (d, ³J_{HH} = 7.9 Hz, ${}^{3}J_{SnH}$ = 55.6, 38.6 Hz, 8H, H-2), 7.21 (d, ${}^{3}J_{HH}$ = 7.9 Hz, ${}^{4}J_{SnH}$ = 20.4 Hz, 8H, H-3), 2.61 (t, ${}^{3}J_{HH}$ = 7.5 Hz, 8H, H-5), 1.63 (p, ³J_{HH} = 7.5 Hz, 8H, H-6), 1.43 – 1.18 (m, 24H, H-7, 8, 9), 0.91 (t, ³J_{HH} = 6.9 Hz, 12H, H-10) ppm; ${}^{13}C{}^{1}H$ NMR² (126 MHz, CDCl₃): δ 143.9 (${}^{4}J_{SnC}$ = 10.8 Hz, C-4), 137.3 (${}^{2}J_{SnC}$ = 38.4 Hz, C-2), 135.0 (¹*J*_{SnC} = 812.4, 773.4 Hz, C-1), 128.8 (³*J*_{SnC} = 54.0 Hz, C-3), 36.2 (C-5), 31.9 (C-8), 31.5 (C-6), 29.2 (C-7), 22.8 (C-9), 14.2 (C-10) ppm; ¹¹⁹Sn{¹H} NMR (187 MHz, CDCl₃): δ -125.9 ppm; HR-MS (C₄₈H₆₈¹²⁰Sn): calcd. 764.43430, found 764.42786 (R = 10,000); MS (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) =764 (2) [M]^{+,}, 442 (100) [M-C₂₄H₃₄]^{+,}.

¹ Coupling constants ⁿJ(¹¹⁹Sn, ¹H) are given in parentheses when signal to noise ratio allowed for determination.

² Coupling constants ⁿJ(¹¹⁹Sn, ¹³C) are given in parentheses when signal to noise ratio allowed for determination.

The analytical data are in agreement with the literature.^{3d, 7}





A solution of 1-bromo-4-hexyloxybenzene (4.00 g, 15.6 mmol) in dry THF (48 mL) was cooled to -78 °C. Then, 2 eq. of t-BuLi (1.7 M in n-pentane, 18.4mL, 31.2 mmol) was added dropwise over the course of 50 min and the reaction mixture was stirred at this temperature for 5 min. Tin(IV)chloride (410 μ L, 3.51 mmol) was slowly added over the course of 2 min and the reaction was stirred at -78 °C for 30 min. The reaction was warmed to 20 °C by removing the cooling bath and it was stirred for 16 h. Then, it was quenched with t-BuOH, n-hexane ($1 \times 80 \text{ mL}$) was added and it was washed with H₂O ($1 \times 100 \text{ mL}$). The organic phase was dried over Na₂SO₄ and filtered. The solvent was removed in vacuo and the excess of 1-bromo-4-hexyloxybenzene was removed by distillation (154-155 °C, 16 mbar). The product was obtained as a light yellow oil, which became a waxy solid at 0-5 °C (2.80 g, 96%). M.p.: 47 °C; ¹H NMR³ (500 MHz, CDCl₃): δ 7.49 (d, ³J_{HH} = 8.5 Hz, ³J_{SnH} = 54.1, 39.1 Hz, 8H, H-2), 6.94 (d, ³J_{HH} = 8.5 Hz, 8H, H-3), 3.97 (t, ³J_{HH} = 6.6 Hz, 8H, H-6), 1.84 – 1.74 (m, 8H, H-7), 1.50 – 1.43 (m, 8H, H-8), 1.39 – 1.31 (m, 16H, H-9, 10), 0.93 (t, ³J_{HH} = 7.1 Hz, 12H, H-11) ppm; ¹³C{¹H} NMR⁴ (126 MHz, CDCl₃): δ 160.1 (⁴J_{SnC} = 11.8 Hz, C-4), 138.4 (²J_{SnC} = 42.4 Hz, C-2), 128.8 (C-1), 115.1 (³J_{SnC} = 55.6 Hz, C-3), 67.9 (C-6), 31.7 (C-9), 29.4 (C-7), 25.9 (C-8), 22.8 (C-10), 14.2 (C-11) ppm; ¹¹⁹Sn{¹H} NMR (187 MHz, CDCl₃): δ -116.0 ppm; IR (ATR): v 3054 (w), 3015 (w), 2925 (m), 2858 (w), 2518 (w), 1896 (w), 1584 (s), 1561 (m), 1494 (s), 1466 (m), 1393 (w), 1311 (w), 1272 (m), 1240 (s), 1177 (s), 1122 (w), 1101 (w), 1073 (s), 1026 (m), 1005 (m), 936 (w), 850 (w), 811 (m), 726 (w) cm⁻¹; HR-MS (C₄₈H₆₈O₄¹¹⁶Sn): calcd. 824.41296, found 824.41249 (R

³ Coupling constants ⁿJ(¹¹⁹Sn, ¹H) are given in parentheses when signal to noise ratio allowed for determination.

⁴ Coupling constants ⁿJ(¹¹⁹Sn, ¹H) are given in parentheses when signal to noise ratio allowed for determination.

= 10,000); MS (EI, 70 eV, direct inlet, 200 °C): m/z (% relative intensity) =828 (4) [M]⁺, 354 (100) $[C_{24}H_{34}O_2]^+$.

Tetrakis[4-(trifluoromethyl)phenyl]stannane (7)⁸



A solution of 1-bromo-4-(trifluoromethyl)benzene (5.00 g, 22.2 mmol) in dry THF (70 mL) was cooled to -78 C and stirred at this temperature. Then, n-BuLi (2.5 M in hexanes, 9.1 mL, 22.6 mmol) was added dropwise over the course of 30 min. The solution was stirred at -78 °C for 2.5 h. To the yellow reaction mixture, tin(IV)chloride (580 µL, 4.99 mmol) was added slowly over a period of 3 min. The reaction was stirred at -78 °C for 1 h and at 20 °C (by removing the cooling bath) for 16 h. Then, it was quenched with t-BuOH. The solution was washed with H_2O (1 x 100 mL). The organic phase was separated, dried over Na₂SO₄ and filtered. The volatiles were removed *in vacuo* to obtain a yellow-white powder. The crude compound was further purified by sublimation (130 °C, 5·10⁻³ mbar) to furnish a colourless solid (2.34 g, 67%). M.p.: 149 °C; ¹H NMR⁵ (500 MHz, CD₂Cl₂): δ 7.72 (d, 16H, H-2, 3) ppm; ¹³C{¹H} NMR⁶ (126 MHz, CD₂Cl₂): δ 141.5 (s, C-1), 137.8 (s, ²J_{CSn} = 39.2 Hz, C-2), 132.2 (q, ²J_{CF} = 32.4 Hz, C-4), 125.8 (q, ³*J*_{CF} = 3.8 Hz, C-3), 124.5 (q, ¹*J*_{CF} = 272.3 Hz, C-5) ppm; ¹¹⁹Sn{¹H} NMR (187 MHz, CD₂Cl₂): δ -132.7 ppm; ¹⁹F NMR (471 MHz, CD₂Cl₂): δ -63.43 ppm; IR (ATR): ν 3033 (w), 1928 (w), 1820 (w), 1675 (w), 1603 (w), 1391 (m), 1317 (s), 1270 (m), 1238 (w), 1174 (s), 1116 (s), 1099 (s), 1082 (s), 1046 (s), 1014 (s), 958 (m), 851 (w), 823 (s), 772 (w), 725 (w), 680 (s) cm⁻¹; HR-MS (EI, C₂₈H₁₆F₁₁¹¹⁶Sn): calcd. 677.00938, found 677.01135 (R = 10,000); MS (EI, 70 eV, direct inlet, 200 °C): m/z (% relative intensity) = 681 (6) [M-F]⁺, 555 (100) [M-C₇H₄F₃]⁺.

The analytical data are in agreement with the literature.⁸

⁵ Coupling constants ⁿJ(¹¹⁹Sn, ¹H) are given in parentheses when signal to noise ratio allowed for determination.

⁶ Coupling constants ⁿJ(¹¹⁹Sn, ¹H) are given in parentheses when signal to noise ratio allowed for determination.

Tetrakis[3,5-bis(trifluoromethyl)phenyl]stannane (8)⁸



A solution of 3,5-bis(trifluoromethyl)bromobenzene (5.00 g, 17.1 mmol) in dry Et₂O (75 mL) was cooled to -78 °C and stirred at this temperature. Then, n-BuLi (2.50 M in hexanes, 7.5 mL, 18.8 mmol) was added dropwise over the course of 15 min. The solution was stirred at -78 °C for 3 h. To the yellow reaction mixture, tin(IV)chloride (450 µL, 3.85 mmol) was added slowly over the course of 3 min, resulting in the formation of a white precipitate. The reaction was stirred at -78 °C for 30 min and at 20 °C (by removing the cooling bath) for 16 h. It was quenched with t-BuOH and washed with H₂O (1 x 100 mL) to remove the salts. The organic phase was separated, dried over Na₂SO₄ and filtered. The solvent was removed in vacuo. The crude compound was purified by sublimation (135 $^{\circ}$ C, 5 \cdot 10⁻³ mbar) to give a colourless solid compound (2.63 g, 70%). M.p.: 158 °C; ¹H NMR⁷ (500 MHz, CDCl₃): δ 8.07 (s, 4H, H-4), 7.95 (s, ³J_{SnH} = 49.3 Hz, 8H, H-2) ppm; ¹³C{¹H} NMR⁸ (126 MHz, CDCl₃): δ 136.5 (s, C-1, 2), 133.0 (q, ${}^{2}J_{CF}$ = 33.7 Hz, C-3), 125.2 (q, ${}^{3}J_{CF}$ = 3.7 Hz, C-4), 123.1 (q, ${}^{1}J_{CF}$ = 273.5 Hz, C-5) ppm; 119 Sn{ ${}^{1}H$ } NMR (187 MHz, CDCl₃): δ -127.0 ppm; ¹⁹F NMR (471 MHz, CDCl₃): δ -63.12 ppm; IR (ATR): ν 3084 (w), 1824 (w), 1617 (w), 1593 (w), 1350 (s), 1273 (s), 1177 (m), 1119 (s), 1103 (s), 1085 (s), 1000 (w), 919 (m), 891 (s), 840 (m), 785 (w), 706 (m), 698 (m), 680 (s) cm⁻¹; HR-MS ([M-F]⁺, C₃₂H₁₂F₂₃¹¹⁶Sn): calcd. 948.95837, found 948.95502 (R = 10,000); MS (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) $= 953 (13) [M-F]^+, 759 (100) [M-C_8H_3F_6]^+.$

The analytical data are in agreement with the literature .⁸

⁷ Coupling constants ⁿJ(¹¹⁹Sn, ¹H) are given in parentheses when signal to noise ratio allowed for determination.

