Synthesis of 1-amino-2,5-di(2-thienyl)benzenes as potential monomers for the preparation of hybrid polythiophene anionic sensors*

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A convenient method for the synthesis of 1-amino-2,5-di(2-thienyl)benzenes was proposed. The method involves *in situ* generation of aryne intermediates from 1-halo-2,5-di-(2-thienyl)benzenes in the presence of strong bases followed by reactions of the arynes with polyfunctional primary and secondary amines. The products obtained in 75—85% yields are promising monomers for the preparation of polythiophene anionic sensors. Polymerization of dibrominated 1-piperidino-2,5-di(2-thienyl)benzene gave the corresponding poly[(bithiophenediyl)(phenylene)].

Key words: amination, aryne, poly[(bithiophenediyl)(phenylene)], cross-coupling.

In the last three decades, polythiophenes have found wide use as active components of transistors,[1] electroluminescent devices,[2] solar panels,[3] photochemical resistors,[4] nonlinear optic devices,[5] solar cell components,[6] diodes,[7] and chemical sensors.[8] Polythiophenes themselves and polythiophene-based materials tend to be applied in two main ways. In static polymer materials prepared by common methods, the conducting properties of polythiophenes[9] are employed with retention of other properties of polymer materials. In dynamic materials, an optical or electrical signal is altered by applying an electric potential or an external stimulus. In this context, the synthesis of anionic sensors based on polythiophenes or hybrid polymers containing aromatic and heteroaromatic (thiophene) fragments is of particular interest. Organic and inorganic anions penetrate into the environment *via* food additives,[10] synthetic detergents,[11] drugs,[12] organic fertilizers,[13] *etc*. Monitoring of the level of organic and inorganic anions in human blood is a promising tool for early diagnostics of serious diseases.[14]

In addition, cationic complexes of polythiophenes have been used for detection of anions (*e.g.*, iodide anions in water[15]). At the same time, cyclic and acyclic polyfunctional amines are very common anionic receptors for organic and inorganic anions.[16]

Therefore, by combining polyfunctional amines and polythiophenes, one could design efficient polyfunctional anionic sensors. Having this in mind, here we tried to introduce cyclic and acyclic amino groups into 1,4-di-(2-thienyl)benzene for subsequent polymerization of the resulting monomers.

We employed the Buchwald—Hartwig amination[17] for direct cross-coupling of 1-iodo- or 1-bromo-2,5-di(2-thienyl)benzenes with amines as the most promising method. To do this, we obtained 1-iodo-2,5-di(2-thienyl)-benzene (**1a**) according to a known procedure.[18] However, its attempted modification with an amino function under standard amination conditions led only to 1,4-di(2-thienyl)benzene **2** as a major product (Scheme 1). 1-Bromo-2,5-di(2-thienyl)benzene (**1b**) reacted in a similar way.

Based on the mechanism postulated for this reaction,[19] one can assume that the steric hindrances at a palladium intermediate preclude subsequent addition of an amine and hence favor the β-transfer of the hydrogen atom (β-H shift), yielding dehalogenated product **2** (Scheme 2).

While investigating possible causes of such low reactivities of compounds **1a**,**b**, we found that heating of compound **1b** with piperidine in toluene in the presence of strong bases ($KOBu^t$ or $NaNH_2$), which are not common bases used under the conditions of the Buchwald reaction, and a decreased amount of the catalyst $Pd(OAc)_2$ (0.2 mol.%) unexpectedly gives amination product **3a** in 50—65% yields, product **2** being formed only in trace amounts (Scheme 3). Moreover, the yield of compound **3a** in the absence of the catalyst increased to 85%. We assumed that a strong base favors the *in situ* formation of an aryne intermediate that reacts with piperidine to give

