Electronic Supplementary Information for

Direct nitroxide mediated (co)polymerization of 4-vinylphenylboronic acid as route to sugar sensors

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Contents:

1.1 Materials

All HPLC grade solvents were purchased from Sigma-Aldrich (*N,N*-dimethylacetamide (DMAc), ethyl acetate and acetone), from Fischer Scientific (toluene, *n*-hexane and dichloromethane) or from Acros. 4-Vinylphenylboronic acid was purchased from TCI Europe and used as received. Disperse Red 1 methacrylate (DR1-MA) and α-D-glucose were obtained from Sigma-Aldrich. All deuterated solvent were bought from Cambridge Isotope Labratories. Blocbuilder$^{(R)}$ was a kind donation from Arkema.

Materials for the synthesis of compounds **1**-**5**: All reactions were carried out under inert conditions (argon). Benzothiadiazole, 3-hexylthiophene, *tert*-butyllithium, 2-*iso*propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane were purchased from Acros, *N*-bromsuccinimide and $Pd(PPh_3)_4$ were purchased from ABCR. 2-(4-Hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1**),[1] 4,7-dibromobenzothiadiazole (**2**),[2] 4,7-*bis*(4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (**3**)[3,4] and 4-(5-bromo-4-hexylthiophen-2-yl)-7-(4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (**4**)[5] were synthesized according to modified procedures known from literature. All solvents and chemicals used in this work were analytical grade and used without further purification.

1.2 Equipment

Size-exclusion chromatography (SEC) was performed on a Agilent 1260-series HPLC system equipped with a 1260 online degasser, a 1260 ISO-pump, a 1260 automatic liquid sampler, a thermostatted column compartment, a 1260 diode array detector (DAD) and a 1260 refractive index detector (RID). Analyses were performed on a PSS Gram30 column in series with a PSS Gram1000 column at 50 ^{o}C. DMAc containing 50 mM of LiCl was used as eluent at a flow rate of 1 ml/min. The spectra were analysed using the Agilent Chemstation software with the GPC add on. Molar mass and PDI values were calculated against Varian PS standards.

UV/Vis spectra were recorded on a Varian Cary 300 Bio UV-VIS spectrophotometer equipped with a Cary temperature and stir control. The emission and excitation spectra were recorded on a Varian Cary Eclipse fluorospectrophotometer also equipped with a Cary temperature and stir control.

Centrifugation was performed on an ALC multispeed refrigerated centrifuge PK 121R from Thermo Scientific using 50 ml centrifuging tubes with screw caps from VWR or 15 ml high clarity polypropylene conical tubes from Falcon.

Proton nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 MHz spectrometer at room temperature. The chemical shifts are given relative to TMS.

Deionised water was prepared with a resistivity less than 18.2 MΩ x cm using an Arium 611 from Sartorius with the Sartopore 2 150 (0.45 + 0.2 µm pore size) cartridge filter.

pH-values were measured using a Consort C561 equipped with a universal pH electrode with build in temperature probe.

Characterization towards the synthesis of compounds **1**-**5**: Infrared studies were conducted on a JASCO FT/IR-4200 Fourier-Transform-Spectrometer. Mass spectra were obtained using a Bruker micrOTOF instrument equipped with an atmospheric pressure laser ionization source (APLI-MS). ^{1}H and ^{13}C-NMR spectra were recorded in deuterated chloroform ($CDCl_3$) with TMS as internal standard on a Bruker ARX 400 and 600. The chemical shift δ is given in ppm. Elemental analyses were performed by means of the Vario Elemental EL analyzer. For the purification of the compounds by means of column chromatography silica gel of particle size 50-200 mesh was utilized as the stationary phase.

2. General polymerization procedure

All the polymerizations were conducted in specially designed Schlenk reaction tubes that ensure tight closure and easy switching between high vacuum and argon atmosphere without decoupling the vials from the Schlenk line. The tubes are fitted with a screw cap with septa to allow easy sampling during the kinetic study. The polymerization mixture is first degassed using so called freeze-pump-thaw cycles (3 times), *i.e.* initial freezing of the mixture with liquid nitrogen after which a high vacuum is applied to remove all the gas in the Schlenk vial. The mixture is subsequently thawed under argon and the cycle is repeated to remove all the gasses that are absorbed or included in the frozen mixture. The polymerizations were all conducted in an oil bath under argon atmosphere.

3. Synthesis and kinetic study for the NMP of 4-vinylphenyl boronic acid

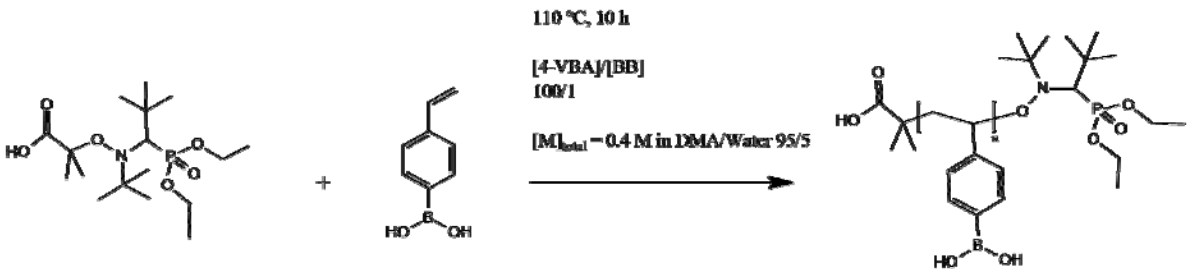


Fig. S1: Schematic overview and reaction conditions for the NMP of 4-VBA.

Poly(4-VBA) was synthesised in solution with a [4-VBA]:[Blocbuilder] ratio of [100]:[1]. 4-VBA (0.5 g, 3.379 mmol) and Blocbuilder (12.8 mg, 0.034 mmol) were dissolved in DMAc/H_2O (8.45 ml, 95/5). After dissolving and degassing, the mixture was heated to 110 °C for 12 h while samples were taken to monitor the polymerization. Afterwards, the polymerization mixture was precipitated in a 10-fold excess of cold ethyl acetate and isolated by centrifugation (6000 rpm, 5 °C, 45 min), resulting in a glassy, white solid after drying.
Yield: 0.4907 g, **Conversion:** 74 % (based on the UV signal at 316 nm in SEC)

^{1}H-NMR spectroscopy (300 MHz, DMSO-6d/drop of D_2O, Fig. S2):
Poly(4-VBA): δ = 1–2 ppm (polymer backbone, H^a); δ = 6.5 ppm, δ = 7.6 ppm (aromatic H, H^b); boronic acid hydrogen atoms are not visible due to exchange with water.
Solvent traces: δ = 1.183 ppm, δ = 4.05 ppm (ethyl acetate); δ = 2.01 ppm, δ = 2.82 ppm, δ = 2.98 ppm (DMAc); δ = 2.56 ppm (DMSO); δ = 4.16 ppm (H_2O).
SEC (DMAc, PS CAL): Mn = 23,700 g/mol, PDI = 1.25