⁸ Coupling constants ⁿJ(¹¹⁹Sn, ¹H) are given in parentheses when signal to noise ratio allowed for determination.

Di-(p-hexylphenyl)-dichlorostannane (9)^{3d, 7}



Tetrakis-(*p*-hexylphenyl)stannane (930 mg, 1.22 mmol) was added to a J. Young's flask under a N₂ atmosphere. Then, tin(IV)chloride (140 μ L, 1.22 mmol) was added. The flask was frozen with liquid N₂ and placed under static vacuum (9·10⁻³ mbar). The reaction mixture was heated at 180 °C for 10 h. A brown suspension was obtained. In a GB, the reaction mixture was dissolved in anhydrous, degassed *n*-pentane (5 mL), filtered through a PTFE syringe filter (0.45 μ m pore size), and dried *in vacuo*. The product was obtained as a brown oil (1.04 g, 83%). ¹H NMR⁹ (600 MHz, CD₂Cl₂): δ 7.62 (d, ³*J*_{HH} = 8.1 Hz, ³*J*_{SnH} = 87.8, 72.0 Hz, 4H, H-2), 7.39 (d, ³*J*_{HH} = 8.1 Hz, ⁴*J*_{SnH} = 36.0, 20.6 Hz 4H, H-3), 2.67 (t, ³*J*_{HH} = 7.5 Hz, 4H, H-5), 1.68 – 1.55 (m, 4H, H-6), 1.40 – 1.25 (m, 12H, H-7, 8, 9), 0.89 (t, ³*J*_{HH} = 7.1 Hz, 6H, H-10) ppm; ¹³C{¹H} NMR¹⁰ (126 MHz, CD₂Cl₂): δ 147.9 (⁴*J*_{SnC} = 16.8 Hz, C-4), 135.3 (²*J*_{SnC} = 67.4, 64.6 Hz, C-2), 134.2 (¹*J*_{SnC} = 797.6, 760.8 Hz, C-1), 130.2 (³*J*_{SnC} = 89.0, 85.2 Hz, C-3), 36.4 (C-5), 31.7 (C-8), 29.3 (C-6), 29.3 (C-7), 23.0 (C-9), 14.3 (C-10) ppm; ¹¹⁹Sn{¹H} NMR (187 MHz, CD₂Cl₂): δ -23.6 ppm.¹¹

The analytical data are in agreement with the literature.^{3d, 7}

Di-(p-hexyloxyphenyl)-dichlorostannane (6)



⁹ Coupling constants ⁿ/(¹¹⁹Sn, ¹H) are given in parentheses when signal to noise ratio allowed for determination.

¹⁰ Coupling constants ⁿJ(¹¹⁹Sn, ¹³C) are given in parentheses when signal to noise ratio allowed for determination.

¹¹ IR data could not be obtained due to the moisture sensitivity of the compound.

Tetrakis-(*p*-hexyloxyphenyl)stannane (1.50 g, 1.81 mmol) was added to a J. Young's flask under a N₂ atmosphere. Tin(IV)chloride (0.21 mL, 1.81 mmol) was added to the flask. Then, the flask was frozen with liquid nitrogen and placed under a static vacuum (9·10⁻³ mbar). The reaction mixture was heated at 230 °C for 10 h and a black-brown melt was obtained. In a GB, the oil was dissolved in anhydrous, degassed *n*-pentane (5 mL), filtered through a PTFE syringe filter (0.45 μ m pore size), and stored for 96 h at -30 °C. A colourless precipitate was obtained in a yield of (1.75 g, 89%). ¹H NMR¹² (600 MHz, CD₂Cl₂): δ 7.62 (d, ³J_{HH} = 8.8 Hz, 4H, H-2), 7.07 (d, ³J_{HH} = 8.8 Hz, 4H, H-3), 4.01 (t, ³J_{HH} = 6.6 Hz, 4H, H-6), 1.83 – 1.75 (m, 4H, H-7), 1.51 – 1.43 (m, 4H, H-8), 1.39 – 1.31 (m, 8H, H-9, 10), 0.91 (t, ³J_{HH} = 7.1 Hz, 6H, H-11) ppm; ¹³C{¹H} NMR¹³ (151 MHz, CD₂Cl₂): δ 162.5 (C-4), 136.8 (²J_{SnC} = 77.8 Hz, C-2), 127.7 (C-1), 116.3 (³J_{SnC} = 97.6 Hz, C-3), 68.6 (C-6), 32.0 (C-9), 29.5 (C-7), 26.0 (C-8), 23.0 (C-10), 14.2 (C-11) ppm; ¹³Sn{¹H} NMR (187 MHz, CD₂Cl₂): δ -16.4 ppm.¹⁴

Di-[4-(trifluoromethyl)phenyl]dichlorostannane (10)⁸



Tetrakis[4-(trifluoromethyl)phenyl]stannane (500 mg, 720 μmol) and tin(IV)chloride (80.0 μL,720 μmol) were added to a J. Young's flask under a N₂ atmosphere. The flask was frozen with liquid nitrogen and placed under a static vacuum ($1.0 \cdot 10^{-2}$ mbar). The reaction mixture was heated at 180 °C for 48 h and a black melt was obtained. In a GB, the brown-black solid was dissolved in anhydrous, degassed DCM (1 mL) and filtered through a PTFE syringe filter (0.45μ m pore size). The solvent was removed *in vacuo*. The crude compound was further purified by sublimation ($65 \circ C, 5.0 \cdot 10^{-3}$ mbar) to produce a colourless solid compound (0.45 g, 66%). ¹H NMR¹⁵ ($500 \text{ MHz}, \text{CD}_2\text{Cl}_2$): $\delta 7.86$ (dd, ³*J*_{HH} = 8.2 Hz, 8H, H-2, 3) ppm; ¹³C{¹H} NMR¹⁶ ($126 \text{ MHz}, \text{CD}_2\text{Cl}_2$): $\delta 141.28$ (m, C-1), 136.0 (m, ²*J*_{SnC} = 68.6, 65.2 Hz, C-2), 134.1 (q, ²*J*_{CF} = 32.7 Hz, C-4), 126.6 (q, ³*J*_{CF} = 4.0 Hz, C-3), 123.9 (q, *J*_{CF} = 272.9 Hz, C-5) ppm; ¹¹⁹Sn{¹H} NMR ($187 \text{ MHz}, \text{CD}_2\text{Cl}_2$): $\delta -35.7 \text{ ppm}$; ¹⁹F NMR ($471 \text{ MHz}, \text{CD}_2\text{Cl}_2$): $\delta -65.09$ (s, ⁶*J*_{FSn} = 3.0 Hz) ppm.¹⁷

¹² Coupling constants ⁿJ(¹¹⁹Sn, ¹H) are given in parentheses when signal to noise ratio allowed for determination.

¹³ Coupling constants ⁿJ(¹¹⁹Sn, ¹H) are given in parentheses when signal to noise ratio allowed for determination.

¹⁴ IR data could not be obtained due to the moisture sensitivity of the compound.

¹⁵ Coupling constants ⁿ*J*(¹¹⁹Sn, ¹H) are given in parentheses when signal to noise ratio allowed for determination.

¹⁶ Coupling constants ⁿ/(¹¹⁹Sn, ¹H) are given in parentheses when signal to noise ratio allowed for determination.

¹⁷ IR data could not be obtained due to the moisture sensitivity of the compound.

The analytical data are in agreement with the literature.⁸

Di-[3,5-bis(trifluoromethyl)phenyl]dichlorostannane (11)⁸



Tetrakis[3,5-bis(trifluoromethyl)phenyl]stannane (1.00 g, 2.03 mmol) was added to a J. Young's flask under a N₂ atmosphere. Then, tin(IV)chloride (120 μ L, 1.03 mmol) was added. The flask was frozen with liquid nitrogen and placed under a static vacuum (3·10⁻² mbar). The reaction mixture was heated at 180 °C for 48 h. A black melt was obtained. In a GB, the brown-black solid was dissolved in anhydrous, degassed DCM (5 mL) and filtered through a PTFE syringe filter (0.45 μ m pore size). Then, it was dried *in vacuo* to obtain brown crystals. The crude compound was further purified by sublimation (80 °C, 4-5 10⁻³ mbar) to furnish a colourless solid compound. The NMR spectra showed that a mixture of di-[3,5-bis(trifluoromethyl)phenyl]dichlorostannane and tri-[3,5-bis(trifluoromethyl)phenyl]chlorostannane was obtained. The product still was used for further stannole syntheses taking into consideration of lower yields in the next step. (884 mg, 70%, purity ca. 75%). ¹H NMR (500 MHz, CD₂Cl₂): δ 8.21 (s, 2H, H-4), 8.12 (s, 4H, H-2,2') ppm; ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 138.9 (s, C-1), 135.5 (m, C-2), 133.0 (q, ²_{JC+F} = 33.7 Hz, C-3), 126.6 (m, C-4), 124.5 (q, ¹_{JC+F} = 273.3 Hz, C-5) ppm; ¹¹⁹Sn{¹H} NMR (187 MHz, CD₂Cl₂): δ -43.3 ppm; ¹⁹F NMR (471 MHz, CD₂Cl₂): δ -64.55 ppm.¹⁸

The analytical data are in agreement with the literature .⁸

2,2-Bis(4-hexylphenyl)-1,3-bis(5-iodothiophen-2-yl)-4,5,6,7-tetrahydro-2*H*-benzo[*c*]stannole (St1)



¹⁸ IR data could not be obtained due to the moisture sensitivity of the compound.