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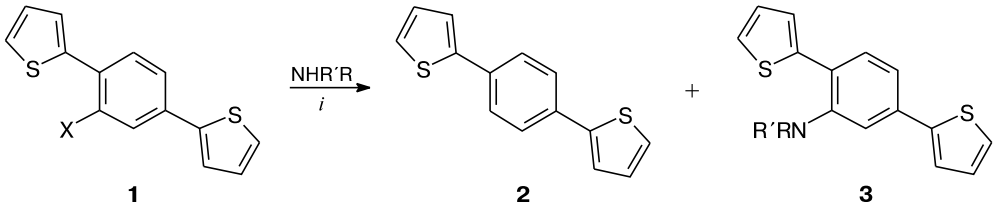
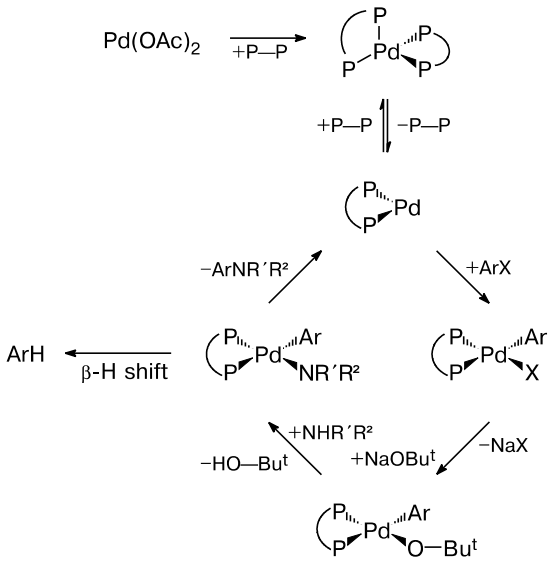
Scheme 1

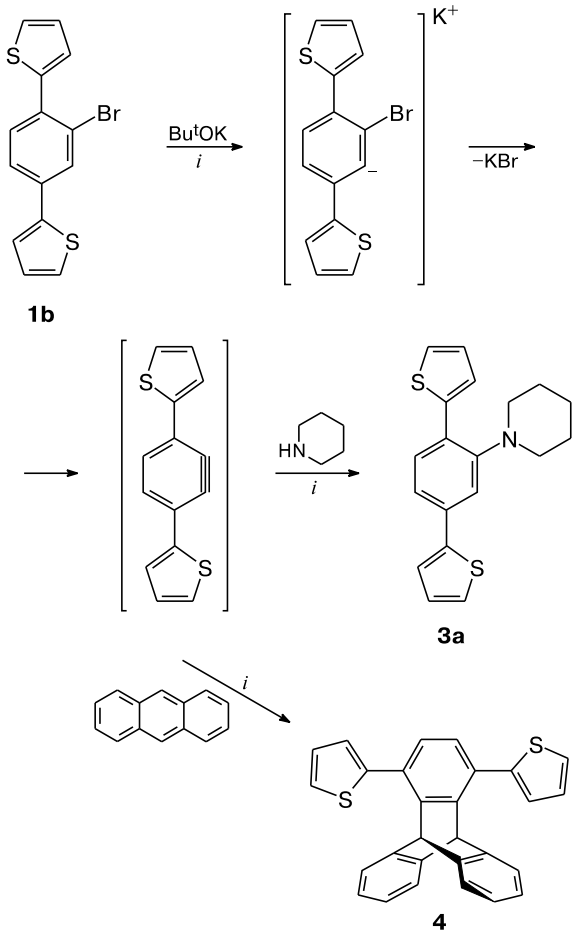


i. Base/P ligand, solvent.

Scheme 2



Scheme 3



i. Toluene, 140 °C.

product **3a**. To verify this assumption, we carried out the above reaction in the presence of an excess of anthracene, a known trap for aryne intermediates, and obtained 3′,6′-di-(2-thienyl)-9,10-dihydro-9,10-[2′,1′]benzoanthracene (triptycene)[20] **4** in 35% yield as a result of the Diels—Alder reaction of aryne with anthracene (Scheme 3).