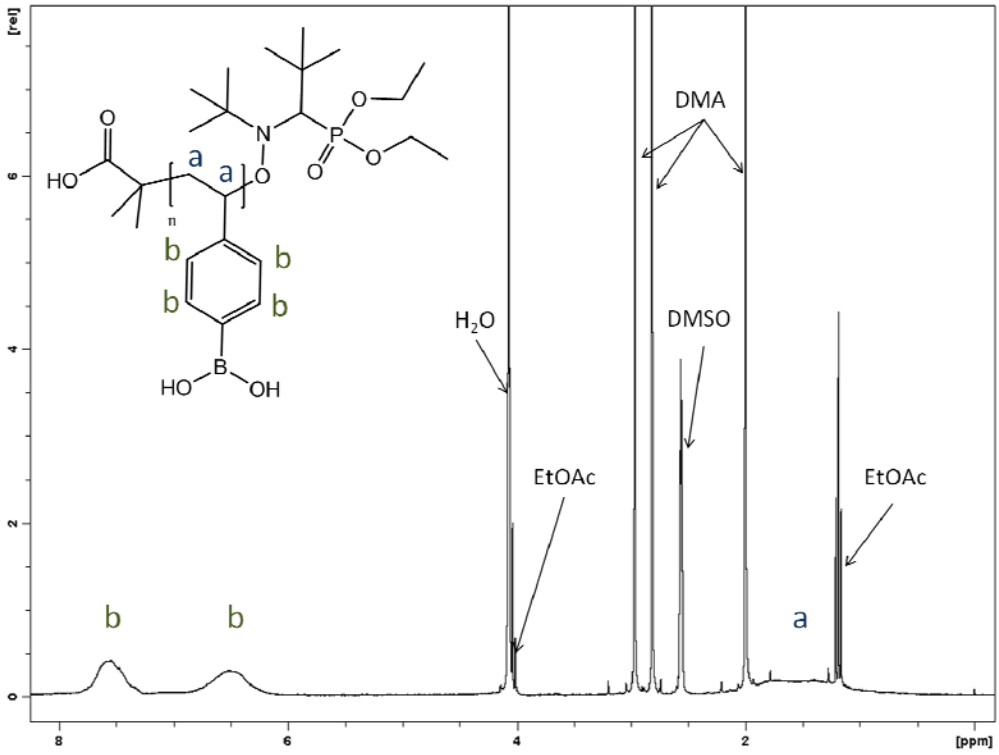


Fig. S2: ^{1}H-NMR spectrum of precipitated poly(4-VBA) obtained by NMP in DMSO-6d with a drop of D_2O.

The monomer conversion was determined by SEC with UV detection at 316 nm, which allows almost exclusive detection of the monomer since the polymer does not significantly absorb at this wavelength due to loss of double bond conjugation upon polymerization. This method was first validated by measuring SEC traces of 4-VBA with various concentrations (60, 45, 30, 15 mg/mL; Fig. S3). Fig. S4 clearly shows the linear dependence of the peak height in function of the monomer concentration and validates that the monomer conversion can be directly calculated based on the peak heights.

The SEC traces obtained for the samples taken during the kinetic study are shown in Fig. S5 and the corresponding non-linear first order kinetic plot of the 4-VBA polymerization by NMP is shown in Fig. S6.

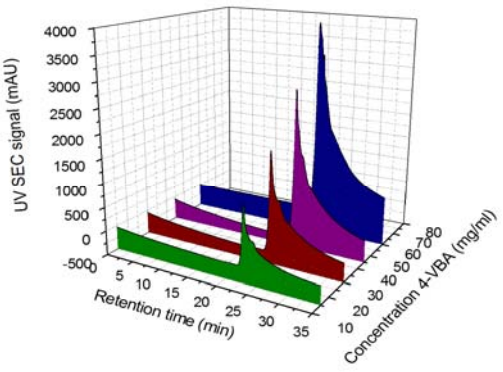


Fig. S3: 3D-plot of UV SEC signal (mAU) at 316 nm in function of 4-VBA concentration (mg/ml) and retention time (min) showing the 4-VBA peak at 23min.

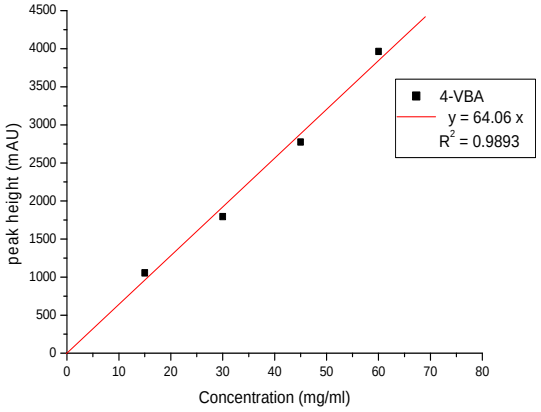


Fig S4. Peak height (mAU) plotted against 4-VBA concentration (mg/ml) and the linear fit to show the linear dependence.

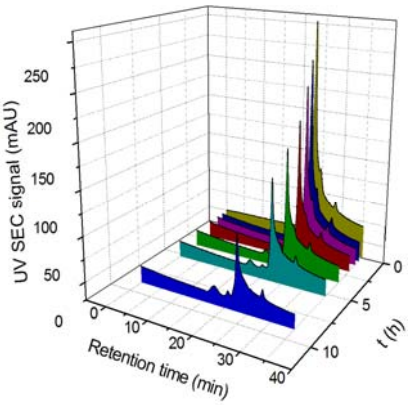


Fig. S5: 3D-plot of UV signal (mAU) at 316 nm in function of sampling time (h) and retention time (min), which shows 4-VBA at 23 min and p-VBA at 17.8 min.

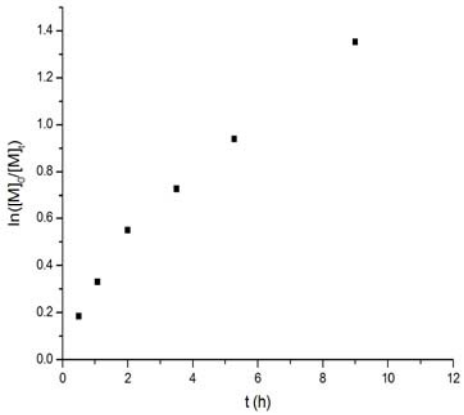


Fig. S6: $ln([M]_0/[M]_t)$ plotted against sampling time t(h) for the kinetic study of 4-VBA with NMP.

4. Synthesis of poly(4-VBA-*co*-DR1-MA) by NMP

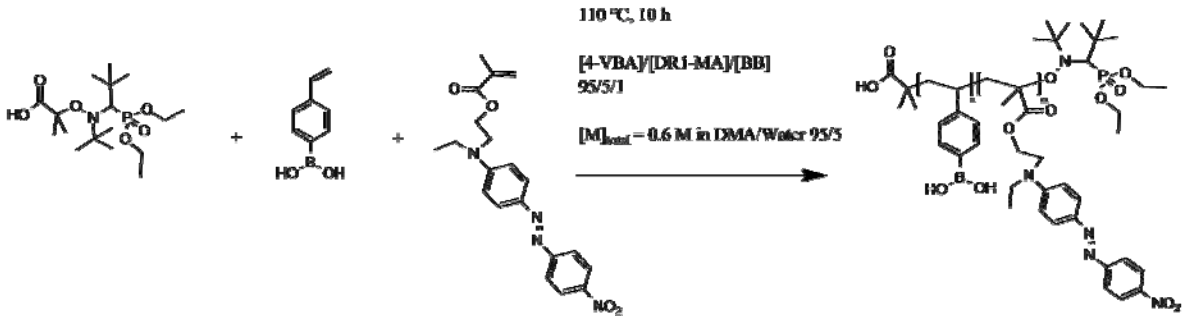


Fig. S7: Schematic overview and reaction conditions for the copolymerization of 4-VBA and DR1-MA by NMP.