In a GB, 1,8-bis(5-iodothiophen-2-yl)octa-1,7-diyne (150 mg, 290 µmol) and Rosenthal's zirconocene (137 mg, 290 µmol) were dissolved in anhydrous, degassed toluene (6 mL). The dark red solution was stirred at 22 °C for 1 h under a N₂-atmosphere. Then, di-(p-hexylphenyl)-dichlorostannane (149 mg, 290 µmol) and Cu(I)Cl (2.9 mg, 29 µmol) in toluene (2 mL) were added. The reaction mixture was stirred at 22 °C for further 6 h and turned to light orange over this time. It was quenched with H₂O $(1 \times 50 \text{ mL})$ and extracted with Et₂O $(3 \times 50 \text{ mL})$. The combined organic layers were dried over MgSO₄, filtered, and concentrated in vacuo. Purification by column chromatography (silica gel, 3% TEA, npentane, R_f = 0.51) gave an orange-yellow oil, which solidified at -10 °C (180 mg, 64%). M.p.: 115 °C; $\lambda_{abs,max}$ (CHCl₃, ϵ = 22,600 L·mol⁻¹·cm⁻¹) = 434 nm; $\lambda_{em,max}$ (CHCl₃) = 522 nm; ¹H NMR¹⁹ (600 MHz, CDCl₃): δ 7.49 (d, ${}^{3}J_{SnH}$ = 51.4, 36.6 Hz, ${}^{3}J_{HH}$ = 7.4 Hz, 4H, H-2′), 7.19 (d, ${}^{4}J_{SnH}$ = 14.6 Hz, ${}^{3}J_{HH}$ = 14.8 Hz, 4H, H-3′), 7.07 (d, ³J_{HH} = 3.8 Hz, 2H, H-8), 6.61 (d, ³J_{HH} = 3.8 Hz, 2H, H-7), 2.82 – 2.76 (m, 4H, H-4), 2.58 (t, ³J_{HH} = 7.9 Hz, 4H, H-5'), 1.82 – 1.77 (m, 4H, H-5), 1.63 – 1.55 (m, 4H, H-6'), 1.37 – 1.27 (m, 12H, H-7', 8', 9'), 0.87 (t, ³J_{HH} = 6.9 Hz, 6H, H-10') ppm; ¹³C{¹H} NMR²⁰ (151 MHz, CDCl₃): δ 151.4 (²J_{SnC} = 73.6 Hz, C-6), 150.1 (²J_{snc} = 74.2 Hz, C-3), 144.7 (⁴J_{snc} = 12.6 Hz, C-4'), 137.1 (²J_{snc} = 43.4 Hz, C-2'), 136.7 (C-8), 133.9 (¹*J*_{SnC} = 534.4, 510.0 Hz, C-1′), 130.8 (C-2), 130.7 (³*J*_{SnC} = 23.6 Hz, C-7), 129.3 (³*J*_{SnC} = 56.2 Hz, C-3′), 74.4 (C-9), 36.2 (C-5'), 32.1 (C-4), 31.9 (C-8'), 31.5 (C-6'), 29.2 (C-7'), 23.3 (C-5), 22.7 (C-9'), 14.3 (C-10') ppm; ¹¹⁹Sn{¹H} NMR (224 MHz, C₆D₆): δ -74.9 ppm; IR (ATR): ν 3051 (w), 2954 (w), 2921 (m), 2848 (w), 1591 (w), 1547 (w), 1492 (w), 1455 (w), 1394 (w), 1376 (w), 1329 (w), 1248 (w), 1231 (w), 1209 (w), 1200 (w), 1187 (m), 1071 (m), 1059 (m), 1015 (m), 965 (w), 944 (w), 924 (w), 901 (w), 864 (w), 796 (m), 772 (m), 720 (m), 655 (w) cm⁻¹; HR-MS (APCI, DCM/MeOH 1:10, [C₄₀H₄₆I₂S₂Sn+H]⁺): calcd. 965.02251, found 965.02283.

¹⁹ Coupling constants ⁿJ(¹¹⁹Sn, ¹H) are given in parentheses when signal to noise ratio allowed for determination.

²⁰ Coupling constants ⁿ*J*(¹¹⁹Sn, ¹H) are given in parentheses when signal to noise ratio allowed for determination.

1,3-Bis(5-iodothiophen-2-yl)-2,2-bis(4-(hexyloxy)phenyl)-4,5,6,7-tetrahydro-2*H*-benzo[*c*]stannole (St2)



In a GB, 1,8-bis(5-iodothiophen-2-yl)octa-1,7-diyne (150 mg, 290 µmol) and Rosenthal's zirconocene (137 mg, 290 µmol) were dissolved in anhydrous, degassed toluene (6 mL). The dark red solution was stirred at 22 °C for 1 h under a N₂-atmosphere. Then, di-(p-hexyloxyphenyl)-dichlorostannane (158 mg, 290 µmol) and Cu(I)Cl (2.9 mg, 29 µmol) in toluene (2 mL) were added to the dark solution. The reaction mixture was stirred at 22 °C for 6 h and turned to light orange over this time. It was quenched with H_2O (1 x 50 mL) and extracted with Et_2O (3 x 50 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by column chromatography (silica gel, 3% TEA, *n*-pentane, $R_f = 0.51$) furnished an orange-yellow oil, which crystallised at -10 °C (196 mg, 68%). Yellow single crystals could be obtained from a sat. soln. of DCM/*n*-hexane. M.p.: 108 °C; $\lambda_{abs,max}$ (CHCl₃, ϵ = 22,400 L·mol⁻¹·cm⁻¹) = 434 nm; $\lambda_{em,max}$ (CHCl₃) = 523 nm; ¹H NMR²¹ (600 MHz, CDCl₃): δ 7.47 (d, ³J_{SnH} = 49.0, 34.2 Hz, ${}^{3}J_{HH}$ = 8.4 Hz, 4H, H-2'), 7.06 (d, ${}^{3}J_{HH}$ = 3.8 Hz, 2H, H-8), 6.92 (d, ${}^{4}J_{SnH}$ = 10.4 Hz, ${}^{3}J_{HH}$ = 8.4 Hz, 4H, H-3[′]), 6.59 (d, ³J_{HH} = 3.8 Hz, 2H, H-7), 3.94 (t, ³J_{HH} = 7.9 Hz, 4H, H-6[′]), 2.82 – 2.75 (m, 4H, H-4), 1.83 – 1.78 (m, 4H, H-5), 1.78 – 1.73 (m, 4H, H-7'), 1.47 – 1.41 (m, 4H, H-8'), 1.36 – 1.30 (m, 8H, H-9', 10'), 0.90 (t, ${}^{3}J_{HH}$ = 6.8 Hz, 6H, H-11') ppm; ${}^{13}C{}^{1}H$ NMR²² (151 MHz, CDCl₃): δ 160.6 (${}^{4}J_{SnC}$ = 13.6 Hz, C-4'), 151.5 (²J_{SnC} = 70.2 Hz, C-6), 150.0 (²J_{SnC} = 76.8 Hz, C-3), 138.4 (²J_{SnC} = 47.8 Hz, C-2'), 136.7 (C-8), 130.8 (C-2), 130.5 (³J_{SnC} = 23.8 Hz, C-7), 127.4 (C-1'), 115.6 (³J_{SnC} = 58.6 Hz, C-3'), 74.3 (C-9), 67.9 (C-6'), 32.1 (C-4), 31.7 (C-9'), 29.3 (C-7'), 25.9 (C-8'), 23.3 (C-5), 22.8 (C-10'), 14.2 (C-11') ppm; ¹¹⁹Sn{¹H} NMR (224 MHz, C_6D_6): δ = -70.2ppm; IR (ATR): ν = 3051 (w), 2946 (w), 2926 (w), 2852 (m), 1584 (m), 1564 (w), 1496 (m), 1473 (m), 1464 (m), 1421 (w), 1398 (w), 1376 (w), 1327 (w), 1316 (w), 1276 (m), 1243 (s), 1203 (m), 1179 (m), 1151 (w), 1131 (w), 1074 (m), 1057 (w), 1028 (m), 942 (w), 919 (w), 889 (w),

²¹ Coupling constants ⁿJ(¹¹⁹Sn, ¹H) are given in parentheses when signal to noise ratio allowed for determination.

²² Coupling constants ⁿJ(¹¹⁹Sn, ¹H) are given in parentheses when signal to noise ratio allowed for determination.

816 (m), 790 (m), 777 (m), 729 (w), 704 (w), 693 (w), 684 (w) cm⁻¹; HR-MS (APCI, DCM/MeOH 1:10, [C₄₀H₄₆I₂O₂S₂Sn+H]⁺): calcd. 997.01234, found 997.01165.





In a GB, 1,8-bis(4-hexyl-5-iodothiophen-2-yl)octa-1,7-diyne (150 mg, 217 µmol) and Rosenthal's zirconocene (102 mg, 217 µmol) were dissolved in anhydrous, degassed toluene (6 mL) and the dark red solution was stirred at 22 °C for 1 h under a N₂-atmosphere. In a GB, di-[4-(trifluoromethyl)phenyl]dichlorostannane (104 mg, 217 µmol) and Cu(l)Cl (2.1 mg, 21.7 µmol) in anhydrous, degassed THF (1 mL) were added to the dark solution. The reaction mixture was stirred at 22 °C for 6 h and turned to light orange. It was quenched with H_2O (1 x 50 mL) and extracted with Et_2O (3 x 50 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by column chromatography (silica gel, 3% TEA, *n*-pentane, $R_f = 0.42$) afforded a yelloworange solid (180 mg, 75%). Orange single crystals could be obtained from a sat. soln. of DCM/nhexane. M.p.: 149 °C; $\lambda_{abs,max}$ (CHCl₃, ϵ = 24,500 L·mol⁻¹·cm⁻¹) = 443 nm; $\lambda_{em,max}$ (CHCl₃) = 534 nm; ¹H NMR²³ (600 MHz, CDCl₃): δ 7.72 (d, ³J_{SnH} = 49.0, 34.2 Hz, ³J_{HH} = 7.5 Hz, 4H, H-2'), 7.64 (d, ⁴J_{SnH} = 11.0 Hz, ³J_{HH} = 7.5 Hz, 4H, H-3′), 6.52 (s, 2H, H-7), 2.86 – 2.74 (m, 4H, H-4), 2.43 (t, ³J_{HH} = 7.4 Hz, 4H, H-10), 1.84 - 1.77 (m, 4H, H-5), 1.42 (p, ³J_{HH} = 7.4 Hz, 4H, H-11), 1.26 - 1.16 (m, 12H, H-12, 13, 14), 0.84 (t, ³J_{HH} = 6.3 Hz, 6H, H-15) ppm; ¹³C{¹H} NMR²⁴ (151 MHz, CDCl₃): δ 150.7 (C-3), 149.3 (C-6), 147.1 (C-8), 142.4 (C-1'), 137.4 (² J_{SnC} = 44.0 Hz, C-2'), 132.0 (q, ² J_{CF} = 32.7 Hz, C-4'), 129.8 (³ J_{SnC} = 25.2 Hz, C-7), 128.9 (C-2), 125.6 (q, ²J_{CF} = 3.7 Hz, C-3'), 124.1 (q, ¹J_{CF} = 272.5 Hz, CF₃), 76.6 (C-9), 32.2 (C-10), 32.0 (C-4), 31.8 (C-13), 29.9 (C-11), 28.8 (C-12), 23.2 (C-5), 22.6 (C-14), 14.1 (C-15) ppm; ¹¹⁹Sn{¹H} NMR (224 MHz, CDCl₃): δ -83.2 ppm; ¹⁹F NMR (565 MHz, CDCl₃): δ -63.13 ppm; IR (ATR): ν = 3051 (w), 2927 (w), 2856 (w), 1600 (w), 1518 (w), 1456 (w), 1390 (w), 1359 (w), 1318 (m), 1270 (w), 1227 (w), 1200 (w), 1154 (m), 1120