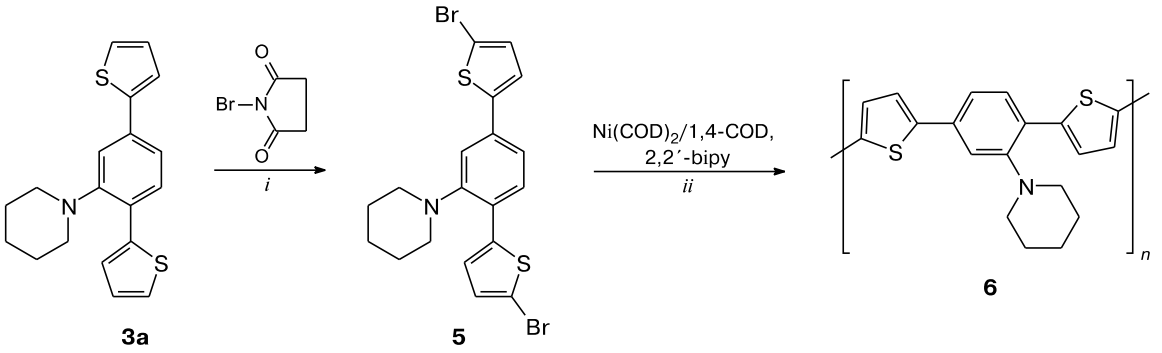
To find out whether it is possible to obtain amino-containing thienylphenylene polymers, we functionalized compound **3a** by room-temperature bromination of its thiophene moieties with *N*-bromosuccinimide in DMF. The Yamamoto polymerization[21] of the resulting dibromide **5** by heating in toluene in the presence of equimolar amounts of bis(cyclooctadiene)nickel(0) ($Ni(COD)_2$), cycloocta-1,5-diene, and 2,2′-bipyridine gave amino-functionalized poly[(bithiophenediyl)(phenylene)] **6** (Scheme 4).

Further optimization of the conditions for the synthesis of compounds **3** revealed that 1-chloro-2,5-di(2-thienyl)benzene (**1c**) is their most convenient precursor, which can be prepared in 80% yield by the Stille cross-coupling[22] of 1-chloro-2,5-diiodobenzene with 2-(trimethylstannyl)thiophene (Scheme 5).

Heating of compound **1c** with amines in toluene in the presence of $KOBu^t$ or $NaNH_2$ gave amination products **3a—d** in high yields (see Scheme 5, Table 1). Note that both primary and secondary polyfunctional amines can be used in this reaction.

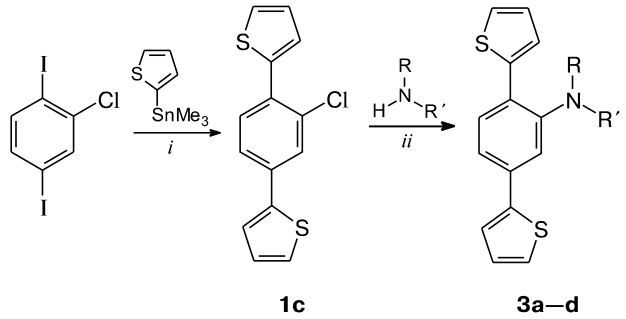
To sum up, we demonstrated that sterically hindered 1-halo-2,5-di(2-thienyl)benzenes can be aminated with primary or secondary polyfunctional amines *via* the aryne mechanism. We obtained 1-amino-2,5-di(2-thienyl)-

Scheme 4



i. DMF, 0—25 °C; *ii*. Toluene, 90 °C.

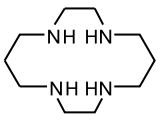
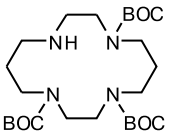
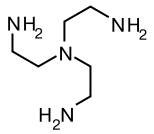
Scheme 5



i. $Pd(PPh_3)_4$, toluene, 110 °C; *ii*. Base, toluene, 140 °C.

benzenes in high yields as monomers for the synthesis of polythiophene anionic receptors. The *in situ* generated aryne intermediate was isolated as its derivative **4** and identified by physicochemical methods. We found that 1-piperidino-2,5-di(2-thienyl)benzene **3a** can be polymerized into an amino-functionalized thienylphenylene polymer.