Poly(4-VBA-*co*-DR1-MA) was synthesised in solution with a [4-VBA]:[DR1-MA]:[Blocbuilder] ratio of [95]:[5]:[1]. 4-VBA (0.2 g, 1.352 mmol), blocbuilder (5.4 mg, 0.014 mmol) and of DR1-MA (26.3 mg, 0.711 mmol) were dissolved in DMAc/H_2O (2.37 ml, 95/5). After dissolving and degassing, the mixture was heated to 110 °C for 12 h. Afterwards the polymerization mixture was precipitated in a 10-fold excess of cold ethyl acetate and isolated by centrifugation (6000 rpm, 5 °C, 45 min) resulting in a red, glassy solid after drying.

Yield: 0.1238 g, **Conversion:** 51.37 % (gravimetrically)

SEC (DMAc, PS CAL): Mn = 12,600 g/mol, PDI = 1.14

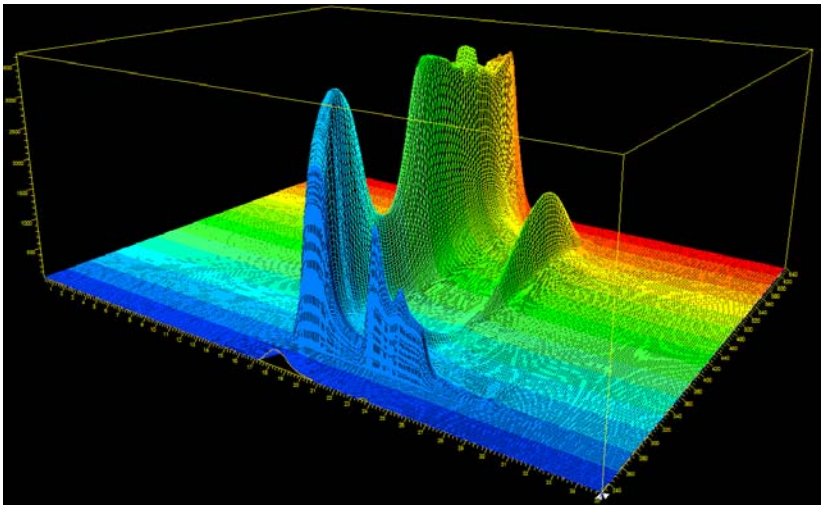


Fig S8: DAD-SEC trace showing the absorbance intensity (µAU) vs. retention time (min) and wavelength (nm) for poly(4-VBA-co-DR1-MA). A minor trace of DR1-MA is also visible, which however is insoluble in water and, thus, will not interfere with sensing studies.

5. Synthesis of poly(4-VBA-*co*-TBTS) by NMP

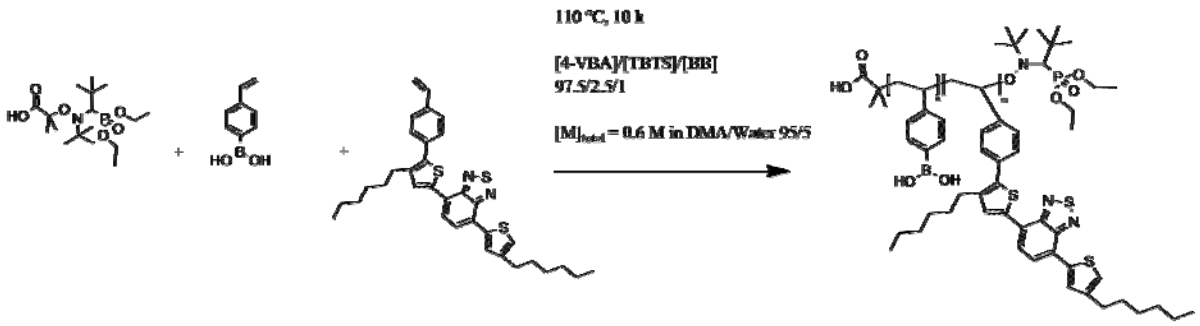


Fig. S9: Schematic overview and reaction conditions for the copolymerization of 4-VBA and TBTS by NMP.

Poly(4-VBA-*co*-TBTS) was synthesised in solution with a [4-VBA]:[TBTS]:[Block builder] ratio of [97.5]:[2.5]:[1]. 4-VBA (0.2 g, 1.352 mmol), block builder (5.4 mg, 0.014 mmol) and TBTS (20.1 mg, 0.035 mmol) were dissolved in DMA/H_2O (2.37 ml, 95/5). After dissolving and degassing, the mixture was heated to 110 °C for 12 h. Afterwards the polymerization mixture was precipitated in a 10-fold excess of cold ethyl acetate and isolated by centrifugation (6000 rpm, 5 °C, 45 min), resulting in a red-orange, glassy solid after drying.
Yield: 0.1356 g, **Conversion:** 58.74 % (gravimetrically)

SEC (DMA, PS CAL): Mn = 18,800 g/mol, PDI = 1.20

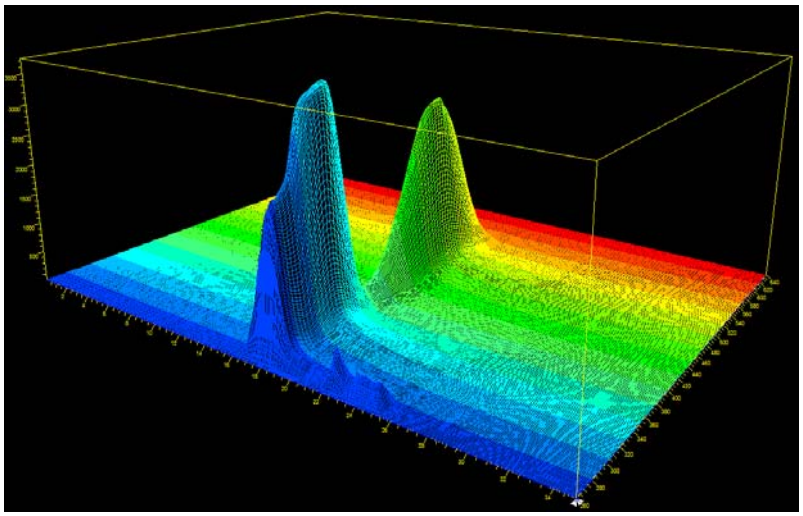


Fig. S10: DAD-SEC trace showing the absorbance intensity (µAU) vs. retention time (min) and wavelength (nm) for poly(4-VBA-co-TBTS).