²³ Coupling constants ⁿJ(¹¹⁹Sn, ¹H) are given in parentheses when signal to noise ratio allowed for determination.

²⁴ Coupling constants ⁿJ(¹¹⁹Sn, ¹H) are given in parentheses when signal to noise ratio allowed for determination.

(m), 1099 (m), 1081 (m), 1049 (m), 1013 (m), 955 (w), 910 (m), 831 (m), 822 (m), 807 (m), 722 (w), 679 (m) cm⁻¹; HR-MS (APCI, DCM/MeOH 1:10, [C₄₂H₄₄F₆I₂S₂Sn+H]⁺): calcd. 1100.99728, found 1100.99761.





In a GB, 1,8-bis(4-hexyl-5-iodothiophen-2-yl)octa-1,7-diyne (150 mg, 217 µmol) and Rosenthal's zirconocene (102 mg, 217 µmol) were dissolved in anhydrous, degassed toluene (6 mL) and the dark red solution was stirred at 22 °C for 1 h under a N₂-atmosphere. In a GB, di-[3,5bis(trifluoromethyl)phenyl]dichlorostannane (134 mg, 217 μmol) and Cu(l)Cl (2.1 mg, 21.7 μmol) in anhydrous, degassed THF (1 mL) were added to the dark solution. The reaction mixture was stirred at 22 °C for 6 h and turned to light orange. It was quenched with H_2O (1 x 50 mL) and extracted with Et_2O (3 x 50 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by column chromatography (silica gel, 3% TEA, *n*-pentane, $R_f = 0.42$) furnished an orange solid (85 mg, 32%²⁵). M.p.: 196 °C; $\lambda_{abs,max}$ (CHCl₃, ϵ = 17,300 L·mol⁻¹·cm⁻¹) = 446 nm; $\lambda_{em,max}$ (CHCl₃) = 543 nm; ¹H NMR²⁶ (600 MHz, CDCl₃): δ 7.97 (s, 4H, H-2'), 7.95 (s, 2H, H-4'), 6.48 (s, 2H, H-7), 2.86 – 2.81 (m, 4H, H-4), 2.42 (t, ³/_{HH} = 7.5 Hz, 4H, H-10), 1.85 – 1.80 (m, 4H, H-5), 1.46 – 1.38 (m, 4H, H-11), 1.25 – 1.17 (m, 12H, H-12, 13, 14), 0.83 (t, ${}^{3}J_{HH}$ = 7.1 Hz, 6H, H-15) ppm; ${}^{13}C{}^{1}H$ NMR²⁷ (151 MHz, CDCl₃): δ 151.3 (C-3), 148.8 (C-6), 147.4 (C-8), 139.9 (C-1'), 136.6 (C-2'), 132.2 (q, ²J_{CF} = 33.1 Hz, C-3'), 129.5 (C-7), 127.2 (C-2), 124.2 (C-4'), 123.3 (q, ¹J_{CF} = 271.4 Hz, CF₃), 76.9 (C-9), 32.2 (C-10), 32.0 (C-4), 31.5 (C-13), 30.0 (C-11), 28.9 (C-12), 23.0 (C-5), 22.6 (C-14), 14.1 (C-15) ppm; ¹¹⁹Sn{¹H} NMR (224 MHz, C₆D₆): δ -82.7 ppm; ¹⁹F NMR (565 MHz, CDCl₃): δ -62.92 ppm; IR (ATR): ν = 3051 (w), 2928 (w), 2858 (w), 1615 (w), 1458 (w), 1349 (m), 1273 (s), 1182 (m), 1133 (s), 1121 (s), 1102 (s), 1087 (s), 915 (w), 891 (m), 840

²⁵ The yield is low due to impure di-[3,5-bis(trifluoromethyl)phenyl]dichlorostannane, which is mixed with tri-[3,5-(trifluoromethyl)phenyl]chlorostannane

²⁶ Coupling constants ⁿJ(¹¹⁹Sn, ¹H) are given in parentheses when signal to noise ratio allowed for determination.

²⁷ Coupling constants ⁿ*J*(¹¹⁹Sn, ¹H) are given in parentheses when signal to noise ratio allowed for determination.

(w), 806 (w), 756 (w), 707 (m), 696 (w), 679 (s) cm⁻¹; HR-MS (APCI, toluene, [C₄₄H₄₂F₁₂I₂S₂Sn+H]⁺): calcd. 1236.97205, found 1236.97202.

Table 3. Test reactions for the formation of polymers with different catalysts (1.3 µmol) and solvents (1.5 mL) under reflux for 3 days. The reaction conditions 1-12 were tested for monomer St2 and the reaction conditions 5, 6, 8, 9 were tested for monomer St3. The resulting polymers were analysed by UV-Vis and GPC measurements. The reaction condition of 9 led to the highest molecular weight and most red-shifted absorption maximum for TStTT2 and the reaction condition of 6 led to the highest molecular weight and most red-shifted absorption maximum for TStTT3.

Reaction	Catalyst	Solvent	Visible colour of	Visible colour of	
number			the product TStTT2	the product TStTT3	
1	[PdCl ₂ (PPh ₃) ₂]	THF	dark red		
2	[PdCl ₂ (PPh ₃) ₂]	Toluene	violet-red		
3	$[PdCl_2(PPh_3)_2]$	Toluene/DMF (2+1)	red-violet		
4	[Pd(PPh ₃) ₄]	THF	orange		
5	[Pd(PPh ₃) ₄]	Toluene	dark wine-red	purple-black	
6	[Pd(PPh ₃) ₄]	Toluene/DMF (2+1)	purple black	purple-black	
7	[Pd(t-Bu ₃ P) ₂]	THF	dark wine-red		
8	$[Pd(t-Bu_3P)_2]$	Toluene	purple black	dark reddish-purple	
9	[Pd(t-Bu ₃ P) ₂]	Toluene/DMF (2+1)	bluish-purple black	dark reddish-purple	
10	[Pd(dba) ₂]	THF	dark orange-red		
11	[Pd(dba) ₂]	Toluene	orange-red		
12	[Pd(dba) ₂]	Toluene/DMF (2+1)	wine-red		

Synthesis of Polymer TStTT1



In a pressure tube, a solution of stannole **St1** (100 mg, 104 μ mol), 2,5-bis(trimethylstannyl)thiophene (43 mg, 104 μ mol) and [Pd(*t*-Bu₃P)₂] (2.5 mg, 5 μ mol) in a mixture of toluene (4 mL) and DMF (2 mL) was heated to reflux for 3 d under N₂-atmosphere. Over this time, the colour changed from orange to dark blue-black. The solution was precipitated into MeOH (300 mL). The polymer was collected by

centrifugation, washed with MeOH (300 mL) and dried *in vacuo* to furnish a bluish-black solid of **TStTT1** (80 mg, 97%). $\lambda_{abs,max}$ (CHCl₃, ε = 35,600 L·mol⁻¹·cm⁻¹) = 556 nm; $\lambda_{abs,max}$ (thin film) = 556 nm; $\lambda_{em,max}$ (CHCl₃) = 717 nm; ¹H NMR (600 MHz, CDCl₃): δ 7.62 – 7.52 (br m, 4H, H-2′), 7.25 – 7.16 (br m, 4H, H-3′), 7.08 – 6.98 (br m, 4H, Tph), 6.87 (br s, 2H, Tph), 2.98 – 2.80 (br m, 4H, H-4), 2.64 – 2.53 (br m, 4H, H-5′), 1.88 – 1.75 (br m, 4H, H-5), 1.63 – 1.56 (br m, 4H, H-6′), 1.37 – 1.25 (br m, 12H, H-7′, 8′, 9′), 0.86 (br t, ³*J*_{HH} = 6.5 Hz, H-10′) ppm; ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 152.8 (C-3), 144.6 (C-4′), 139.6 (Tph), 137.4 (Tph), 137.3 (C-2′), 134.5 (C-1′), 133.7 (Tph), 131.0 (C-2), 129.3 (C-3′), 129.2 (Tph), 124.0 (Tph), 36.2 (C-5′), 31.9 (C-4), 31.5 (C-8′), 29.9 (C-6′), 29.2 (C-7′), 23.3 (C-5), 22.7 (C-9′), 14.2 (C-10′) ppm; ¹¹⁹Sn{¹H} NMR (224 MHz, CDCl₃): δ -76.4 ppm; IR (ATR): ν = 3051 (w), 2921 (w), 2851 (w), 1591 (w), 1557 (w), 1484 (w), 1454 (w), 1393 (w), 1375 (m), 1249 (w), 1186 (w), 1131 (w), 1068 (w), 1015 (w), 925 (w), 823 (w), 771 (m), 722 (w), 688 (w) cm⁻¹; M_n (GPC) = 4,900 Da; M_w (GPC) = 11,200 Da; PDI = 2.3.