Table 1. Synthesis of compounds **3a—d**

Amine	Base	Product	Yield (%)
	$KOBu^t$	**3a**	55
	$NaNH_2$	**3a**	85
	$KOBu^t$	**3b**	75
	$NaNH_2$	**3b**	86
	$KOBu^t$	**3c**	80
	$KOBu^t$	**3d**	85
	$NaNH_2$	**3d**	85

Experimental

The starting materials and $Ni(COD)_2$ were prepared according to known procedures; the other starting materials were used as purchased. TLC analysis was performed on Silica gel $60F_{254}$ plates (Merck); spots were visualized under UV light. Products were purified by column chromatography on Silica gel 60 (Merck). ^1H NMR spectra were recorded on a Bruker WH-250 instrument. Melting points were determined on a Boetius instrument. Mass spectra of polymer **6** were measured on a MicrOTOF-Q II mass spectrometer (Bruker Daltonics, Bremen, Germany) (ESI) equipped with a six-port valve and a kd Scientific system for direct inlet probe (flow rate 180 μL h). The mass spectrometer was controlled by the micrOTOFcontrol 2.3 patch 1 and HyStar 3.2 software (Bruker Daltonics). The operating parameters of the mass spectrometer were as follows: rated resolution 17 500, positive ion mode, m/z scan range 50—8000 Da, ion source capillary voltage 4500 V, glass capillary outlet voltage 166 V, spraying gas pressure 0.8 bar, drying gas flow rate 4 L min^{-1}, gas heater temperature 250 °C, averaging setting 3, summation setting 5000 (corresponding to a spectrum per second), ion travel time 70 μs, and radio frequency of the hexapole 100 Vpp.

1-Chloro-2,5-di(2-thienyl)benzene (1c). 2-(Trimethylstannyl)thiophene (0.750 g, 3 mmol) and $Pd(PPh_3)_4$ (0.110 g, 0.10 mmol) were added under argon to a solution of 1-chloro-2,5-diiodobenzene[23] (0.364 g, 1 mmol) in dry toluene (25 mL). The reaction mixture was stirred at 110 °C for 24 h. On cooling, silica gel (10 g) was added and the mixture was stirred and concentrated under reduced pressure. The resulting silica gel was transferred on top of a column packed with silica gel. The product was separated by column chromatography with 30% CH_2Cl_2 in hexane as an eluent and recrystallized from MeOH—CH_2Cl_2 (1 : 1). The yield of compound **1c** was 85%, colorless crystals, m.p. 75 °C. ^1H NMR (250 MHz, $CDCl_3$), δ: 7.75 (s, 1 H, Ph); 7.54—7.59 (m, 2 H, Ph); 7.42—7.46 (m, 2 H, $CH_{thiophene}$); 7.34—7.38 (m, 2 H, $CH_{thiophene}$); 7.12—7.16 (m, 2 H, $CH_{thiophene}$). Found (%): C, 60.80; H, 2.99. $C_{14}H_9ClS_2$. Calculated (%): C, 60.75; H, 3.28.

1,4-Di(2-thienyl)benzene (2). The catalyst $Pd(OAc)_2$ or $Pd_2(dba)_3$ (2—5 mol.%), the P ligand (10 mol.%), a base (3 mmol), and an appropriate amine (3 mmol) were added under argon to a solution of 1-iodo- or 1-bromo-2,5-di(2-thienyl)-benzene **1** (0.5 mmol) in dry toluene (10 mL). The reaction mixture was stirred at 140 °C for 22 h and diluted with water (10 mL). The product was extracted from the organic layer with ethyl acetate (3×10 mL). The combined extracts were washed with water (2×10 mL) and brine (10 mL), dried over $CaCl_2$, filtered, and evaporated to dryness under reduced pressure. The product was separated by column chromatography on silica gel with 10% acetone in hexane as an eluent. The physicochemical and spectroscopic characteristics of the resulting colorless precipitate agree with the literature data.[24]

