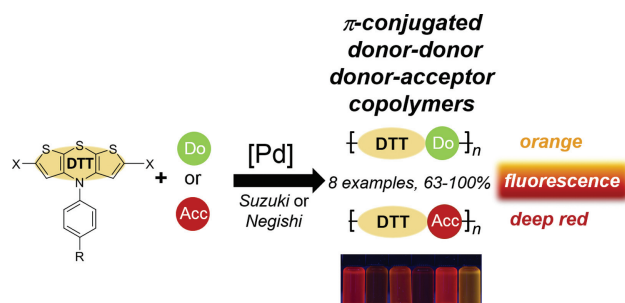# Dithienothiazine Copolymers – Synthesis and Electronic Properties of Novel Redox-Active Fluorescent Polymers

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π-conjugated donor-donor donor-acceptor copolymers

[Pd]
Suzuki or Negishi

8 examples, 63–100%

orange fluorescence deep red

Abstract Dithienothiazine copolymers are efficiently obtained by Suzuki polymerization or in situ lithiation–Negishi polymerization in good to excellent yields. Gel permeation chromatography was applied to characterize the dispersities and degrees of polymerization of these novel materials. Thermogravimetric analysis shows that the copolymers are stable towards side-chain cleavage up to 200 °C. The materials are deep red to black amorphous solids or resins and their absorption and emission spectra in solution reveal broad absorption bands in the visible and orange to deep red luminescence upon UV excitation. According to the optical band gaps these novel copolymers qualify as a new class of low band gap organic semiconductors.

Introduction

Organic macromolecules with π-conjugated ligation throughout the backbone, so-called π-conjugated polymers, can become electrical (semi)conductors upon doping with oxidants (p-doping) or reductants (n-doping).[1] Although conjugated organic polymers have been known for more than 150 years, it was not before the early 1960s that their conductivity was first discovered.[2] In the past decades, they have conquered numerous applications, such as molecular electronics,[3] photocatalysis,[4] biomedical applications,[5] and organic photovoltaics.[6] Among these π-conjugated polymers, regioregular narrow band gap polymers containing alternating donor and acceptor

moieties have aroused interest for use in plastic electronics.[7]

As donor components, ensuring high lying HOMO energies and generation of stable radical cations upon oxidation with triarylamines[8] and thiophene motifs[9] have received significant prominence as hole transporters. Furthermore, S,N-containing tricycles, such as 3,7-disubstituted phenothiazines, exhibit fully reversible one-electron oxidations at low potentials,[10] extraordinarily stable radical cations,[11] and pronounced luminescence. For instance, organic light-emitting diodes[12] as well as redox switchable luminophores[13] have been developed based on oligomeric and polymeric phenothiazines.

Just very recently, we have introduced dithieno[1,4]thiazines, electron-density enriched congeners of phenothiazines,[14] which even have lower oxidation potentials with higher radical cation stability, as novel types of donors for organic chromophores and electrophores.[15] The paramount practical advantage of dithieno[1,4]thiazines over phenothiazines is their ready functionalization in the α,α'-positions of the thieno cores. Based upon versatile transformations by lithiation-electrophilic trapping sequences,[16] halogenated and organometallic build blocks became accessible, which were employed to the efficient synthesis of dithienothiazine dimers, trimers and homopolymers.[17] Here, we report on the synthesis and characterization of dithienothiazine copolymers based upon Suzuki and Negishi polymerization as well as on the electronic properties of these polymers.

Results and Discussion

Synthesis and Polymer Characterization

For ensuring high solubility in common organic solvents, we decided to introduce *p*-phenoxy to an aliphatic swallow tail in the *4H*-dithieno[2,3-b:3',2'-e][1,4]thiazine **1**

Scheme 1 Synthesis of *syn,syn*-dithienothiazine starting materials **1** and **2**.
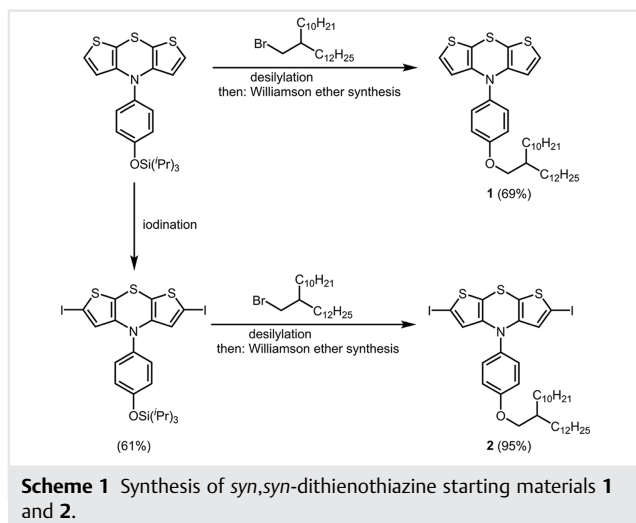
(conveniently we will abbreviate this unit as *syn,syn*-dithienothiazine since the sulfur atoms are in a *syn–syn* relationship). Starting with a TIPS-protected precursor that is obtained in good yield via (5 + 1)-Buchwald–Hartwig cyclization, compound **1** is directly formed by one-pot fluoride-induced desilylation and Williamson ether synthesis, whereas for the diiodo derivative **2** the TIPS-protected precursor is first selectively iodinated followed by one-pot desilylation–etherification synthesis (Scheme 1).[17]

With dithienothiazine monomers **1** and **2** in hand, we synthesized dithienothiazine copolymers **4** by Suzuki polymerization of diiodo dithienothiazine **2** and (hetero)-aryl bis(boronate) **3** (Scheme 2) and by Negishi polymerization in situ dilithiated dithienothiazine **1** and diiodo (hetero)arene **5** (Scheme 3) as dark red to black solids or resins in good to excellent yields.
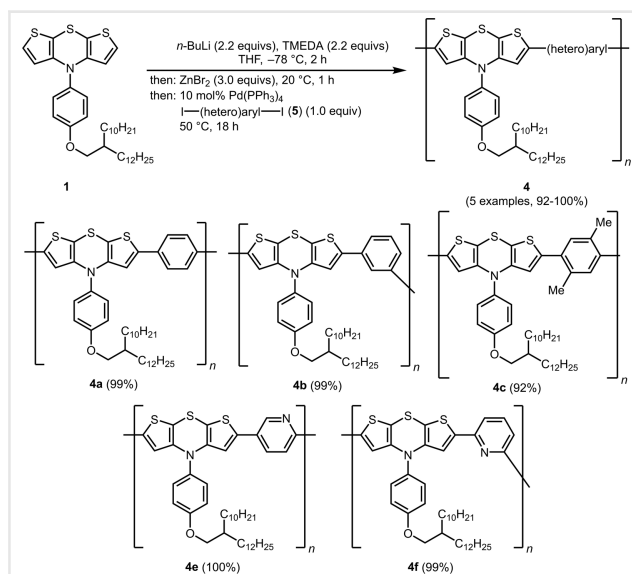
The novel dithienothiazine copolymers **4** were characterized by IR spectroscopy and gel permeation chromatography (GPC).[18] For the THF-soluble copolymers **4a**, **4b**, **4c**, **4e**, **4f**, and **4h**, ^{1}H and ^{13}C NMR spectra were recorded showing broad, poorly resolved signals, yet, showing approximate integral ratios that support the corresponding proposed ligation. For some polymers prepared by the Negishi polymerization protocol, residual TMEDA stemming from the lithiation of monomer **1**, which cannot be completely removed by multiple suspension–sonication cycles and extensive high vacuum drying, is discernable in the NMR spectra. MALDI TOF mass spectra rather revealed several molecular peaks for short oligomers with various end groups, such as pinacolyl boryl or iodo substituents.