Synthesis of Polymer TStTT2



In a pressure tube, a solution of stannole **St2** (100 mg, 100 µmol), 2,5-bis(trimethylstannyl)thiophene (41 mg, 100 µmol) and [Pd(*t*-Bu₃P)₂] (2.5 mg, 5 µmol) in a mixture of toluene (4 mL) and DMF (2 mL) was heated to reflux for 3 d under N₂-atmosphere. Over this time, the colour changed from orange to dark blue-black. The solution was precipitated into MeOH (300 mL). The polymer was collected by centrifugation, washed with MeOH (300 mL) and dried *in vacuo* to obtain a bluish-black solid of **TStTT2** (79 mg, 96%). $\lambda_{abs,max}$ (CHCl₃, $\varepsilon = 28,600 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) = 560 nm; $\lambda_{abs,max}$ (thin film) = 595 nm; $\lambda_{em,max}$ (CHCl₃) = 716 nm; ¹H NMR (600 MHz, CDCl₃): δ 7.60 – 7.47 (br m, 4H, H-2'), 7.05 – 6.98 (br m, 4H, Tph), 6.96 – 6.90 (br m, 4H, H-3'), 6.89 – 6.81 (br m, 2H, Tph), 4.01 – 3.86 (br m, 4H, H-6'), 3.00 – 2.80 (br m, 4H, H-4), 1.91 – 1.79 (br m, 4H, H-5), 1.80 – 1.69 (br m, 4H, H-7'), 1.48 – 1.36 (br m, 4H, H-8'), 1.35 – 1.23 (br m, 8H, H-9', 10'), 0.89 (br t, ³J_{HH} = 6.2 Hz, H-11') ppm; ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 160.7 (C-4'), 149.5 (C-3), 145.1 (Tph), 138.5 (C-2'), 136.5 (Tph), 133.1 (Tph), 131.0 (Tph), 128.1 (C-2), 128.0 (C-1'), 123.5 (Tph), 115.6 (C-3'), 67.9 (C-6'), 31.7 (C-4), 29.9 (C-9'), 29.3 (C-7'), 25.9 (C-8'), 23.4 (C-5),

22.7 (C-10′), 14.2 (C-11′) ppm; ¹¹⁹Sn{¹H} NMR (224 MHz, CDCl₃): δ -71.8 ppm; IR (ATR): ν = 3051 (w), 2950 (w), 2919 (w), 2867 (w), 1584 (w), 1563 (w), 1492 (w), 1455 (w), 1376 (w), 1276 (w), 1240 (m), 1177 (m), 1071 (w), 998 (w), 973 (w), 937 (w), 900 (w), 781 (m), 724 (w) cm⁻¹; M_n (GPC) = 5,100 Da; M_w (GPC) = 9,600 Da; PDI = 1.9.

Synthesis of Polymer TStTT3



In a pressure tube, a solution of stannole St3 (100 mg, 91.0 µmol), 2,5-bis(trimethylstannyl)thiophene $(37.0 \text{ mg}, 91.0 \mu \text{mol})$ and $[Pd(PPh_3)_4]$ (3 mg, 5 μ mol) in a mixture of toluene (4 mL) and DMF (2 mL) was heated to reflux for 3 d under N₂-atmosphere. Over this time, the colour changed from orange to dark purple-black. The solution was precipitated into MeOH (300 mL). The polymer was collected by centrifugation, washed with MeOH (300 mL) and dried in vacuo to furnish a purple-black solid of **TStTT3** (83 mg, 98%). $\lambda_{abs,max}$ (CHCl₃, ϵ = 32,000 L·mol⁻¹·cm⁻¹) = 532 nm; $\lambda_{abs,max}$ (thin film) = 568 nm; $\lambda_{em,max}$ (CHCl₃) = 654 nm; ¹H NMR (600 MHz, CDCl₃): δ 7.87 – 7.73 (br m, 4H, H-2'), 7.70 – 7.60 (br m, 4H, H-3'), 7.12 – 6.99 (br m, 2H, Tph), 6.77 – 6.70 (br m, 2H, Tph), 2.99 – 2.84 (br m, 4H, H-4), 2.78 – 2.57 (br m, 4H, H-10), 1.91 – 1.80 (br m, 4H, H-5), 1.60 – 1.44 (br m, 4H, H-11), 1.38 – 1.13 (br m, 12H, H-12, 13, 14), 0.84 (br t, ${}^{3}J_{HH}$ = 6.4 Hz, 6H, H-15) ppm; ${}^{13}C{}^{1}H$ NMR (151 MHz, CDCl₃): δ 150.4 (C-3), 142.7 (C-1'), 139.3(Tph), 137.4 (C-2'), 136.0 (Tph), 135.9 (Tph), 133.0 (Tph),132.1 (Tph), 131.7 (C-4'), 128.8 (C-2), 125.7 (Tph), 125.5 (q, ²J_{CF} = 4.1 Hz, C-3'), 124.0 (q, ¹J_{C-F} = 272.3 Hz, CF₃), 31.9 (C-4), 31.7 (C-13), 30.3 (C-11), 29.2 (C-10), 29.0 (C-12), 23.1 (C-5), 22.5 (C-14), 14.0 (C-15) ppm; ¹¹⁹Sn{¹H} NMR (224 MHz, CDCl₃): δ -83.9 ppm; ¹⁹F NMR (565 MHz, CDCl₃): δ -63.09 ppm; IR (ATR): ν = 3051 (w), 2925 (w), 2855 (w), 1600 (w), 1494 (w), 1454 (w), 1390 (w), 1318 (w), 1272 (w), 1161 (w), 1120 (w), 1099 (w), 1080 (w), 1048 (w), 1013 (w), 911 (w), 819 (w), 791 (w), 723 (w), 679 (w) cm⁻¹; M_n (GPC) = 10,900 Da; M_w (GPC) = 21,900 Da; PDI = 2.0.

Synthesis of Polymer TStTT4



In a pressure tube, a solution of stannole **St4** (100 mg, 80.9 µmol), 2,5-bis(trimethylstannyl)thiophene (33.2 mg, 80.9 µmol) and [Pd(PPh₃)₄] (2 mg, 4 µmol) in a mixture of toluene (4 mL) and DMF (2 mL) was heated to reflux for 3 d under N₂-atmosphere. Over this time, the colour changed from orange to dark red/purple-black. The solution was precipitated into MeOH (300 mL). The polymer was collected by centrifugation, washed with MeOH (300 mL) and dried *in vacuo* to afford a reddish/purple-black solid of **TStTT4** (81 mg, 94%). $\lambda_{abs,max}$ (CHCl₃, $\varepsilon = 26,400 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) = 522 nm; $\lambda_{abs,max}$ (thin film) = 550 nm; $\lambda_{em,max}$ (CHCl₃) = 655 nm; ¹H NMR (600 MHz, CDCl₃): δ 8.12 – 8.02 (br m, 4H, H-2'), 7.98 – 7.90 (br m, 2H, H-4'), 7.13 – 7.02 (br m, 2H, Tph), 6.79 – 6.65 (br m, 2H, Tph), 3.01 – 2.88 (br m, 4H, H-4), 2.74 – 2.62 (br m, 4H, H-10), 1.92 – 1.81 (m, 4H, H-5), 1.59 – 1.44 (br m, 4H, H-11), 1.39 – 1.10 (br m, 12H, H-12, 13, 14), 0.87 – 0.72 (br m, 6H, H-15) ppm; ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 151.2 (C-3), 142.6 (Tph), 140.4 (C-1'), 139.9 (TpH), 136.8 (C-2'), 136.1 (Tph), 132.5 (Tph), 132.2 (q, ²_{JCF} = 33.6 Hz, C-3'), 127.3 (C-2), 126.1 (Tph), 124.1 (C-4'), 123.4 (q, ¹_{JCF} = 273.3 Hz, CF₃), 32.1 (C-4), 31.5 (C-13), 30.4 (C-11), 29.4 (C-10), 29.2 (C-12), 23.1 (C-5), 22.6 (C-14), 14.1 (C-15) ppm; ¹¹⁹Sn{¹H} NMR (224 MHz, CDCl₃):

δ -84.2 ppm; ¹⁹F NMR (565 MHz, CDCl₃): δ -62.89 ppm; IR (ATR): ν = 3051 (w), 2926 (w), 2855 (w), 1614 (w), 1456 (w), 1377 (w), 1348 (w), 1274 (w), 1171 (w), 1119 (w), 1102 (w), 1086 (w), 914 (w), 889 (w), 839 (w), 788 (w), 749 (w), 705 (w), 695 (w), 680 (w) cm⁻¹; M_n (GPC) = 10,300 Da; M_w (GPC) = 21,500 Da; PDI = 2.1.

3 Crystallography



Figure S1. Molecular structure of stannole **St2** showing 50% probability ellipsoids and the crystallographic numbering scheme. All hydrogen atoms are omitted for clarity.



Figure S2. Molecular structure of stannole **St3** showing 50% probability ellipsoids and the crystallographic numbering scheme. All hydrogen atoms are omitted for clarity.

Table S4. Crystal data and structure refinement for St2 and St3.