6. Synthesis of 4-(4-hexyl-5-(4-vinylphenyl)thiophen-2-yl)-7-(4-hexylthiophen-2-yl)-benzo[c][1,2,5]thiadiazole (TBTS)

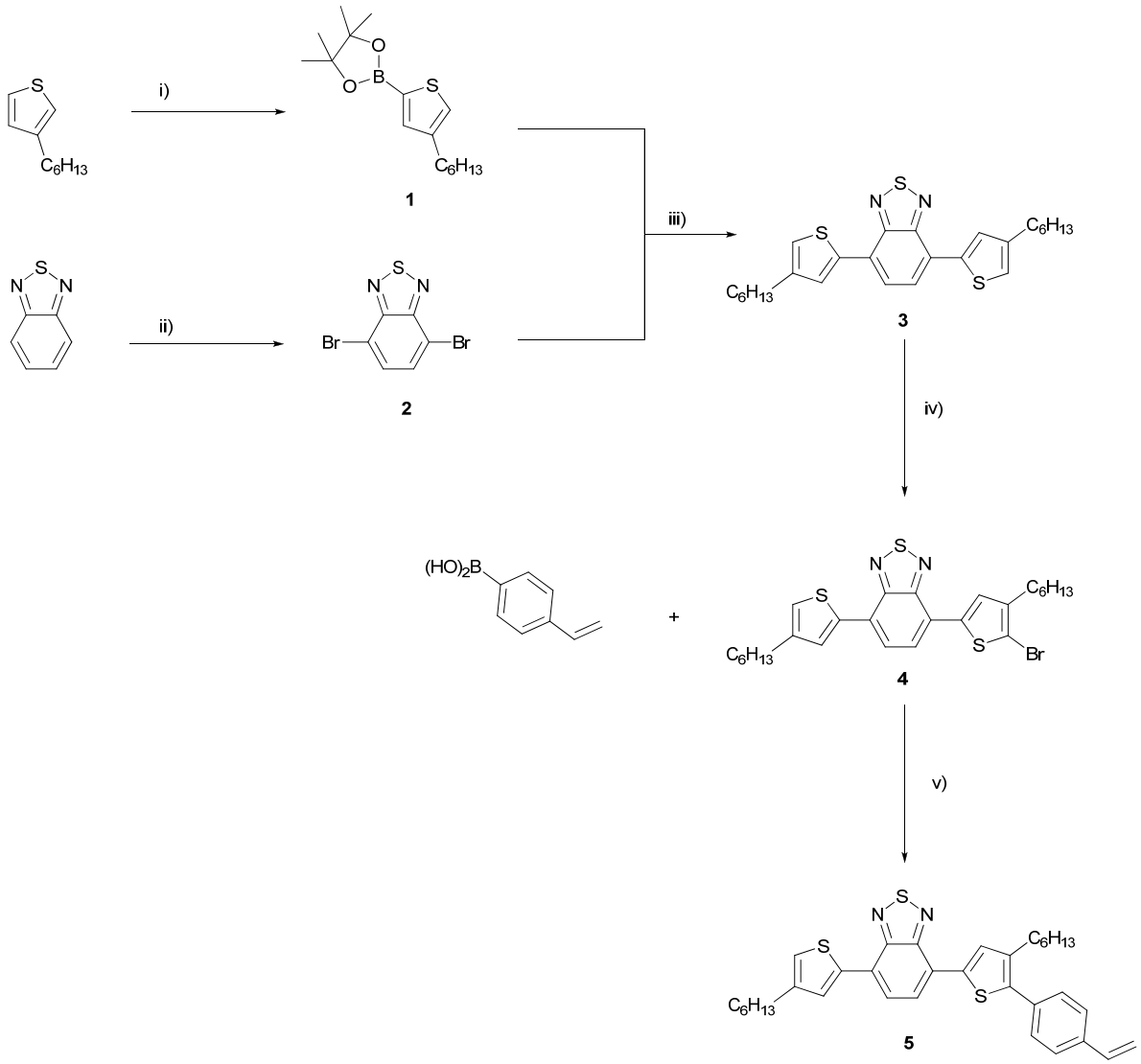


Fig S11: Schematic reaction scheme for the synthesis of TBTS monomer (5): conditions i) t-buthyllithium, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. ii) Br_2, HBr. iii) $Pd(PPh_3)_4$. iv) NBS. v) $Pd(PPh_3)_4$.

6.1 Synthesis of 2-(4-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1)

A solution of 3-hexylthiophene (6 g, 35.65 mmol) in THF (50 ml) at -78 °C was added drop-wise to 22.3 ml (35.65 ml) *tert*-butyllithium (1.6 M in *n*-pentane). The resulting mixture was stirred for 2 h at -78 °C and afterwards 2-*iso*propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7.3 ml, 35.65 mmol) was added in one portion by using a syringe. After stirring an additional hour at -78 °C the reaction mixture was warmed to room temperature and stirred overnight. The reaction was stopped by adding 30 ml of saturated aqueous ammonium chloride solution followed by the addition of 50 ml diethyl ether. The organic phase was washed three times with 200 ml water and dried over magnesium sulfate. The solvent was evaporated and no further purification was carried out (yield 9.96 g, 95 %).

IR $\nu_{max.}$ (cm^{-1}): 2974 (C=C-H); 2929; 2857 (C-C-H); 1545; 1445 (C=C); 1380; 1326; 1270; 1214; 1144; 1027; 961; 854; 772; 685.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 (d, *J* = 1.0 Hz, 1H); 7.21 (d, *J* = 0.8 Hz, 1H); 2.63 (t, 2H); 1.62 (m, 2H); 1.34 (s, 12H); 1.32 – 1.28 (m, 6H); 0.90 (t, *J* = 4.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 144.85; 138.63; 127.68; 84.12; 77.37; 77.16; 76.95; 31.81; 30.77; 30.12; 29.12; 27.06; 24.90; 24.75; 22.72; 14.21.

GC-MS (EI) $C_{16}H_{27}BO_2S$ (*m/z*): calcd. For 294.3; found 294.3.

Elem. Anal. Calcd for $C_{16}H_{27}BO_2S$: C 65.31%; H 9.25%; O 10.87%; S 10.90%. Found: C 65.44%; H 8.97%; O 10.64%; S 10.94%.

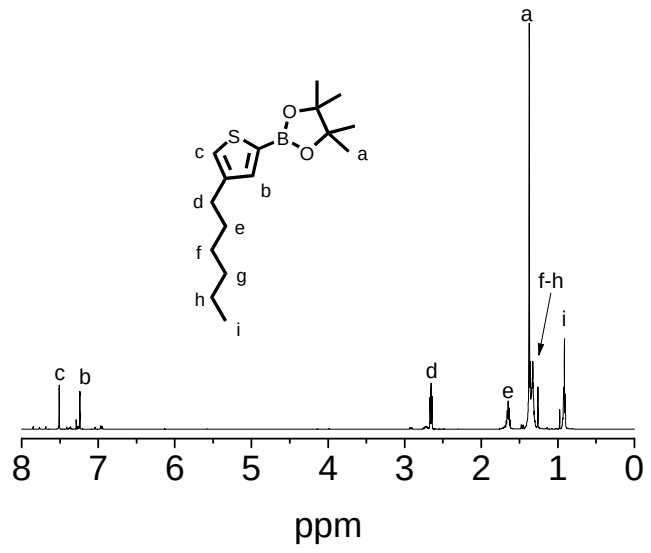


*Fig. S12: ^{1}H-NMR spectrum of **1**.*

6.2 Synthesis of 4,7-dibromobenzothiadiazole (2)

To a solution of benzothiadiazole (10 g, 73.4 mmol) in HBr (150 ml, 48 %) was added drop-wise and fairly slow a solution containing Br_2 (35.2 g, 220.3 mmol) in HBr (100 ml). After complete addition the reaction mixture was heated at reflux for 6 h. The solution was then allowed to cool to room temperature and any access of Br_2 was compensated by addition of a saturated solution of $NaHSO_3$. The resulting precipitate was filtered and washed with cold diethyl ether (yield 20.7 g, 95 %).