GPC in THF with polystyrene as a standard[19] allows determining the number average molecular weight (M_n), the weight average molecular weight (M_w), the molecular weight of the detector signal maximum (M_p) as well as the dispersity $Đ_M = M_w/M_n$ and the degree of polymerization DP. For the interpretation the globular structure of
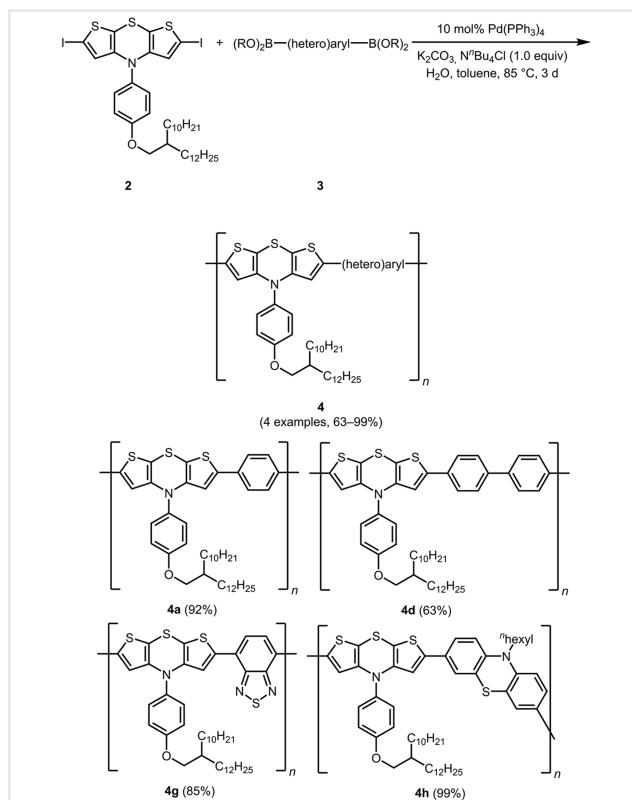
Scheme 2 Suzuki polymerization synthesis of dithienothiazine copolymers **4**.

polystyrene chains in comparison to the bacillary nature of poly(dithienothiazines) has to be taken into account, overestimating the molecular weights of poly

Scheme 3 Negishi polymerization synthesis of dithienothiazine copolymers **4**.

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Table 1 Molecular weight distributions of the copolymers **4** according to GPC (eluent THF, flow rate 1 mL/min, T = 293 K)

Polymer	Molecular weight [Da]				Dispersity	Degree of polymerization
	$M_0{}^a$	$M_n{}^b$	$M_w{}^c$	$M_p{}^d$	$Đ_M{}^e$	DP^f
4a^g	714.1	$3.76 \cdot 10^3$	$6.22 \cdot 10^3$	$9.47 \cdot 10^3$	1.65	8.7
4a^h		$5.93 \cdot 10^3$	$8.96 \cdot 10^3$	$6.74 \cdot 10^3$	1.51	12.5
4b^h	714.1	$3.74 \cdot 10^3$	$6.14 \cdot 10^3$	$1.64 \cdot 10^3$	1.64	8.6
4c^h	742.2	$4.24 \cdot 10^3$	$7.27 \cdot 10^3$	$1.78 \cdot 10^3$	1.71	9.8
4d^g	790.2	$1.04 \cdot 10^4$	$1.65 \cdot 10^4$	$1.61 \cdot 10^4$	1.59	20.9
4e^h	715.1	$8.41 \cdot 10^3$	$1.41 \cdot 10^4$	$1.72 \cdot 10^4$	1.68	19.7
4f^h	715.1	$4.44 \cdot 10^3$	$6.02 \cdot 10^3$	$3.79 \cdot 10^3$	1.35	8.4
4g^g	772.2	$2.46 \cdot 10^3$	$2.95 \cdot 10^3$	$2.46 \cdot 10^3$	1.20	3.8
4h^g	919.5	$1.01 \cdot 10^4$	$1.37 \cdot 10^4$	$1.50 \cdot 10^4$	1.36	14.9

$^a M_0$: molecular weight of the repeating unit.
$^b M_n$: number average molecular weight.
$^c M_w$: weight average molecular weight.
$^d M_p$: molecular weight of the detector signal maximum.
$^e Đ_M = M_w/M_n$: dispersity.
^{f}DP $= M_w/M_0$: degree of polymerization.
^{g}Suzuki polymer synthesis.
^{h}Negishi polymer synthesis.

(dithienothiazines). The GPC data of the copolymers **4** are summarized in Table 1.

The average molecular weights of the dithienothiazine copolymers **4** fall into a range between 3000 and 18000 g/mol. In the GPC traces of copolymers **4a**, **4b**, **4c**, **4g**, **4e**, and **4f**, lower oligomers are also visible (Figure 1).
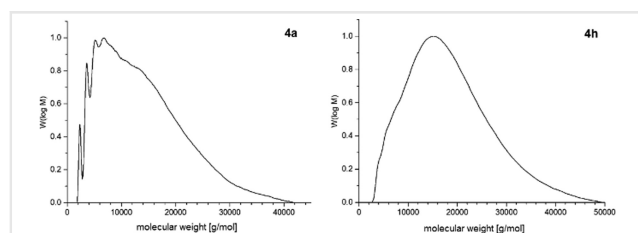
Figure 1 Representative GPC traces of copolymers **4a** (left) and **4h** (right) (eluent THF, flow rate 1 mL/min, T = 293 K).

Thermal Properties

The copolymers **4a** and **4d**–**h** were furthermore investigated by thermogravimetric analysis for obtaining an insight into their thermal stability (Table 2). Our interest was focused on the stability of the N-substituent towards thermal cleavage. After extrusion of solvent residues above 100 °C, all investigated copolymers **4** are thermally stable up to a temperature of 205 °C. While copolymer **4f** starts to decompose at 205 °C, copolymer **4d** only starts to decompose above 275 °C. In the range of 350 to 395 °C, the pyrolytic cleavage of the solubilizing swallowtail

**Table 2** Thermogravimetric analysis of copolymers **4**

Copolymer	Decomposition			Weight loss [%]	Molecular mass percentage of the swallowtail [%]
	Start [°C]	Maximum [°C]	End [°C]		
4a	235	360	495	47.12	47.1
4d	275	365	500	40.97	42.6
4e	250	395	485	50.60	47.0
4f	205	350	480	48.05	47.0
4g	220	380	450	43.53	43.6
4h	230	380	450	44.61	45.9^a

^{a}With concomitant cleavage of the phenothiazine's hexyl chain.

proceeds. This is indicated, depending on the corresponding copolymer **4**, by a loss of weight between 40.97 and 50.60%, in accordance with the proportional molecular weight of the swallowtail. At temperatures between 450 and 500 °C, the pyrolytic cleavage of the swallowtail ceases.