	St2	St3
CCDC number	2052178	2052177
Empirical formula	$C_{40}H_{46}I_2O_2S_2Sn$	$C_{42}H_{44}F_6I_2S_2Sn$
Formula weight	995.38	1099.38
Temperature [K]	100.0	100.0
Crystal system	'orthorhombic'	'triclinic'
Space group (number)	<i>P</i> bcn (60)	P1 (2)
<i>a</i> [Å]	10.3597(10)	8.6422(4)
<i>b</i> [Å]	11.9739(10)	16.3118(8)
<i>c</i> [Å]	32.004(3)	16.7929(9)
α [Å]	90	63.057(2)
β [Å]	90	79.804(2)
γ [Å]	90	85.769(2)
Volume [ų]	3970.0(6)	2076.96(18)
Ζ	4	2
$ ho_{calc}$ [g/cm ³]	1.665	1.758
μ [mm⁻¹]	2.336	2.258
F(000)	1960	1076
Crystal size [mm ³]	0.1×0.1×0.01	0.29×0.27×0.13
Crystal colour	yellow	yellow
Crystal shape	plate	plate
Radiation	Mo <i>K</i> _α (λ=0.71073 Å)	Mo <i>K</i> _α (λ=0.71073 Å)
20 range [°]	5.09 to 56.99 (0.74 Å)	4.73 to 62.00 (0.69 Å)
Index ranges	-13 ≤ h ≤ 13	-12 ≤ h ≤ 12
	-16 ≤ k ≤ 14	-23 ≤ k ≤ 23
	-42 ≤ I ≤ 42	-24 ≤ l ≤ 24
Reflections collected	63429	63734
Independent reflections	5028	13233
	$R_{\rm int} = 0.0506$	<i>R</i> _{int} = 0.0371
	R _{sigma} = 0.0264	R _{sigma} = 0.0295
Completeness to θ = 25.242°	99.9 %	99.9 %
Data / Restraints / Parameters	5028/0/215	13233/0/480
Goodness-of-fit on <i>F</i> ²	1.074	1.051
Final <i>R</i> indexes	$R_1 = 0.0289$	$R_1 = 0.0242$
[<i>I</i> ≥2σ(<i>I</i>)]	w <i>R</i> ₂ = 0.0450	w <i>R</i> ₂ = 0.0494
Final <i>R</i> indexes	$R_1 = 0.0457$	$R_1 = 0.0329$
[all data]	$wR_2 = 0.0494$	$wR_2 = 0.0531$
Largest peak/hole [eų]	1.01/-0.66	0.92/-0.71
Extinction coefficient	0.00046(3)	

Table S5. Selected bond parameters of molecular structures St2 and St3.

Bond lengths [Å] and angles [°]	St2	St3
Sn1–C1	2.140(2)	2.127(3)
C1–C2	1.366(3)	1.366(2)
Sn1-C20	2.126(2)	-
Sn1-C30	-	2.140(3)
C2–C2A	1.490(5)	-
C2–C7	-	1.496(2)
C1–Sn1–C1A	83.0(2)	-
C1-Sn1-C8	-	84.23(7)
C20-Sn1-C1	120.61(9)	-
C1-Sn1-C30	-	118.20(7)
C20–Sn1–C20A	109.4(3)	-
C40-Sn1-C30	-	106.40(7)
C2-C1-Sn1	108.9(2)	107.9(2)
C2-C1-C10	129.6(2)	129.9(3)
C1–C2–C2A	119.4(3)	-
C1–C2–C7	-	119.8(3)
Sn1–C1–C2–C2A	-3.6(3)	-
Sn1-C1-C2-C7	-	5.2(2)
Sn1-C1-C10-C11	-14.5(3)	-10.5(3)
C1–C2–C3–C4	-166.9(2)	168.4(2)
C1-Sn1-C20-C21	105.5(3)	-
C1-Sn1-C30-C31	-	-71.(2)

4 **Optical Properties**

Monomer	Solvent	$\lambda_{abs,max}$ / nm	$\lambda_{\text{em,max}}/\text{ nm}$	$\Delta \tilde{\nu}/ \text{ cm}^{-1}$	Φ _F / %
		(ε/ L·mol ⁻¹ ·cm ⁻¹)			
St1	CHCl₃	434 (22,600)	522	3,884	0.57
	PhMe	438	522	3,674	0.95
	THF	434	519	3,774	0.50
St2	CHCl₃	434 (22,400)	523	3,921	0.42
	PhMe	437	523	3,763	0.87
	THF	434	520	3,811	0.38
St3	CHCl₃	443 (24,500)	534	3,847	1.32
	PhMe	446	535	3,730	2.72
	THF	443	533	3,812	1.93
St4	CHCl₃	446 (17,300)	543	4,005	3.51
	PhMe	451	545	3,824	6.75
	THF	445	543	4,055	2.45

Table S6. Optical properties of monomers St1-St4 in solutions (10⁻⁵ M) of chloroform, toluene and 2-methyltetrahydrofuran at 295 K.

Table S7. Optical properties of monomers St1-St4 in the solid state at 295 K.

Monomer	$\lambda_{exc}/$ nm	$\lambda_{\text{em,max}}/$ nm	$\Delta \tilde{\nu} / \text{ cm}^{-1}$	$\Phi_{\rm F}$ /%	$arPhi_{ extsf{F}}$ / % (thin film)
St1	373	537	8,188	0.22	0.77
St2	355	530	9,302	0.21	0.29
St3	368	583	1,0021	8.15	3.71
St4	344	561	1,1244	9.36	8.89

Table S8. Optical properties of polymers TStTT1-4 in solution (CHCl₃) and thin film.

Polymer	$\lambda_{abs,max}/nm$	ε/	$\lambda_{abs,max}/nm$	$\lambda_{\text{em,max}}$	$\Delta \tilde{\nu}$ / cm ⁻¹	Φ _F / %
	(CHCl₃)	L·mol⁻¹·cm⁻¹	(thin film)	nm		
TStTT1	556	35,600	556	717	4,038	0.26
TStTT2	560	28,600	595	716	3,891	<0.1
TStTT3	532	32,000	568	654	3,506	0.32
TStTT4	522	26,400	550	655	3,890	<0.1



Figure S3. CIE1931 chromaticity plot with emission colour coordinates of stannoles St1-St4 at 295 K in toluene.



Figure S4. CIE1931 chromaticity plot with emission colour coordinates of stannoles St1-St4 at 100 K in 2-methyl-tetrahydrofuran.



Figure S5. CIE1931 chromaticity plot with emission colour coordinates of stannoles St1-St4 at 295 K in the solid state.



4.1 Monomer St1





Figure S7. Normalised emission spectra of monomer St1 in various solvents ($c = 10^{-5} \text{ mol } L^{-1}$) at 295 K.



Figure S8. Normalised absorption (red line) and emission (blue line) spectra of **St1**; solvent: chloroform ($c = 10^{-5}$ mol L⁻¹), 295 K. The emission was monitored by excitation at 434 nm.



Figure S9. Normalised absorption (red line) and emission (blue line) spectra of **St1**; solvent: toluene ($c = 10^{-5} \text{ mol } L^{-1}$), 295 K. The emission was monitored by excitation at 434 nm.



Figure S10. Normalised absorption (red line) and emission (blue line) spectra of **St1**; solvent: tetrahydrofuran ($c = 10^{-5} \text{ mol } L^{-1}$), 295 K. The emission was monitored by excitation at 434 nm.



Figure S11. Normalised excitation (red line) and emission (blue line) spectra of **St1** in the solid state at 295 K. The emission was monitored by excitation at 369 nm, the excitation was monitored at 537 nm.



Figure S12. Temperature dependent emission spectra of **St1** in 2-methyltetrahydrofuran (c = 10^{-5} mol L⁻¹) during heating from 100 K to 280 K with excitation at 434 nm.



Figure S13. Irradiation of a frozen solution (10⁻⁵ M, 2-methyltetrahydrofuran) of St1 at 434 nm at 100 K.



Figure S14. Trend of the wavelength of the emission maximum of stannole **St1** at the given temperature (with respect to Figure S9). Starting from 523 nm at 280 K the wavelength drops to 517 nm at 100 K.



Figure S15. Trend of the Intensity of the emission maximum of **St1** at the given temperature (with respect to Figure S9). Compared to 280 K the emission intensity has multiplied by the factor of 122 at 100 K.

4.2 Monomer St2



Figure S16. Normalised absorption spectra of monomer St2 in various solvents ($c = 10^{-5} \text{ mol } L^{-1}$) at 295 K.



Figure S17. Normalised emission spectra of monomer St2 in various solvents ($c = 10^{-5} \text{ mol } L^{-1}$) at 295 K.



Figure S18. Normalised absorption (red line) and emission (blue line) spectra of **St2**; solvent: chloroform ($c = 10^{-5}$ mol L⁻¹), 295 K. The emission was monitored by excitation at 434 nm.


Figure S19. Normalised absorption (red line) and emission (blue line) spectra of **St2**; solvent: toluene ($c = 10^{-5} \text{ mol } L^{-1}$), 295 K. The emission was monitored by excitation at 434 nm.



Figure S20. Normalised absorption (red line) and emission (blue line) spectra of **St2**; solvent: tetrahydrofuran ($c = 10^{-5} \text{ mol } L^{-1}$), 295 K. The emission was monitored by excitation at 434 nm.



Figure S21. Normalised excitation (red line) and emission (blue line) spectra of St2 in the solid state at 295 K. The emission was monitored by excitation at 355 nm, the excitation was monitored at 531 nm.



Figure S22. Temperature dependent emission spectra of **St2** in 2-methyltetrahydrofuran (c = 10^{-5} mol L⁻¹) during heating from 100 K to 280 K with excitation at 434 nm.



Figure S23. Irradiation of a frozen solution (10⁻⁵ M, 2-methyltetrahydrofuran) of St2 at 434 nm at 100 K.



Figure S24. Trend of the wavelength of the emission maximum of stannole **St2** at the given temperature (with respect to Figure S19).



Figure S25. Trend of the Intensity of the emission maximum of **St2** at the given temperature (with respect to Figure S19). Compared to 280 K the emission intensity has multiplied by the factor of 237 at 100 K.

4.3 Monomer St3



Figure S26. Normalised absorption spectra of monomer St3 in various solvents ($c = 10^{-5} \text{ mol } L^{-1}$) at 295 K.



Figure S27. Normalised emission spectra of monomer St3 in various solvents ($c = 10^{-5} \text{ mol } L^{-1}$) at 295 K.



Figure S28. Normalised absorption (red line) and emission (blue line) spectra of **St3**; solvent: chloroform ($c = 10^{-5}$ mol L⁻¹), 295 K. The emission was monitored by excitation at 445 nm.



Figure S29. Normalised absorption (red line) and emission (blue line) spectra of **St3**; solvent: toluene ($c = 10^{-5} \text{ mol } L^{-1}$), 295 K. The emission was monitored by excitation at 445 nm.



Figure S30. Normalised absorption (red line) and emission (blue line) spectra of **St3**; solvent: tetrahydrofuran ($c = 10^{-5} \text{ mol } L^{-1}$), 295 K. The emission was monitored by excitation at 445 nm.







Figure S32. Crystals of St3 under normal daylight.