IR $\nu_{max.}$ (cm^{-1}): 3079; 3046; 2993; 2965 (C=C-H); 1874; 1857; 1666; 1498 (C=C); 1272; 1206.

^1H NMR (600 MHz, $CDCl_3$): δ 7.72. ^{13}C NMR (151 MHz, $CDCl_3$): δ 153.13; 132.49; 114.07.

GC-MS $C_6H_2N_2S$ (*m/z*): calcd for 293.91. Found 293.9.

Elem. Anal. Calcd for $C_6H_2N_2S$: C 24.51%; H 0.69%; N 9.53%; S 10.91%. Found C 24.97%; H 0.88%; N 9.44%; S 10.93%.

6.3 Synthesis of 4,7-*bis*(4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (3)

Compounds **1** (8 g, 27.19 mmol), **2** (2.6 g, 9.06 mmol) and $Pd(PPh_3)_4$ (0.63 g, 6 mol%) were dissolved in toluene (180 ml) and aqueous solution of K_2CO_3 (120 ml, 2M) was added. The reaction mixture was stirred for 24 h at 90 °C and then cooled to ambient temperatures followed by addition of chloroform (200 ml). The organic layer was washed three times with water (200 ml) and dried over magnesium sulfate. After the solvent was removed the product was purified by silica gel column chromatography (*n*-hexane/chloroform 4/1 *v*/*v*) to yield **3** (3.42 g) as orange needles (yield 80%).

IR $\nu_{max.}$ (cm^{-1}): 3095; 3011 (C=C-H); 2954; 2920; 2849 (C-C-H); 1492; 1450 (C=C; C=N); 1189.

^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 1.3 Hz, 2H); 7.83 (s, 2H); 7.04 (d, J = 1.1 Hz, 2H); 2.66 (m, 4H); 1.70 (m, 4H); 1.38 (m, 12H); 0.89 (t, J = 4.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.82; 144.53; 139.17; 129.17; 128.44; 126.21; 125.69; 125.16; 121.68; 119.90; 118.86; 77.48; 77.16; 76.84; 31.86; 31.84; 30.82; 30.68; 30.63; 30.51; 30.44; 29.20; 29.16; 22.79; 22.76; 14.25.

APLI-MS calcd for $C_{26}H_{32}N_2S_3$ (*m/z*): 468.17. Found 468.15.

Elem. Anal. Calcd. For $C_{26}H_{32}N_2S_3$: C 66.62%; H 6.88%; N 5.98%; S 20.52%. Found C 66.61%; H 7.56%; N 5.92%; S 21.54%.

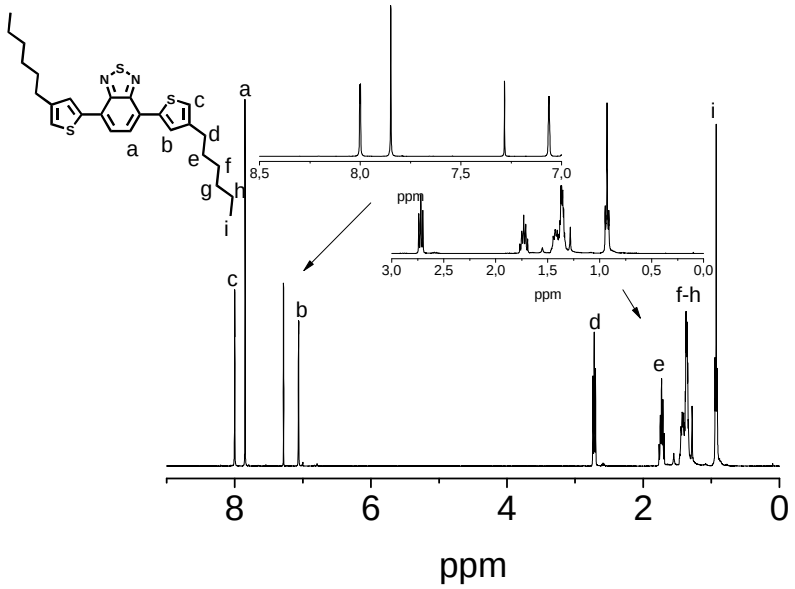
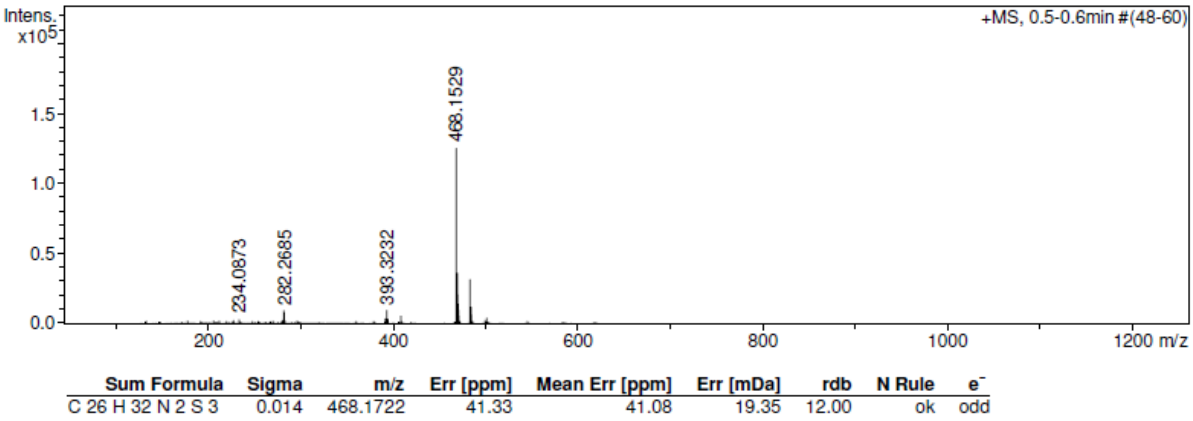


*Fig. S13: ^{1}H-NMR spectrum of **3**.*



Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 26 H 32 N 2 S 3	0.014	468.1722	41.33	41.08	19.35	12.00	ok	odd

*Fig. S14: APLI MS spectra of **3**.*

6.4 Synthesis of 4-(5-bromo-4-hexylthiophen-2-yl)-7-(4-hexylthiophen-2-yl)-benzo[c][1,2,5]thiadiazole (4)

Compound **3** (2 g, 4.26 mmol) was dissolved in dichloromethane (100 ml) and acetic acid (100 ml) and cooled to 0 °C. Then *N*-bromosuccinimide (0.68 g, 3.84 mmol) in dichloromethane (50 ml) was added slowly *via* dropping funnel. The reaction mixture was then stirred for 2 h followed by the addition of chloroform (100 ml). The organic phase was washed with a saturated aqueous solution of $NaHCO_3$ (200 ml) and water (200 ml) and dried over magnesium sulfate. After evaporation and purification by silica gel column chromatography (*n*-hexane) the product was obtained as orange needles (1.3 g, 62%).