Electronic Properties

The electronic properties of the dithienothiazine copolymers **4** were investigated by cyclic voltammetry and absorption and emission spectroscopy. Upon comparison of the cyclic voltammograms of copolymers **4** with the CV of the previously reported dithienothiazine homopolymer,[17] a similar behavior becomes apparent. Only broad oxidation and reduction waves are displayed, which cannot be elaborated further (Figure 2).
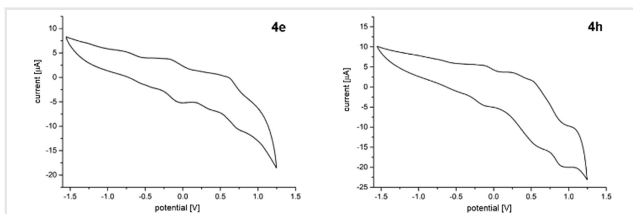
Figure 2 Cyclic voltammograms of dithienothiazine copolymers **4e** (left) and **4h** (right) (recorded in CH_2Cl_2, $T = 293$ K, 0.1 m electrolyte [$^nBu_4N$][PF_6]; $v = 100$ mV/s; Pt working electrode, Ag/AgCl reference electrode and Pt counter electrode).

The solutions of copolymers **4a**, **4b**, **4c**, **4e**, **4f**, and **4h** are orange to red under daylight and they fluoresce with orange to deep red color under the handheld UV lamp (Figure 3).
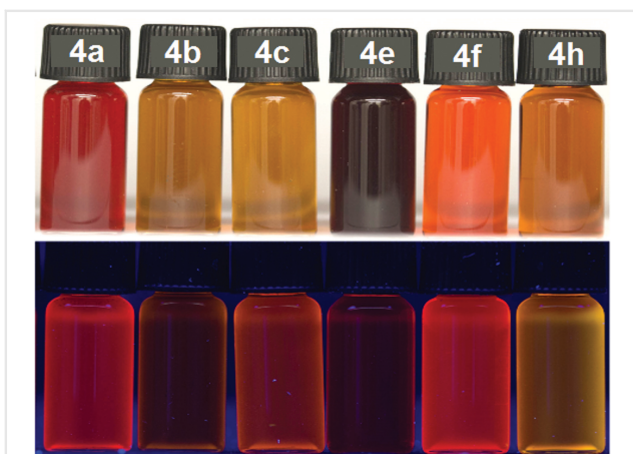
Figure 3 Solutions of selected dithienothiazine copolymers **4** (recorded in CH_2Cl_2, $T = 293$ K, $c(\mathbf{4}) = 10^{-6}$ M, under daylight (top) and under the handheld UV lamp, $\lambda_{exc} = 365$ nm).

Absorption and emission spectra of the dithienothiazine copolymers **4** were recorded in dichloromethane or in THF, depending on the solubility (Table 3, Figure 4). For copolymer
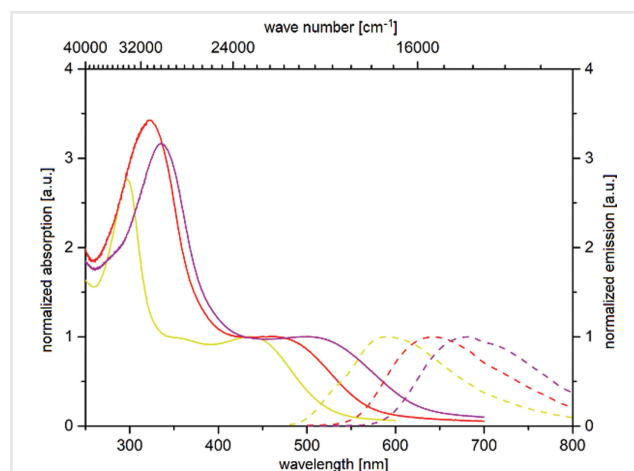
Figure 4 Normalized absorption (solid lines) and emission (dashed lines) spectra of copolymers **4a** (red lines), **4e** (magenta lines), and **4h** (yellow lines) (absorption spectra recorded in CH_2Cl_2, $T = 293$ K, $c(\mathbf{4}) = 10^{-5}$ M; emission spectra recorded in CH_2Cl_2, $T = 293$ K, $c(\mathbf{4}) = 10^{-5}$ M, $\lambda_{exc} = 470$ nm).

4a, the absorption bands essentially are at the same energy in both solvents, dichloromethane and THF. Only the emission maximum experiences a slight redshift upon changing from THF to the polar solvent dichloromethane.

All copolymers **4** possess two characteristic absorption bands, the higher energy absorptions fall into a range from 291 to 336 nm and lower energy longest wavelength absorption band appears in a broad range from 436 to

Table 3 Selected absorption and emission data of dithienothiazine copolymers **4**

	Solvent	$\lambda_{max,abs}$ [nm] (ε [L mol^{-1} cm^{-1}])[a]	$\lambda_{max,em}$[nm][b]	Stokes shift $\Delta_{\tilde{\nu}}$ [cm^{-1}][c]	$\Delta E_{opt(HOMO-LUMO)}$ (E_{0-0})[d] [eV (nm)]
4a	CH_2Cl_2	322 (18100), 461 (5300)	643	6100	2.18 (569)
4a	THF	322 (22200), 461 (6700)	631	5800	2.21 (562)
4b	CH_2Cl_2	295 (26300), 442sh (3600)	608	6200	2.29 (542)
4c	CH_2Cl_2	291 (21600), 437 (4000)	637	7200	2.24 (553)
4d	THF	328 (26200), 471 (8700)	628	5300	2.19 (565)
4e	CH_2Cl_2	336 (21000), 501 (6600)	681	5300	2.03 (610)
4f	CH_2Cl_2	316 (17600), 465 (3400)	640	5900	2.18 (570)
4g	THF	300 (21600), 747 (11200)	–	–	–
4h	CH_2Cl_2	297 (42800), 436 (15500)	587	5900	2.40 (516)

[a]Recorded at $T = 293$ K, $c(\mathbf{4}) = 10^{-5}$ M.
[b]Recorded at $T = 293$ K, $c(\mathbf{4}) = 10^{-6}$ M, $\lambda_{exc} = 470$ nm.
[c]$\Delta_{\tilde{\nu}} = \lambda_{max,abs}^{-1} - \lambda_{max,em}^{-1}$ [cm^{-1}].
[d]E_{0-0} was determined at the intersection of the corresponding normalized absorption and emission bands.[20]

747 nm. Expectedly, an electron-withdrawing bridging unit, such as 2,5-pyridylene or 4,7-benzothiadiazolylene, causes a considerable bathochromic shift in comparison to electron neutral or electron-donating bridging units. Therefore, most blueshifted is the absorption band of the electron-rich dithienothiazine–phenothiazine copolymer **4h**.