Figure S33. Crystals of St3 under UV irradiation at 366 nm.



Figure S34. Temperature dependent emission spectra of **St3** in 2-methyltetrahydrofuran (c = 10^{-5} mol L⁻¹) during heating from 100 K to 280 K with excitation at 445 nm.



Figure S35. Irradiation of a frozen solution (10⁻⁵ M, 2-methyltetrahydrofuran) of St3 at 445 nm at 100 K.



Figure S36. Trend of the wavelength of the emission maximum of stannole **St3** at the given temperature (with respect to Figure S29). Starting from 534 nm at 280 K the wavelength drops to 528 nm at 100 K.



Figure S37. Trend of the Intensity of the emission maximum of **St3** at the given temperature (with respect to Figure S29). Compared to 280 K the emission intensity has multiplied by the factor of 71 at 100 K.

4.4 Monomer St4



Figure S38. Normalised absorption spectra of monomer St4 in various solvents ($c = 10^{-5} \text{ mol } L^{-1}$) at 295 K.



Figure S39. Normalised emission spectra of monomer St4 in various solvents ($c = 10^{-5} \text{ mol } L^{-1}$) at 295 K.



Figure S40. Normalised absorption (red line) and emission (blue line) spectra of **St4**; solvent: chloroform ($c = 10^{-5} \text{ mol } L^{-1}$), 295 K. The emission was monitored by excitation at 449 nm.



Figure S41. Normalised absorption (red line) and emission (blue line) spectra of **St4**; solvent: toluene ($c = 10^{-5}$ mol L⁻¹), 295 K. The emission was monitored by excitation at 449 nm.



Figure S42. Normalised absorption (red line) and emission (blue line) spectra of **St4**; solvent: tetrahydrofuran ($c = 10^{-5} \text{ mol } L^{-1}$), 295 K. The emission was monitored by excitation at 449 nm.



Figure S43. Normalised excitation (red line) and emission (blue line) spectra of **St4** in the solid state at 295 K. The emission was monitored by excitation at 361 nm, the excitation was monitored at 560 nm.



Figure S44. Temperature dependent emission spectra of **St4** in 2-methyltetrahydrofuran (c = 10^{-5} mol L⁻¹) during heating from 100 K to 280 K with excitation at 449 nm.



Figure S45. Irradiation of a frozen solution (10⁻⁵ M, 2-methyltetrahydrofuran) of St4 at 449 nm at 100 K.



Figure S46. Trend of the wavelength of the emission maximum of stannole **St4** at the given temperature (with respect to Figure S39). Starting from 544 nm at 280 K the wavelength drops to 530 nm at 100 K.



Figure S47. Trend of the Intensity of the emission maximum of **St4** at the given temperature (with respect to Figure S39). Compared to 280 K the emission intensity has multiplied by the factor of 61 at 100 K.

4.5 Polymers



Figure S48. Normalised absorption spectra of TStTT1-4; solvent: chloroform (c = 10⁻⁵ mol L⁻¹), 295 K.



Figure S49. Normalised absorption spectra of TStTT1-4 in the solid state.



Figure S50. Normalised absorption (purple line) and emission (red line) spectra of **TStTT1**; solvent: chloroform ($c = 10^{-5} \text{ mol } L^{-1}$), 295 K. The emission was monitored by excitation at 557 nm.

b



Figure S51. Normalised absorption (purple line) and emission (red line) spectra of **TStTT2**; solvent: chloroform ($c = 10^{-5} \text{ mol } L^{-1}$), 295 K. The emission was monitored by excitation at 560 nm.



Figure S52. Normalised absorption (purple line) and emission (red line) spectra of **TStTT3**; solvent: chloroform ($c = 10^{-5} \text{ mol } L^{-1}$), 295 K. The emission was monitored by excitation at 533 nm.



Figure S53. Normalised absorption (purple line) and emission (red line) spectra of **TStTT4**; solvent: chloroform ($c = 10^{-5} \text{ mol } L^{-1}$), 295 K. The emission was monitored by excitation at 522 nm.



Figure S54. Photographs of polymer TStTT1 under normal daylight.



Figure S55. Photographs of polymer TStTT2 under normal daylight.





Figure S56. Photographs of polymer TStTT3 under normal daylight.



Figure S57. Photographs of polymer TStTT4 under normal daylight.

5 Theoretical Calculations

Optimised equilibrium geometries were calculated on a DFT level with the Gaussian 16, revision A.03⁹ quantum software package for a single molecule in the gas phase using the PBE1PBE/6-311++G(2d,2p)¹⁰ level of theory including empirical dispersion corrections according to Grimme's D3¹¹ method involving Becke-Johnson damping (GD3BJ). For the Sn atom, we employed the Stuttgart/Dresden (SDD) pseudo potential.¹² The orbital energies of HOMO and LUMO and their energy differences were calculated for these optimised molecules. Frequency analyses were performed in all cases to confirm the absence of imaginary frequencies and thus prove that the obtained geometries corresponded to minima on the potential energy surface. The isodensity value for the molecular orbital isosurface representations was set to 0.02 a.u. in all cases. Absorption data was calculated using time-dependent DFT (TD-DFT) level on the optimised ground state geometries with the same functional and basis set as described above, i.e., TD-PBE1PBE-GD3BJ/6-311++G(2d,2p)//PBE1PBE-GD3BJ/6-311++G(2d,2p) employing SDD pseudo potentials for Sn.¹⁰⁻¹²

Table S9. HOMO, HOMO-1, LUMO and LUMO+1 energy levels, HOMO-LUMO energy gaps and calculated absorption maxima of monomers St1-St4.

Stannole	HOMO-1/	номо/	LUMO/	LUMO+1/	E_{gap}/eV	$\lambda_{abs,calc}$	$\lambda_{abs,calc}$
	eV	eV	eV	eV		nm ²⁸	nm ²⁹
St1	-6.52	-5.31	-2.07	-1.00	3.24	269	451
St2	-6.39	-5.26	-2.02	-0.97	3.24	272	450
St3	-6.66	-5.52	-2.33	-1.56	3.19	274	463
St4	-6.76	-5.65	-2.48	-1.86	3.17	274	469

²⁸ These absorption maxima arise from a large number of different transitions.

²⁹ These absorption maxima arise from HOMO-LUMO transitions.

Bond lengths [Å] and	St1	St2	St3	St4			
angles [°]							
Sn1–C1	2.151	2.152	2.144	2.137			
Sn1–C30	2.139	2.135	2.148	2.153			
C1–Sn1–C8	82.9	82.8	83.3	83.7			
C1–Sn1–C30	112.4	111.7	112.2	113.9			
Sn1-C1-C2-C3	0.5	0.6	0.4	-2.1			
Sn1-C1-C10-C11	8.5	9.5	10.0	8.9			
Sn1-C8-C20-C21	8.5	8.2	7.1	3.3			

Table S10. Selected bond lengths [Å] and angles [°] of optimised geometries of St1-4.



Figure S58. Optimised geometry of monomer St1.



Figure S59. HOMO and LUMO of stannole St1.



Figure S60. Normalised calculated absorption spectrum of St1.



Figure S61. Optimised geometry of monomer St2.



Figure S62. HOMO and LUMO of stannole St2.



Figure S63. Normalised calculated absorption spectrum of St2.



Figure S64. Optimised geometry of monomer St3.



Figure S65. HOMO and LUMO of stannole St3.



Figure S66. Normalised calculated absorption spectrum of St3.



Figure S67. Optimised geometry of monomer St4.



Figure S68. HOMO and LUMO of stannole St4.



Figure S69. Normalised calculated absorption spectrum of St4.



Figure S70. HOMO (E_{HOMO} = -4.83 eV) of a cyclopentadiene-thiophenyl oligomer.



Figure S71. LUMO (E_{LUMO} = -2.59 eV) of a cyclopentadiene-thiophenyl oligomer.



Figure S72. HOMO (E_{HOMO} = -4.80 eV) of a stannole-thiophenyl oligomer.



Figure S73. LUMO (E_{LUMO} = -2.70 eV) of a stannole-thiophenyl oligomer.

7 GPC and MALDI



Figure S74. GPC measurement of **TStTT1** using CHCl₃ (0.5 mg/mL) as the eluent at a flow rate of 1mL/min. The signals from the refraction index (RI) and UV-Vis detectors are shown.



Figure S75. GPC plot of **TStTT1** using CHCl₃ (0.5 mg/mL) as the eluent at a flow rate of 1 mL/min; calibrated against polystyrene standards.



Figure S76. MALDI spectrum of TStTT1 showing its mass repeating unit *m*/*z* 792.



Figure S77. GPC measurement of TStTT2 using $CHCl_3$ (0.5 mg/mL) as the eluent at a flow rate of 1mL/min. The signals from the refraction index (RI) and UV-Vis detectors are shown.



Figure S78. GPC plot of TStTT2 using CHCl₃ (0.5 mg/mL) as the eluent at a flow rate of 1 mL/min; calibrated against polystyrene standards.



Figure S79. MALDI spectrum of TStTT2 showing its mass repeating unit *m/z* 824.



Figure S80. GPC measurement of **TStTT3** using $CHCl_3$ (0.5 mg/mL) as the eluent at a flow rate of 1 mL/min. The signals from the refraction index (RI) and UV-Vis detectors are shown.



Figure S81. GPC plot of TStTT3 using CHCl₃ (0.5 mg/mL) as the eluent at a flow rate of 1 mL/min; calibrated against polystyrene standards.



Figure S82. MALDI spectrum of TStTT3 showing its mass repeating unit *m*/z 928.



Figure S83. GPC measurement of **TStTT4** using CHCl₃ (0.5mg/mL) as eluent at a flow rate of 1mL/min. The signals from the refraction index (RI) and UV-Vis detectors are shown.



Figure S84. GPC plot of TStTT4 using CHCl₃ (0.5 mg/mL) as the eluent at a flow rate of 1 mL/min; calibrated against polystyrene standards.



Figure S85. MALDI spectrum of TStTT4 showing its mass repeating unit *m*/*z* 1064.

8 TGA Measurements



Figure S86. TGA Plot of TStTT1.



Figure S87. TGA Plot of TStTT2.


Figure S88. TGA Plot of TStTT3.



Figure S89. TGA Plot of TStTT4.