IR $\nu_{max.}$ (cm^{-1}): 3097; 3053; 3019 (C=C-H); 2951; 2923; 2852 C-C-H); 1539; 1489; 1462 (C=C; C=N); 1188.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 1.3 Hz, 1H); 7.81 (d, *J* = 7.6 Hz, 1H); 7.76 (s, 1H); 7.75 (d, *J* = 7.7 Hz, 1H); 7.05 (d, *J* = 0.9 Hz, 1H); 2.69 (t, *J* = 7.7 Hz, 2H); 2.64 (t, *J* = 7.7 Hz, 2H); 1.69 (m, 4H); 1.38 (m, 12H); 0.91 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.70; 152.53; 144.60; 143.17; 139.02; 138.83; 129.35; 128.06; 126.54; 125.55; 125.16; 121.90; 111.51; 31.86; 31.80; 30.80; 30.63; 29.90; 29.85; 29.20; 29.12; 22.77; 14.25.

APLI-MS calcd. For $C_{26}H_{31}BrN_2S_3$ (*m/z*): 548.10. Found 548.10.

Elem. Anal. Calcd. For $C_{26}H_{31}BrN_2S_3$: C 57.02%; H 5.71%; N 5.12%; S 17.57%. Found C 57.25%; H 5.86%; N 5.13%; S 18.11%.

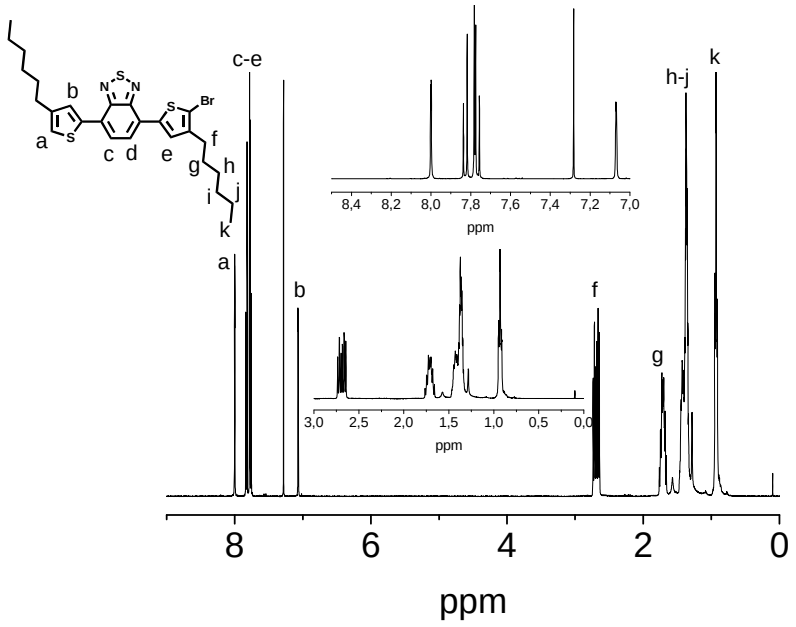


*Fig. S14: ^{1}H-NMR spectra of **4**.*

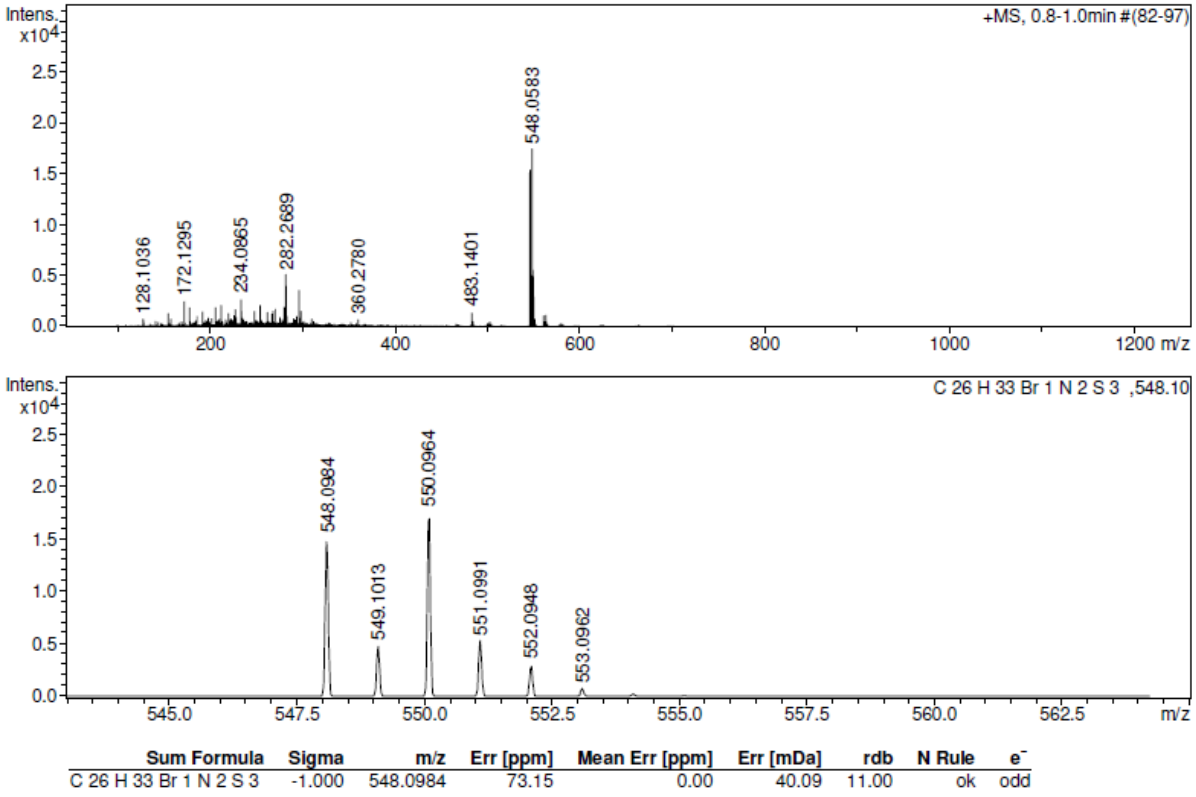


Fig. S15: APLI MS spectra of ***4****.*

6.5 Synthesis of 4-(4-hexyl-5-(4-vinylphenyl)thiophen-2-yl)-7-(4-hexylthiophen-2-yl)-benzo[c][1,2,5]thiadiazole (5)[6]

A solution of 4-vinylphenylboronic acid (0.405 g, 2.739 mmol), compound **4** (1 g, 1.826 mmol) and $(PdPPh_3)_4$ (0.189 g, 6 mol%) in 60 ml toluene and 60 ml aqueous K_2CO_3 solution (2M) was heated to 90 °C and stirred overnight. The reaction mixture was then cooled to ambient temperature and was taken in chloroform. The organic phase was washed three times with 100 ml water and dried over $MgSO_4$. The solvent was removed by reduced pressure and further purification by column chromatography (*n*-hexane/dichloromethane 4:1) yielded a red powder (67 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (1 H, s), 7.98 (1 H, s), 7.83 (1 H, d, *J* 4.2), 7.54 – 7.46 (2 H, m), 7.04 (1 H, s), 6.77 (1 H, dd, *J* 17.6, 10.9), 5.82 (1 H, d, *J* 17.6), 5.31 (1 H, d, *J* 10.9), 2.78 – 2.73 (1 H, m), 2.72 – 2.67 (1 H, m), 1.77 – 1.66 (2 H, m), 1.46 – 1.24 (8 H, m), 0.93 – 0.86 (4 H, m, *J* 10.5, 6.8).