Most distinctly, the emission maxima of the dithieno-thiazine copolymers **4** appear in a range from 587 to 681 nm, again in agreement with the electronic nature of the bridging unit. In contrast to many simple dithienothiazines with 2,6-diaryl substitution, which are only weakly luminescent,[16a] this novel type of low-band gap polymers is intensely luminescent with orange to deep red color. Furthermore, from the intersection of the absorption and emission spectra, the optical band gap ΔE_{opt} that corresponds to the E_{0-0} transition[20] can be estimated for the copolymers **4**, and lies in a range between 2.03 and 2.40 eV. Therefore, the dithieno-thiazine-2,5-pyridine copolymer **4e** possesses the smallest and the dithienothiazine–phenothiazine copolymer **4h** the largest band gap. Since the typical window for optical band gaps of organic semiconductors encompasses a range from 1.5 to 3.0 eV,[21] all these novel dithienothiazine copolymers qualify as low band gap semiconductors.

Conclusions

In summary, we have employed the previously published organometallic synthesis of dithienothiazine homopolymers and oligomers to the generation of dithienothiazine copolymers. Indeed, two complementary polymerizations, Suzuki polymerization and in situ lithiation–Negishi polymerization, were successfully probed to give a series of eight dithieno-thiazine copolymers in good to excellent yields. The dispersities and degrees of polymerization were determined by GPC measurements of the molecular weight distribution. The copolymers are remarkably stable with respect to thermal cleavage of the solubilizing side chains, which does not proceed up to 200 °C. The copolymers are deep colored amorphous solids or resins that dissolve readily in organic solvents. The absorption and emission spectra not only reveal broad absorption bands in the visible, but also orange to deep red luminescence upon excitation with UV light. The determined optical band gaps qualify these novel copolymers as a new class of potential low band gap organic semi-conductors. A more detailed treatment of the electronic structure of dithienothiazine-bridge-dithienothiazine models of the copolymers is currently underway.

Experimental Section

Reagents, catalysts, and solvents were purchased reagent grade and used without further purification. Mono-mers **1** and **2** were synthesized according to our previously published protocol.[17] Bisboronate **3d** was prepared according to our previously published protocol[22] and bisboronate **3c** was prepared from the corresponding 4,7–dibromo-benzo[*c*][1,2,5]thiadiazole[23] by Miyaura coupling.[24] Anhydrous THF was obtained from a drying system (*MBraun systemMB*-SPS-800) and toluene was dried over MS 3Å for at least 24 h. The reaction progress was monitored qualitatively by using TLC silica gel 60 UV_{254} sheets obtained by Macherey-Nagel GmbH & Co. KG. The spots were detected with UV light at 254 and 365 nm. The ^{1}H and ^{13}C NMR spectra were determined on a 600 MHz NMR spectrometer. Chemical shifts δ are reported in ppm relative to the internal solvent signals of THF-d_8 ([1]H δ 3.58, [13]C δ 67.6). By using DEPT-135 spectra the quaternary C, CH, CH_2, and CH_3 signals were assigned. Infrared spectra were recorded with neat compounds under attenuated total reflection and the intensities were characterized as strong (s), middle (m), and weak (w). The elemental analyses were carried out in the microanalytical laboratory of the Pharmazeutisches Institut, Heinrich-Heine-Universität Düsseldorf. Absorption and emission spectra were recorded in dichloromethane HPLC grade at 293 K on a Perkin Elmer UV/Vis/NIR Lambda 19 (absorption) and Hitachi F7000 (emission) spectrometer. The cyclic voltammetry experiments were performed under argon in dry and degassed dichloromethane at 293 K using a small-scale set-up with a three-electrode arrangement (2 mm platinum working electrode, platinum wire counter electrode, Ag/AgCl reference electrode) with tetrabutylammonium hexafluorophosphate as the electrolyte. The oxidation potentials were determined against the internal standard decamethylferrocene ($E^{0/+1} = -95$ mV). The potential of this standard was determined against ferrocene ($E^{0/+1} = 450$ mV[25]).

General Procedure for the Suzuki Polymerization (GP1)

In an oven-dried Schlenk flask with a magnetic stir bar, a mixture of 4-(4-((2-decyltetradecyl)oxy)phenyl)-2,6-diiodo-*4H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (**2**) (357 mg, 0.40 mmol), diboronic acid/diboronate **3** (0.40 mmol), tetra-butylammonium chloride (111 mg, 0.40 mmol), toluene (16 mL) and a saturated aqueous solution of potassium carbonate (4 mL) was degassed with argon for 20 min (for experimental details, see Table 4). Then, tetrakis(triphenyl-phosphane)palladium(0) (10 mol%, 46.0 mg, 0.04 mmol) was added to the reaction mixture and the reaction mixture was heated under an argon atmosphere at 85 °C (oil bath) for 3 d. After cooling to room temperature, water (20 mL) was added to stop the reaction. The organic layer was separated and the aqueous phase was extracted with dichloromethane (3 × 20 mL). The combined organic layers were dried with

Table 4 Experimental details of the Suzuki polymerization synthesis of dithienothiazine copolymers **4**

Entry	Diboronic acid/diboronate **3**	Dithienothiazine copolymer **4** (yield)
1	66.0 mg (0.40 mmol) of **3a**	272 mg (92%) of **4a**
2	97.0 mg (0.40 mmol) of **3b**	204 mg (63%) of **4d**
3[a]	155 mg (0.40 mmol) of **3c**	290 mg (85%) of **4g**
4	214 mg (0.40 mmol) of **3d**	374 mg (99%) of **4h**

[a] Reaction time at 85 °C for 4 d.

anhydrous magnesium sulfate, filtered and the solvent was removed under reduced pressure to give the crude product **4**.

General Procedure for the Negishi Polymerization (GP2)

In an oven-dried Schlenk flask with a magnetic stir bar, a mixture of 4-(4-((2-decyltetradecyl)oxy)phenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine (**1**) (192 mg, 0.30 mmol), TMEDA (0.10 mL, 0.66 mmol), and dry THF (6 mL) under argon was cooled to −78 °C (dry ice/acetone). Then, *n*-butyllithium in hexanes (1.58 m, 0.42 mL, 0.60 mmol) was added dropwise over 10 min and stirring at −78 °C was continued for 2 h. Then, a solution of freshly dried zinc bromide (203 mg, 0.90 mmol) in dry THF (1 mL) was added to the reaction mixture, which was then allowed to come to room temperature. After stirring at room temperature for 1 h, tetrakis(triphenylphosphane)palladium(0) (10 mol%, 35.0 mg, 0.03 mmol) and diiodo(hetero)-arene **5** (1.0 equiv, 0.30 mmol) were added and the mixture was stirred at 50 °C (oil bath) for 3 d (for experimental details, see Table 5). After cooling to room temperature, brine (15 mL) was added to stop the reaction. The aqueous phase was extracted with dichloromethane (3 × 20 mL). The combined organic layers were dried with anhydrous magnesium sulfate, filtered and the solvent was removed under reduced pressure to give the crude product **4**.