Figure S91. ${}^{13}C{}^{1}H$ NMR (151 MHz) spectrum of 1 in CDCl₃.

S73



Figure S93. ¹³C{¹H} NMR (126 MHz) spectrum of 2 in CDCl₃.



Figure S95. ¹³C{¹H} NMR (126 MHz) spectrum of 5 in CDCl₃.

Figure S97. ¹H NMR (500 MHz) spectrum of 6 in CDCl₃.



Figure S96. $^{119}Sn\{^{1}H\}$ NMR (187 MHz) spectrum of 5 in CDCl3.

ò

-20

-40

-60

00

80

60

40

20

-100 δ (ppm)

-80

-120

-140

-160

-180

-220

-200



-3

-280

-260





-100 δ (ppm)

-80

-120

-140

-160

-180

-200

-220

-240

-260

-280 -3

Figure S99. ¹¹⁹Sn{¹H} NMR (187 MHz) spectrum of 6 in CDCl₃.

0

-20

-40

-60

00

80

60

40



Figure S100. ¹H NMR (500 MHz) spectrum of 7 in CD₂Cl₂.



Figure S101. ${}^{13}C{}^{1}H$ NMR (126 MHz) spectrum of 7 in CD₂Cl₂.



whether welle grow when the stand of the sta

)0 -100 δ (ppm) 80 60 -120 40 20 -140 -160 -180 ó -20 -40 -60 -80 -200 -220 -240 -260 -280 -3

Figure S102. $^{119}\text{Sn}\{^{1}\text{H}\}$ NMR (187 MHz) spectrum of 7 in CD_2Cl_2.





Figure S103. ¹⁹F NMR (471 MHz) spectrum of 7 in CD₂Cl₂.



Figure S104. ¹H NMR (500 MHz) spectrum of 8 in CDCl₃.



Figure S105. ¹³C{¹H} NMR (126 MHz) spectrum of 8 in CDCl₃.



-120

-140

-160

-180

-200

-220

-240

-260

-40 -100 δ (ppm) Figure S106. $^{119}\text{Sn}\{^{1}\text{H}\}$ NMR (187 MHz) spectrum of 8 in CDCl₃.

-60

---63.12

-80

-20



40

20

ó

00

80

60



Figure S107. ¹⁹F NMR (471 MHz) spectrum of 8 in CDCl₃.

-3

-280



Figure S109. ${}^{13}C{}^{1}H$ NMR (126 MHz) spectrum of 9 in CD₂Cl₂.



www.www.www.weiner.

1				1						
50	200	150	100	50	0	-50	-100	-150	-200	
δ (ppm)										

Figure S110. ¹¹⁹Sn{¹H} NMR (187 MHz) spectrum of $\mathbf{9}$ in CD₂Cl₂.



Figure S111. ¹H NMR (600 MHz) spectrum of 10 in CD₂Cl₂.



Figure S112. $^{13}\text{C}\{^{1}\text{H}\}$ NMR (151 MHz) spectrum of 10 in CD_2Cl_2.





Figure S113. $^{119}\text{Sn}\{^{1}\text{H}\}$ NMR (187 MHz) spectrum of 10 in CD_2Cl_2.



Figure S114. ¹H NMR (500 MHz) spectrum of 11 in CD₂Cl₂.







Figure S115. $^{13}\text{C}\{^{1}\text{H}\}$ NMR (126 MHz) spectrum of 11 in CD₂Cl₂.





---35.66

Figure S116. $^{119}Sn\{^{1}H\}$ NMR (187 MHz) spectrum of 11 in CD₂Cl₂.





Figure S117. ^{19}F NMR (471 MHz) spectrum of 11 in CD_2Cl_2.



Figure S118. ¹H NMR (500 MHz) spectrum of 12 in CD_2CI_2 .





Figure S119. $^{13}\text{C}\{^{1}\text{H}\}$ NMR (126 MHz) spectrum of 12 in CD₂Cl₂.





Figure S121. ¹⁹F NMR (471 MHz) spectrum of **12** in CD₂Cl₂.



Figure S123. ${}^{13}C{}^{1}H$ NMR (151 MHz) spectrum of St1 in CDCl₃.





Figure S124. ¹¹⁹Sn{¹H} NMR (224 MHz) spectrum of St1 in CDCl₃.



Figure S125. ¹H NMR (600 MHz) spectrum of St2 in CDCl₃.



Figure S126. $^{13}\text{C}\{^{1}\text{H}\}$ NMR (151 MHz) spectrum of St2 in CDCl3.



Figure S127. ¹¹⁹Sn{¹H} NMR (224 MHz) spectrum of St2 in CDCl₃.





Figure S129. ${}^{13}C{}^{1}H$ NMR (151 MHz) spectrum of St3 in CDCl₃.





Figure S130. ¹¹⁹Sn{¹H} NMR (224 MHz) spectrum of St3 in CDCl₃.



Figure S131. ¹⁹F NMR (565 MHz) spectrum of St3 in CDCl₃.





Figure S133. ${}^{13}C{}^{1}H$ NMR (151 MHz) spectrum of St4 in CDCl₃.





Figure S134. $^{119}\mbox{Sn}{}^{1}\mbox{H}$ NMR (224 MHz) spectrum of St4 in CDCl3.





Figure S135. ¹⁹F NMR (565 MHz) spectrum of St4 in CDCl₃.



Figure S136. ¹H NMR (600 MHz) spectrum of TStTT1 in CDCl₃.



Figure S137. ¹³C{¹H} NMR (151 MHz) spectrum of TStTT1 in CDCl₃.





-76.39

Figure S138. ¹¹⁹Sn{¹H} NMR (224 MHz) spectrum of TStTT1 in CDCl₃.



Figure S139. ¹H NMR (600 MHz) spectrum of TStTT2 in CDCl₃.



Figure S140. $^{13}C\{^{1}H\}$ NMR (151 MHz) spectrum of TStTT2 in CDCl_3.



Figure S141. ¹¹⁹Sn{¹H} NMR (224 MHz) spectrum of TStTT2 in CDCl₃.







Figure S142. ¹H NMR (600 MHz) spectrum of TStTT3 in CDCl₃.



Figure S143. ¹³C{¹H} NMR (151 MHz) spectrum of TStTT3 in CDCl₃.





ο δ(ppm) -50

-100

Figure S144. $^{119}\text{Sn}\{^{1}\text{H}\}$ NMR (224 MHz) spectrum of TStTT3 in CDCl3.

200

150

100

50

250



350

300

500

450

400



Figure S145. ¹⁹F NMR (565 MHz) spectrum of TStTT3 in CDCl₃.

-500

-450

-300

-350

-400

-250



Figure S146. ¹H NMR (600 MHz) spectrum of TStTT4 in CDCl₃.



Figure S147. ¹³C{¹H} NMR (151 MHz) spectrum of TStTT4 in CDCl₃.





Figure S148. $^{119}\text{Sn}\{^{1}\text{H}\}$ NMR (224 MHz) spectrum of TStTT4 in CDCl3.





Figure S149. ¹⁹F NMR (565 MHz) spectrum of TStTT4 in CDCl₃.

Literature

- (a) G. Sheldrick, Acta Cryst. A, 2008, 64, 112-122; (b) L. Farrugia, J. Appl. Cryst., 1999, 32, 837-838.
- 2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.
- (a) J. Linshoeft, E. J. Baum, A. Hussain, P. J. Gates, C. Näther and A. Staubitz, Angew. Chem. Int. Ed., 2014, 53, 12916–12920; (b) S. Urrego-Riveros, I.-M. Ramirez y Medina, D. Duvinage, E. Lork, F. D. Sönnichsen and A. Staubitz, Chem. Eur. J., 2019, 25, 13318–13328; (c) I.-M. Ramirez y Medina, M. Rohdenburg, F. Mostaghimi, S. Grabowsky, P. Swiderek, J. Beckmann, J. Hoffmann, V. Dorcet, M. Hissler and A. Staubitz, Inorg. Chem., 2018, 57, 12562–12575; (d) I.-M. Ramirez y Medina, M. Rohdenburg, E. Lork and A. Staubitz, Chem. Commun., 2020, 56, 9775–9778.
- 4. A. C. J. Heinrich, B. Thiedemann, P. J. Gates and A. Staubitz, *Org. Lett.*, 2013, **15**, 4666–4669.
- (a) I. Barlow, S. Sun, G. J. Leggett and M. Turner, *Langmuir*, 2010, 26, 4449–4458; (b) M. P.
 Aldred, P. Vlachos, A. E. A. Contoret, S. R. Farrar, W. Chung-Tsoi, B. Mansoor, K. L. Woon, R.
 Hudson, S. M. Kelly and M. O'Neill, *J. Mater. Chem.*, 2005, 15, 3208–3213.
- 6. M. Shellaiah, Y. C. Rajan and H.-C. Lin, J. Mater. Chem., 2012, 22, 8976–8987.
- 7. V. Y. Lu and T. D. Tilley, *Macromolecules*, 2000, **33**, 2403–2412.
- 8. T. B. D. Miles, A. Lough, D. Foucher, J. Inorg. Organomet. Polym., 2010, 20, 544–553.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, H. P. H. X. Li, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 16 Revision A.03, Gaussian, Inc., Wallingford CT*, 2016.
- 10. (a) A. D. McLean and G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639–5648; (b) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650–654; (c) R. C. Binning Jr. and L. A. Curtiss, *J. Comput. Chem.*, 1990, **11**, 1206–1216; (d) M. P. McGrath and L. Radom, *J. Chem. Phys.*, 1991, **94**, 511–516; (e) L. A. Curtiss, M. P. McGrath, J. Blaudeau, N. E. Davis, R. C. Binning

and L. Radom, *J. Chem. Phys.*, 1995, **103**, 6104–6113; (f) C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158–6170.

- (a) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, 132, 154104; (b) S.
 Grimme, S. Ehrlich and L. Goerigk, J. Comput. Chem., 2011, 32, 1456–1465.
- 12. (a) G. Igel-Mann, H. Stoll and H. Preuss, *Mol. Phys.*, 1988, 65, 1321–1328; (b) A. Bergner, M. Dolg, W. Küchle, H. Stoll and H. Preuß, *Mol. Phys.*, 1993, 80, 1431–1441.