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.82, 152.78, 144.53, 140.12, 139.40, 139.20, 137.43, 136.94, 136.51, 134.13, 130.49, 129.45, 129.16, 126.55, 126.14, 125.90, 125.70, 125.40, 121.69, 114.35, 31.87, 31.80, 31.13, 30.82, 30.63, 29.40, 29.21, 29.17, 22.79, 14.26, 14.23. APLI-MS calcd for $C_{34}H_{38}N_2S_3$(*m/z)*: 570.22. Found 570.22.

Elem.Anal. Calcd for $C_{34}H_{38}N_2S_3$: C 71.53; H 6.71; N 4.91; S 16.85. Found C 71.95; H 6.90; N 4.62; S 16.53.

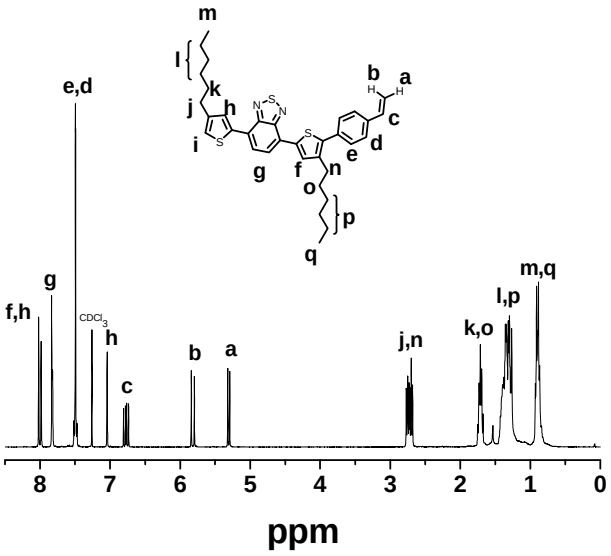
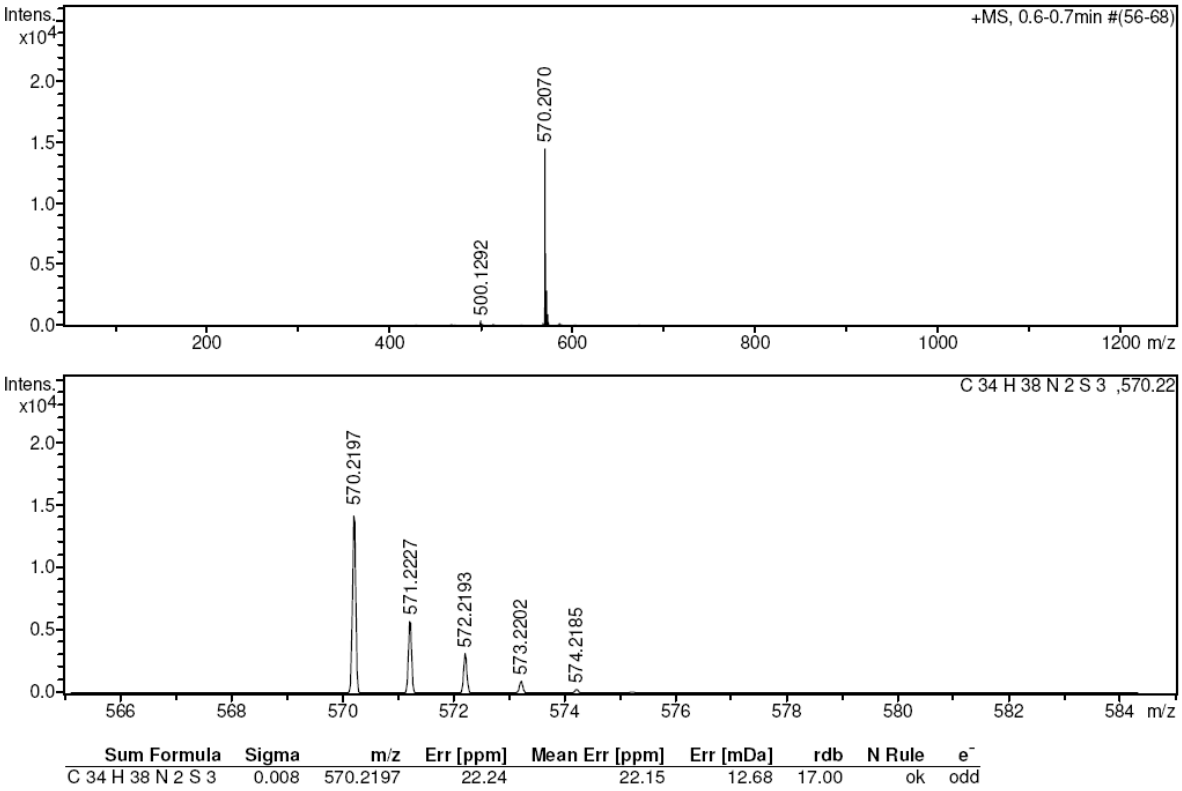


*Fig. S16: ^{1}H-NMR spectra of TBTS (**5**).*



Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 34 H 38 N 2 S 3	0.008	570.2197	22.24	22.15	12.68	17.00	ok	odd

*Fig. S17: APLI MS spectra of TBTS (**5**).*

7. Solvatochromic properties of TBTS

The solvatochromic properties of TBTS were evaluated by measuring the UV-VIS spectra and the fluorescent excitation and emission spectra in 5 different solvents. The solvents were selected to cover a broad range of polarities, including (with increasing polarity) n-hexane, toluene, dichloromethane, acetone and DMAc. The pictures of these solutions (Fig. S18) already clearly indicate a solvatochromic behaviour but whether this is due to changing adsorption or emission bands cannot be concluded.

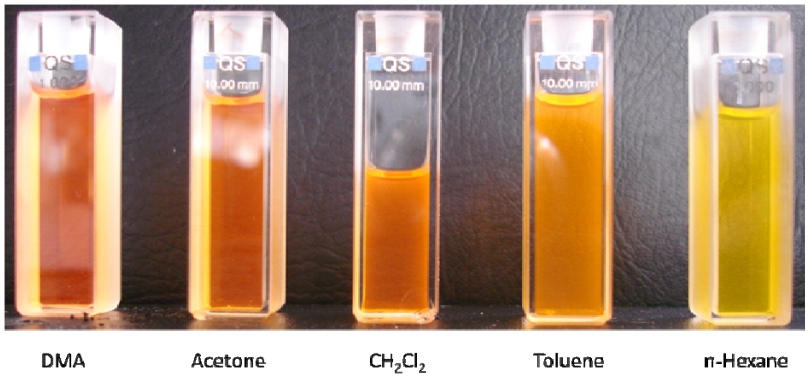


Fig. S18: Picture of TBTS in different solvents.