Table 5 Experimental details of the Negishi polymerization synthesis of dithienothiazine copolymers **4**

Entry	Diiodo(hetero)arene **5**	Dithienothiazine copolymer **4** (yield)
1	99 mg (0.30 mmol) of **5a**	220 mg (99%) of **4a**
2	99 mg (0.30 mmol) of **5b**	225 mg (99%) of **4b**
3	107 mg (0.30 mmol) of **5c**	212 mg (92%) of **4c**
4	99 mg (0.30 mmol) of **5d**	229 mg (100%) of **4e**
5	99 mg (0.30 mmol) of **5e**	228 mg (100%) of **4f**

Poly[4-(4-((2-decyltetradecyl)oxy)phenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazin-2,6-yl-*alt*-1,4-phenylene] (4a)

The crude product obtained according to GP1 was suspended in acetone (25 mL), placed in the ultrasound bath for 25 min and after filtration the residue was dried under reduced pressure to give polymer **4a** (272 mg, 92%) as a dark brown solid, Mp 174–180 °C.

GPC-RI-LS (THF): M_w = 6.22 kDa, M_n = 3.76 kDa, M_w/M_n = 1.65. M_0 = 714.14 g/mol. DP = $\frac{M_w}{M_0}$ = $\frac{6220}{714.14}$ = 8.7.

The crude product obtained according to GP2 was suspended in acetone (20 mL), placed in the ultrasound bath for 15 min and after filtration the residue was dried under reduced pressure to give polymer **4a** (220 mg, 99%) as a dark brown solid, Mp 174–180 °C.

GPC-RI-LS (THF): M_w = 8.9 kDa, M_n = 5.9 kDa, M_w/M_n = 1.51. M_0 = 714.14 g/mol. DP = $\frac{M_w}{M_0}$ = $\frac{8900}{714.14}$ = 12.5.

IR $\tilde{\nu}$ [cm^{-1}]: 2920 (m), 2850 (w), 1504 (s), 1493 (m), 1483 (w), 1463 (w), 1456 (w), 1427 (w), 1409 (w), 1377 (w), 1276 (w), 1240 (m), 1165 (w), 1103 (w), 1062 (w), 1045 (w), 1024 (w), 997 (w), 977 (w), 947 (w), 839 (w), 808 (m), 765 (w), 721 (w), 692 (w), 681 (w), 665 (w).

^{1}H NMR (THF-d_8, 600 MHz): δ = 6.03–7.80 (m, 10 H), 3.70–3.99 (m, 2 H), 1.81–184 (m, 1 H), 1.29–1.55 (m, 40 H), 0.78–0.97 (m, 6 H).

^{13}C NMR (THF-d_8, 150 MHz): δ = 160.1 (C$_{quat}$), 143.4 (C$_{quat}$), 139.0 (C$_{quat}$), 133.3 (C$_{quat}$), 133.2 (C$_{quat}$), 131.32 (CH), 131.28 (CH), 127.4 (CH), 126.1 (CH), 116.92 (C$_{quat}$), 116.89 (C$_{quat}$), 116.1 (CH), 101.6 (C$_{quat}$), 72.0 (CH$_2$), 39.4 (CH), 33.1 (CH$_2$), 32.6 (CH$_2$), 31.2 (CH$_2$), 30.85 (CH$_2$), 30.81 (CH$_2$), 30.5 (CH$_2$), 28.1 (CH$_2$), 23.8 (CH$_2$), 14.7 (CH$_3$).

MS (MALDI): m/z = 1043.219 ([I-*p*-ph-(DTT-ph)-I)]$^+$), 1554.675 ([(DTT-*p*-ph)$_2$-I]$^+$), 1756.602 ([I-*p*-ph-[(DTT-*p*-ph)$_2$-I]$^+$), 2269.053 ([(DTT-*p*-ph)$_3$-I]$^+$), 2471.245 ([I-(*p*-ph-DTT)$_3$-*p*-ph-I]$^+$).

Poly[4-(4-((2-decyltetradecyl)oxy)phenyl)-4*H*-dithieno[2,3-*b*:3',2'-*e*][1,4]thiazin-2,6-yl-*alt*-1,3-phenylene] (4b)

The crude product obtained according to GP2 was suspended in acetone (15 mL), placed in the ultrasound bath for 15 min and after filtration the residue was dried under reduced pressure to give polymer **4b** (225 mg, 99%) as a dark red resin, Mp >300 °C.

GPC-RI-LS (THF): M_w = 6.14 kDa, M_n = 3.74 kDa, M_w/M_n = 1.64. M_0 = 714.14 g/mol. DP = $\frac{M_w}{M_0}$ = $\frac{6140}{714.14}$ = 8.6.

IR $\tilde{\nu}$ [cm^{-1}]: 2958 (w), 2920 (s), 2870 (w), 1597 (w), 1585 (w), 1568 (w), 1533 (w), 1506 (m), 1464 (m), 1456 (w), 1435 (w), 1417 (w), 1377 (w), 1363 (w), 1338 (w), 1257 (m), 1242 (m), 1184 (w), 1165 (w), 1093 (m), 1016 (s), 937 (w), 864 (w), 837 (w), 817 (m), 789 (s), 742 (w), 719 (w), 690 (m), 659 (w).

^{1}H NMR (THF-d_8, 600 MHz): δ = 6.02–7.74 (m, 10 H), 3.70–4.00 (br, 2 H), 1.82–1.85 (br, 1 H), 1.28–1.56 (m, 40 H), 0.80–0.89 (m, 6 H).

^{13}C NMR (THF-d_8, 150 MHz): δ = 160.1 (C$_{quat}$), 154.3 (C$_{quat}$), 145.5 (C$_{quat}$), 137.0 (C$_{quat}$), 134.3 (C$_{quat}$), 133.3 (CH), 133.1 (CH), 133.0 (CH), 132.6 (C$_{quat}$), 132.3 (C$_{quat}$), 131.2 (CH), 129.34 (CH), 129.29 (CH), 117.0 (CH), 116.9 (CH), 115.8 (CH), 101.1 (C$_{quat}$), 72.0 (CH$_2$), 39.4 (CH), 33.1 (CH$_2$), 32.6 (CH$_2$), 31.2 (CH$_2$), 30.9 (CH$_2$), 30.8 (CH$_2$), 30.5 (CH$_2$), 28.1 (CH$_2$), 26.6 (CH$_2$), 23.8 (CH$_2$), 14.7 (CH$_3$).

MS (MALDI): m/z = 841.248 ([(DTT-m-ph)-I]$^+$), 1043.279 ([I-m-ph-(DTT-m-ph)-I]$^+$), 1555.746 ([(DTT-m-ph)$_2$-I]$^+$), 1757.701 ([I-m-ph-(DTT-m-ph)$_2$-I]$^+$), 2269.150 ([(DTT-m-ph)$_3$-I]$^+$).

Poly[4-(4-((2-decyltetradecyl)oxy)phenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazin-2,6-yl-alt-2,5-dimethyl-1,4-phenylene] (4c)

The crude product obtained according to GP2 was suspended in acetone (15 mL), placed in the ultrasound bath for 15 min and after decantation of the supernatant the residue was dried under reduced pressure to give polymer **4c** (212 mg, 92%) as a dark red resin.

GPC-RI-LS (THF): M_w = 7.27 kDa, M_n = 4.24 kDa, M_w/M_n = 1.71. M_0 = 742.20 g/mol. DP = $\frac{M_w}{M_0}$ = $\frac{7270}{742.2}$ = 9.8.

IR $\tilde{\nu}$ [cm^{-1}]: 2987 (w) 2920 (s), 2872 (m), 1701 (w), 1558 (w), 1504 (s), 1456 (w), 1435 (w), 1379 (w), 1354 (w), 1296 (w), 1278 (w), 1240 (m), 1166 (w), 1072 (w), 1037 (w), 997 (w), 974 (w), 889 (w), 742 (w), 721 (w), 692 (w), 620 (m).

^{1}H NMR (THF-d_8, 600 MHz): δ = 6.01–7.75 (m, 8 H), 3.75–3.95 (br, 2 H), 2.08–2.57 (m, 6 H), 1.75–1.83 (br, 1 H), 1.28–1.52 (m, 40 H), 0.79–0.90 (m, 6 H).

^{13}C NMR (THF-d_8, 150 MHz): δ = 145.4 (C$_{quat}$), 141.8 (C$_{quat}$), 134.2 (C$_{quat}$), 133.3 (C$_{quat}$), 133.2 (C$_{quat}$), 132.8 (CH), 131.3 (CH), 131.01 (CH), 130.03 (CH), 129.34 (C$_{quat}$), 129.26 (C$_{quat}$), 119.9 (CH), 116.8 (C$_{quat}$), 115.8 (CH), 101.1 (C$_{quat}$), 71.8 (CH$_2$), 47.9 (C$_{quat}$), 39.3 (CH), 33.0 (CH$_2$), 32.55 (CH$_2$), 32.50 (CH$_2$), 31.2 (CH$_2$), 30.82 (CH$_2$), 30.78 (CH$_2$), 30.5 (CH$_2$), 28.0 (CH$_2$), 23.7 (CH$_2$), 14.7 (CH$_3$).

MS (MALDI): m/z = 869.280 ([(DTT-2,6-p-xyl)-I]$^+$), 1099.232 ([I-2,6-p-xyl-(DTT-2,6-p-xyl)-I]$^+$), 1610.670

([(DTT-2,6-p-xyl)$_2$-I]$^+$), 1840.620 ([I-2,6-p-xyl-(DTT-2,6-p-xyl)$_2$-I]$^+$), 2353.052 ([(DTT-2,6-p-xyl)$_3$-I]$^+$), 2582.997 ([I-2,6-p-xyl-(DTT-2,6-p-xyl)$_3$-I]$^+$).

Poly[4-(4-((2-decyltetradecyl)oxy)phenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazin-2,6-yl-alt-4,4'-biphenylene] (4d)

The crude product obtained according to GP1 was suspended in acetone (25 mL), placed in the ultrasound bath for 25 min and after filtration the residue was dried under reduced pressure to give polymer **4d** (204 mg, 63%) as a sparingly soluble black solid, Mp >300 °C.

GPC-RI-LS (THF): M_w = 16.5 kDa, M_n = 10.4 kDa, M_w/M_n = 1.59. M_0 = 790.24 g/mol. DP = $\frac{M_w}{M_0}$ = $\frac{16500}{790.24}$ = 20.9.

IR $\tilde{\nu}$ [cm^{-1}]: 2920 (s), 2850 (m), 1504 (s), 1490 (s), 1465 (m), 1435 (m), 1411 (w), 1400 (w), 1377 (w), 1298 (w), 1274 (w), 1240 (s), 1165 (w), 1105 (w), 1029 (w), 1001 (w), 839 (w), 808 (s), 763 (w), 719 (w), 694 (w).

MS (MALDI): m/z = 839.445 ([(DTT-4,4'-biph)-B(OH)$_2$]$^+$), 1428.834 ([DTT-4,4'-biph-DTT]$^+$), 2219.263 ([(DTT-4,4'-biph)$_2$-DTT]$^+$), 3008.729 ([(DTT-4,4'-biph)$_3$-DTT]$^+$).

Poly[4-(4-((2-decyltetradecyl)oxy)phenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazin-2,6-yl-alt-2,5-pyridyl] (4e)

The crude product obtained according to GP2 was suspended in acetone (20 mL), placed in the ultrasound bath for 15 min and after filtration the residue was dried under reduced pressure to give polymer **4e** (229 mg, 100%) as a black solid, Mp >300 °C (dec.).

GPC-RI-LS (THF): M_w = 14.1 kDa, M_n = 8.41 kDa, M_w/M_n = 1.68. M_0 = 715.12 g/mol. DP = $\frac{M_w}{M_0}$ = $\frac{14100}{715.13}$ = 19.7.

IR $\tilde{\nu}$ [cm^{-1}]: 2920 (s), 2850 (m), 1573 (w), 1556 (w), 1531 (w), 1504 (s), 1471 (s), 1417 (m), 1377 (w), 1365 (w), 1292 (w), 1276 (w), 1240 (s), 1186 (w), 1166 (w), 1134 (w), 1101 (w), 1076 (w), 1047 (w), 1022 (w), 997 (w), 975 (w), 964 (w), 945 (w), 918 (w), 893 (w), 839 (w), 813 (w), 765 (w), 742 (w), 721 (w), 692 (w), 667 (w), 615 (w).

^{1}H NMR (THF-d_8, 600 MHz): δ = 6.01–8.59 (m, 9 H), 3.74–3.93 (br, 2 H), 1.83 (br, 1 H), 1.28–1.54 (m, 40 H), 0.80–0.90 (m, 6 H).

^{13}C NMR (THF-d_8, 150 MHz): δ = 160.8 (C$_{quat}$), 145.6 (C$_{quat}$), 134.0 (C$_{quat}$), 133.6 (C$_{quat}$), 132.5 (C$_{quat}$), 131.43 (CH), 131.37 (CH), 129.4 (C$_{quat}$), 117.0 (CH), 116.97 (CH), 116.94 (CH), 101.1 (C$_{quat}$), 71.8 (CH$_2$), 39.4 (CH), 33.1 (CH$_2$), 32.6 (CH$_2$), 31.2 (CH$_2$), 30.8 (CH$_2$), 30.5 (CH$_2$), 28.0 (CH$_2$), 23.8 (CH$_2$), 14.7 (CH$_3$).

MS (MALDI): $m/z = 1556.659$ ([(DTT-2,5-py)$_2$-I]$^+$), 1759.579 ([I-2,5-py-(DTT-2,5-py)$_2$-I]$^+$), 2272.027 ([(DTT-2,5-py)$_3$-I]$^+$), 2474.958 ([I-2,5-py-(DTT-2,5-py)$_3$-I]$^+$), 3189.435 ([I-2,5-py-(DTT-2,5-py)$_4$-I]$^+$).

Poly[4-(4-((2-decyltetradecyl)oxy)phenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazin-2,6-yl-alt-2, 6-pyridyl] (4f)

The crude product obtained according to GP2 was suspended in acetone (20 mL), placed in the ultrasound bath for 15 min and after filtration the residue was dried under reduced pressure to give polymer **4f** (228 mg, 100%) as a dark brown solid, Mp 95–98 °C.