7.1 UV-vis solvatochromic behaviour

Solutions of TBTS with equal concentrations in different solvents showed quite different extinction coefficients in different solvents (Table S1). The overlay of the normalized UV-VIS spectra (Fig. S19) revealed almost no difference in the maximum absorption wavelengths for the different solvents and no clear trend could be identified, demonstrating that TBTS has no solvatochromic absorption behaviour.

Table S1. Extinction coefficients and maximum absorption wavelengths for TBTS in different solvents.

Solvent	ε	$\lambda_{max,1}$ (nm)	$\lambda_{max,2}$ (nm)
DMA	38.85	478	330
Acetone	21.01	472	334
Dichloromethane	8.93	472	322
Toluene	2.38	476	329
n-Hexane	1.89	475	324

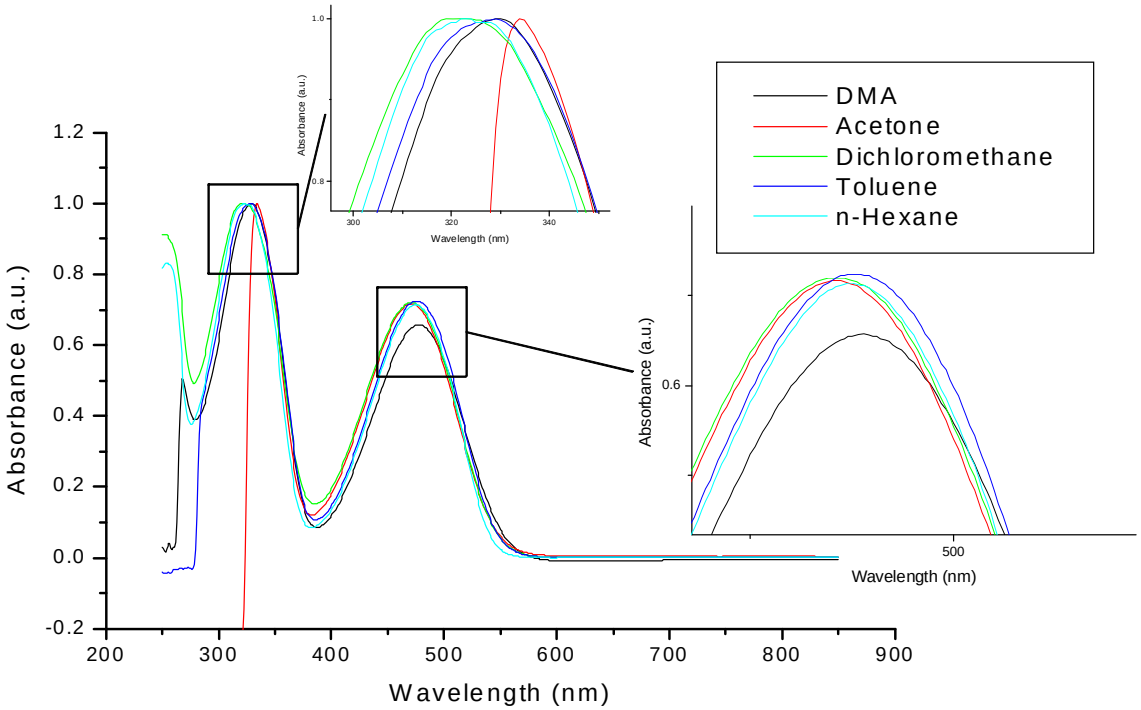


Fig. S19: Overlay of the UV-VIS spectra of TBTS in 5 different solvent.

7.2 Fluorescence solvatochromic behaviour

The solvatochromic behaviour of TBTS was measured in different solvents using a fixed excitation wavelength of 449 nm revealing that the maximum emission wavelength shifts from 564 nm in *n*-hexane to 620 nm in DMAc (Fig. S20). The shift in maximum emission wavelength increases with increasing dielectric constant of the solvent (Fig. S21). This observed emission trend represents a clear positive solvatochromic shift demonstrating that TBTS can be used as solvatochromic fluorescent dye. This shift is similar to the shift reported for 5-dimethylamino-5'-nitro-2,2'-bithiophene, which suggests that the mechanisms of solvatochromism for this reported thiophene containing dye and TBTS are similar. The presence of the benzothiadazole and the absence of pronounced electron donating and accepting groups will, however, reduce the solvatochromic shift of TBTS compared to 5-dimethylamino-5'-nitro-2,2'-bithiophene.[7]

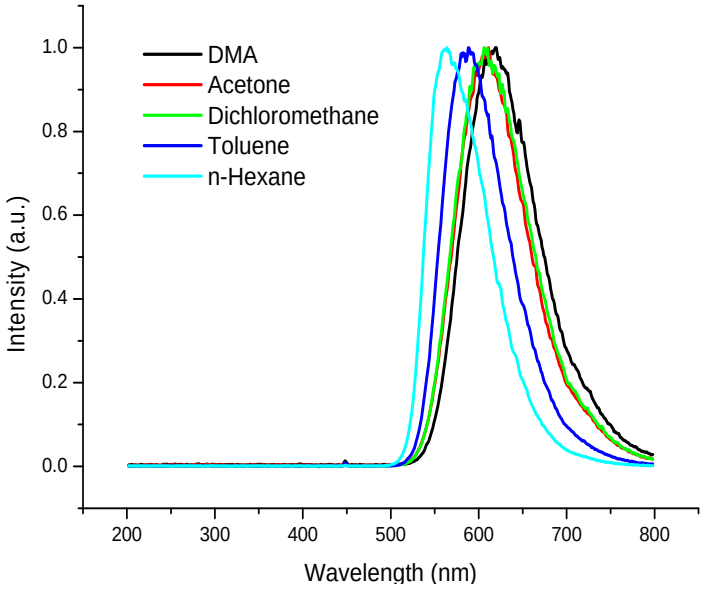


Fig. S20: Overlay of the emission spectra with fixed excitation wavelength at 449 nm.

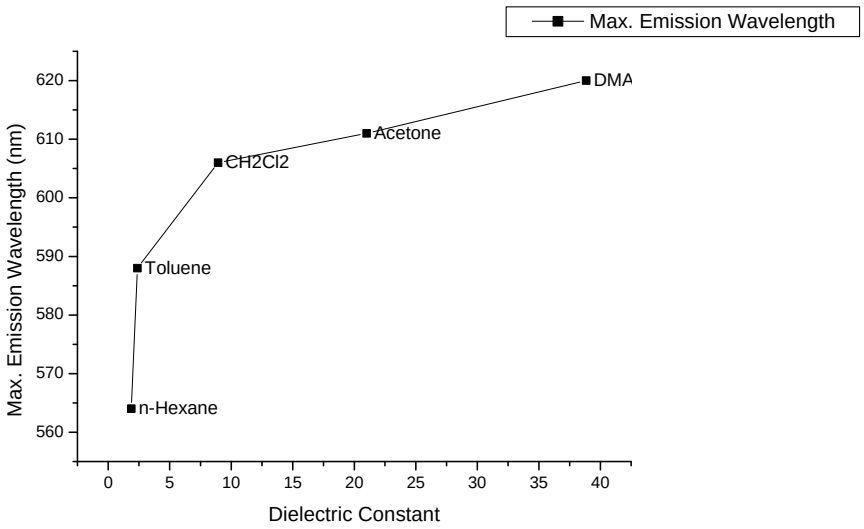


Fig. S21: Emission wavelength (nm) in function of dielectric constant.

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