GPC-RI-LS (THF): $M_w = 6.02$ kDa, $M_n = 4.41$ kDa, $M_w/M_n = 1.35$. $M_0 = 715.13$ g/mol. DP = $\frac{M_w}{M_0} = \frac{6020}{715.13} = 8.4$.

IR $\tilde{\nu}$ [cm^{-1}]: 2920 (s), 2850 (m), 2160 (w), 1575 (w), 1558 (m), 1541 (w), 1504 (m), 1442 (s), 1419 (m), 1394 (w), 1377 (w), 1367 (w), 1298 (w), 1242 (m), 1186 (w), 1159 (w), 1109 (w), 1078 (w), 1045 (w), 1026 (w), 1004 (w), 997 (w), 979 (w), 950 (w), 894 (w), 839 (w), 825 (w), 792 (m), 783 (w), 763 (w), 723 (w), 704 (w), 692 (w), 621 (m).

^{1}H NMR (THF-d_8, 600 MHz): δ = 6.02–7.75 (m, 9 H), 3.75–3.95 (br, 2 H), 1.82–1.85 (br, 1H), 1.28–1.57 (m, 40 H), 0.83–0.89 (m, 6 H).

^{13}C NMR (THF-d_8, 150 MHz): δ = 163.0 (C$_{quat}$), 151.8 (C$_{quat}$), 142.6 (C$_{quat}$), 133.7 (C$_{quat}$), 133.32 (C$_{quat}$), 133.28 (C$_{quat}$), 131.4 (CH), 129.6 (C$_{quat}$), 129.4 (C$_{quat}$), 129.3 (C$_{quat}$), 126.1 (C$_{quat}$), 117.7 (CH), 117.0 (CH), 116.8 (CH), 104.4 (C$_{quat}$), 101.1 (C$_{quat}$), 72.0 (CH$_2$), 39.4 (CH), 33.0 (CH$_2$), 32.6 (CH$_2$), 31.2 (CH$_2$), 30.82 (CH$_2$), 30.79 (CH$_2$), 30.5 (CH$_2$), 28.1 (CH$_2$), 23.7 (CH$_2$), 14.6 (CH$_3$).

MS (MALDI): $m/z = 1045.221$ ([I-2,6-py-(DTT-2,6-py)-I]$^+$), 1557.680 ([(DTT-2,6-py)$_2$-I]$^+$), 1759.602 ([I–2,6-py-(DTT-2,6-py)$_2$-I]$^+$), 2272.054 ([(DTT-2,6-py)$_3$-I]$^+$), 2474.987 ([I-2,6-py-(DTT-2,6-py)$_3$-I]$^+$), 2986.498 ([(DTT-2,6-py)$_4$-I]$^+$), 3189.435 ([I-2,6-py-(DTT-2,6-py)$_4$-I]$^+$).

Poly[4-(4-((2-decyltetradecyl)oxy)phenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazin-2,6-yl-alt-4, 7-benzo[c][1,2,5]thiadiazolyl] (4g)

The crude product obtained according to GP1 was suspended in acetone (20 mL), placed in the ultrasound bath for 15 min. Then the solid was suspended twice in acetone (2 × 10 mL) and the supernatant was decanted. After filtration the residue was dried under reduced pressure to give polymer **4g** (290 mg, 85%) as a sparingly soluble dark green solid, Mp > 300 °C (dec.).

GPC-RI-LS (THF): $M_w = 2.95$ kDa, $M_n = 2.46$ kDa, $M_w/M_n = 1.20$. $M_0 = 772.20$ g/mol. DP = $\frac{M_w}{M_0} = \frac{2950}{772.20} = 3.8$.

IR $\tilde{\nu}$ [cm^{-1}]: 2920 (m), 2850 (m), 1506 (m), 1483 (s), 1467 (m), 1426 (s), 1411 (s), 1375 (m), 1352 (w), 1338 (w), 1298 (w), 1240 (m), 1184 (w), 1165 (w), 1103 (w), 1049 (w), 1022 (w), 1008 (w), 864 (w), 837 (m), 819 (m), 788 (w), 765 (w), 719 (w), 638 (w).

MS (MALDI): $m/z = 1410.746$ ([DTT-(BTD-DTT)]$^+$), 2183.107 ([DTT-(BTD-DTT)$_2$]$^+$), 2955.468 ([DTT-(BTD-DTT)$_3$]$^+$).

Poly[4-(4-((2-decyltetradecyl)oxy)phenyl)-4H-dithieno[2,3-b:3',2'-e][1,4]thiazin-2,6-yl-alt-10-hexyl-10H-phenothiazin-3,7-yl] (4h)

The crude product obtained according to GP1 was suspended in acetone (20 mL), placed in the ultrasound bath for 30 min and after filtration the residue was dried under reduced pressure to give polymer **4h** (374 mg, 99%) as a dark brown resin, Mp 124–128 °C.

GPC-RI-LS (THF): $M_w = 13.7$ kDa, $M_n = 10.1$ kDa, $M_w/M_n = 1.36$. $M_0 = 919.46$ g/mol. DP = $\frac{M_w}{M_0} = \frac{13700}{919.46} = 14.9$.

IR $\tilde{\nu}$ [cm^{-1}]: 2953 (w), 2920 (m), 2850 (w), 1620 (w), 1575 (w), 1571 (w), 1550 (w), 1508 (m), 1469 (s), 1463 (s), 1460 (s), 1452 (m), 1438 (w), 1400 (w), 1354 (w), 1332 (w), 1296 (w), 1244 (s), 1190 (w), 1165 (w), 1141 (w), 1103 (w), 1020 (w), 869 (w), 839 (w), 802 (m), 765 (w), 746 (w), 721 (w), 692 (w).

^{1}H NMR (THF-d_8, 600 MHz): δ = 6.00–7.75 (m, 12 H), 3.78–3.98 (m, 4 H), 1.83–1.87 (br, 1 H), 1.29–1.62 (m, 46 H), 0.78–1.00 (m, 9 H).

^{13}C NMR (THF-d_8, 150 MHz): δ = 160.1 (C$_{quat}$), 156.5 (C$_{quat}$), 145.7 (C$_{quat}$), 145.3 (C$_{quat}$), 141.3 (C$_{quat}$), 137.1 (C$_{quat}$), 133.0 (C$_{quat}$), 132.9 (C$_{quat}$), 131.2 (CH), 129.4 (CH), 129.3 (CH), 129.2 (CH), 125.8 (C$_{quat}$), 125.0 (CH), 124.2 (CH), 116.9 (CH), 116.6 (CH), 116.4 (CH), 115.5 (CH), 101.4 (C$_{quat}$), 84.5 (C$_{quat}$), 72.0 (CH), 48.2 (CH$_2$), 39.4 (CH), 32.6 (CH$_2$), 32.6 (CH$_2$), 31.2 (CH$_2$), 30.9 (CH$_3$), 30.8 (CH$_2$), 30.5 (CH$_2$), 28.1 (CH$_2$), 27.7 (CH$_2$), 27.5 (CH$_2$), 23.8 (CH$_2$), 23.7 (CH$_2$), 20.8 (CH$_2$), 14.7 (CH$_3$), 14.5 (CH$_3$), 14.3 (CH$_3$).

MS (MALDI): $m/z = 1327.681$ ([pinB-PT-(DTT-PT)]$^+$), 1453.764 ([pinB-PT-(DTT-PT)-Bpin]$^+$), 2247.143 ([pinB-PT-(DTT-PT)$_2$]$^+$), 2372.227 ([pinB-PT-(DTT-PT)$_2$-Bpin]$^+$), 3165.621 ([pinB-PT-(DTT-PT)$_3$]$^+$), 3291.700 ([pinB-PT-(DTT-PT)$_3$-Bpin]$^+$), 4087.500 ([pinB-PT-(DTT-PT)$_4$]$^+$), 4213.300 ([pinB-PT-(DTT-PT)$_4$-Bpin]$^+$).

Supporting Information

Supporting Information for this article is available online at https://doi.org/10.1055/a-1528-6301.

References

(1) (a) MacDiarmid, A. G. *Angew. Chem. Int. Ed.* **2001**, *40*, 2581. (b) Kiess, H. G. Conjugated conducting polymers. *Vol. 102,* Springer: Heidelberg, **1992**.

(2) Rasmussen, S. C. *ChemPlusChem* **2020**, *85*, 1412.

(3) (a) Fratini, S.; Nikolka, M.; Salleo, A.; Schweicher, G.; Sirringhaus, H. *Nat. Mater.* **2020**, *19*, 491. (b) Wang, C.; Zhang, X.; Hu, W. *Chem. Soc. Rev.* **2020**, *49*, 653. (c) Bronstein, H.; Nielsen, C. B.; Schroeder, B. C.; McCulloch, I. *Nat. Rev. Chem.* **2020**, *4*, 66. (d) Bhosale, M. E.; Chae, S.; Kim, J. M.; Choi, J.-Y. *J. Mater. Chem. A* **2018**, *6*, 19885. (e) Bujak, P.; Kulszewicz-Bajer, I.; Zagorska, M.; Maurel, V.; Wielgus, I.; Pron, A. *Chem. Soc. Rev.* **2013**, *42*, 8895. (f) Dong, H.; Zhu, H.; Meng, Q.; Gong, X.; Hu, W. *Chem. Soc. Rev.* **2012**, *41*, 1754.

(4) (a) Jayakumar, J.; Chou, H.-H. *ChemCatChem* **2020**, *12*, 689. (b) Dai, C.; Liu, B. *Energy Environ. Sci.* **2020**, *13*, 24.

(5) (a) Li, J.; Pu, K. *Chem. Soc. Rev.* **2019**, *48*, 38. (b) Nezakati, T.; Seifalian, A.; Tan, A.; Seifalian, A. M. *Chem. Rev.* **2018**, *118*, 6766.

(6) (a) Mazzio, K. A.; Luscombe, C. K. *Chem. Soc. Rev.* **2015**, *44*, 78. (b) Facchetti, A. *Chem. Mater.* **2011**, *23*, 733. (c) Cheng, Y.-J.; Yang, S.-H.; Hsu, C.-S. *Chem. Rev.* **2009**, *109*, 5868.

(7) Ying, L.; Huang, F.; Bazan, G. C. *Nat. Commun.* **2017**, *8*, 14047.

(8) Wang, J.; Liu, K.; Ma, L.; Zhan, X. *Chem. Rev.* **2016**, *116*, 14675.

(9) Cinar, M. E.; Ozturk, T. *Chem. Rev.* **2015**, *115*, 3036.

(10) Aitken, R. A.; Aitken, K. M. 1,4-Thiazines and their Benzo Derivatives. In: Comprehensive Heterocyclic Chemistry III. Katritzky, A. R.; Ramsden, A. C.; Scriven, E. F. .. V.; Taylor, R. J. K.; Elsevier: Amsterdam, **2008**, 607.

(11) Perețeanu, I. S.; Müller, T. J. J. *Org. Biomol. Chem.* **2013**, *11*, 5127.

(12) (a) Park, Y.; Kim, B.; Lee, C.; Hyun, A.; Jang, S.; Lee, J.-H.; Gal, Y.-S.; Kim, T. H.; Kim, K.-S.; Park, J. *J. Phys. Chem. C* **2011**, *115*, 4843. (b) Salunke, J. K.; Wong, F. L.; Feron, K.; Manzhos, S.; Lo, M. F.; Shinde, D.; Patil, A.; Lee, C. S.; Roy, V. A. L.; Sonar, P.; Wadgaonkar, P. P. *J. Mater. Chem. C* **2016**, *4*, 1009. (c) Qu, B.; Chen, Z.; Liu, Y.; Cao, H.; Xu, S.; Cao, S.; Lan, Z.; Wang, Z.; Gong, Q. *J. Phys. D: Appl. Phys.* **2006**, *39*, 2680. (d) Zhu, Y.; Champion, R. D.; Jenekhe, S. A. *Macromolecules* **2006**, *39*, 8712.

(13) (a) Urselmann, D.; Deilhof, K.; Mayer, B.; Müller, T. J. J. *Beilstein J. Org. Chem.* **2016**, *12*, 2055. (b) Müller, T. J. J.; Franz, A. W., Barkschat (née Krämer) C. S.Sailer, M.; Meerholz, K.; Müller, D.; Colsmann, A.; Lemmer, U. *Macromol. Symp.* **2010**, *287*, 1. (c) Sailer, M.; Franz, A. W.; Müller, T. J. J. *Chem. Eur J.* **2008**, *14*, 2602.

(14) May, L.; Müller, T. J. J. *Chem. Eur J.* **2020**, *26*, 12111.

(15) May, L.; Müller, T. J. J. *Molecules* **2020**, *25*, 2180.

(16) (a) Dostert, C.; Müller, T. J. J. *Org. Chem. Front.* **2015**, *2*, 481. (b) Dostert, C.; Czajkowski, D.; Müller, T. J. J. *Synlett* **2014**, *25*, 371.

(17) Nau, J.; Schneeweis, A. P. W.; Müller, T. J. J. *Mater. Chem. Front.* **2020**, *4*, 621.

(18) Mori, S.; Barth, H. G. Size Exclusion Chromatography. Springer Science & Business Media: Berlin, **2013**.

(19) Netopilík, M.; Kratochvíl, P. *Polymer* **2003**, *44*, 3431.

(20) Meyer, T.; Ogermann, D.; Pankrath, A.; Kleinermanns, K.; Müller, T. J. J. *J. Org. Chem.* **2012**, *77*, 3704.

(21) Brutting, W.; Rieß, W. *Phys. J.* **2008**, *7*, 33.

(22) Krämer, C. S.; Zimmermann, T. J.; Sailer, M.; Müller, T. J. J. *Synthesis* **2002**, 1163.

(23) Heiskanen, J. P.; Vivo, P.; Saari, N. M.; Hukka, T. I.; Kastinen, T.; Kaunisto, K.; Lemmetyinen, H. J.; Hormi, O. E. O. *J. Org. Chem.* **2016**, *81*, 1535.

(24) Han, F. S.; Higuchi, M.; Kurth, D. G. *Org. Lett.* **2007**, *9*, 559.

(25) Zanello, P. InFerrocenes. A. Togni, A.; Hayashi, T.VCH: Weinheim, **1995**, 317.