Synthesis of compounds 3a—d (general procedure). Potassium *tert*-butoxide (1.12 g, 10 mmol) (method *A*) or sodium amide (0.390 g, 10 mmol) (method *B*) and an appropriate amine (5 mmol) were added under argon to a solution of 1-chloro-2,5-di(2-thienyl)benzene (**1c**) (0.276 g, 1 mmol) in dry toluene (20 mL). The reaction mixture was stirred at 140 °C for 22 h and diluted with water (10 mL). The product was extracted from the organic layer with ethyl acetate (3×10 mL). The combined extracts were washed with brine (2×10 mL), dried over $CaCl_2$, filtered, and evaporated to dryness under reduced pressure. The product as a colorless crystalline or amorphous precipitate was separated by column chromatography on silica gel with $MeOH—NH_4OH—CH_2Cl_2$ (5 : 0.5 : 72) as an eluent.

1-[2,5-Di(2-thienyl)phenyl]piperidine (3a). Yield 55% (*A*), 85% (*B*), m.p. 78 °C (from hexane). ^{1}H NMR (250 MHz, $CDCl_3$), δ: 7.52 (d, 1 H, Ph, J = 7.5 Hz); 7.51—7.52 (m, 1 H, Ph); 7.39 (br.s, 1 H, Ph); 7.28—7.34 (m, 4 H, $CH_{thiophene}$); 7.07—7.12 (m, 2 H, $CH_{thiophene}$); 2.91 (t, 4 H, $(CH_2)_2$, J = 5.1 Hz); 1.56—1.63 (m, 2 H, CH_2); 1.72—1.79 (m, 4 H, $(CH_2)_2$). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 151.7, 144.3, 141.2, 134.1, 129.8, 128.8, 127.9, 126.2, 125.9, 124.8, 124.7, 123.0, 121.0, 117.9, 77.2, 53.8, 25.9, 24.2. Found (%): C, 70.03; H, 6.23; N, 4.14. $C_{19}H_{19}NS_2$. Calculated (%): C, 70.11; H, 5.88; N, 4.30.

1-[2,5-Di(2-thienyl)phenyl]-1,4,8,11-tetraazacyclotetradecane 3b. Yield 75% (*A*), 86% (*B*), oil. ^{1}H NMR (250 MHz, $CDCl_3$), δ: 7.49—7.52 (m, 2 H, Ph); 7.38—7.42 (m, 3 H, Ph + + $CH_{thiophene}$); 7.28—7.34 (m, 2 H, $CH_{thiophene}$); 7.08—7.12 (m, 2 H, $CH_{thiophene}$); 3.16 (t, 2 H, CH_2, J = 5.7 Hz); 2.99—3.03 (m, 2 H, CH_2); 2.67—2.83 (m, 10 H, 5 CH_2); 2.52 (t, 2 H, CH_2, J = 5.4 Hz); 2.18 (s, 3 H, NH); 1.77 (t, 2 H, CH_2, J = 5.4 Hz); 1.67 (t, 2 H, CH_2, J = 5.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 149.8, 143.9, 140.9, 134.5, 131.6, 131.2, 128.0, 126.7, 126.6, 125.8, 124.9, 123.2, 122.1, 120.9, 77.1, 56.7, 48.7, 48.0, 47.2, 46.6, 45.3, 30.8, 26.5. Found (%): C, 65.12; H, 8.00. $C_{24}H_{32}N_4S_2$. Calculated (%): C, 65.41; H, 7.72.

Tri(*tert*-butyl) 11-[2,5-di(2-thienyl)phenyl]-1,4,8,11-tetraazacyclotetradecane-1,4,8-tricarboxylate 3c. Yield 80% (*A*), oil. ^{1}H NMR (250 MHz, $CDCl_3$), δ: 7.52 (d, 1 H, Ph, J = 6.5 Hz); 7.48 (s, 1 H, Ph); 7.28—7.39 (m, 5 H, Ph + $CH_{thiophene}$); 7.06—7.12 (m, 2 H, $CH_{thiophene}$); 3.30—3.43 (m, 14 H, 7 CH_2); 2.85—2.95 (m, 2 H, CH_2); 1.84—1.95 (m, 4 H, 2 CH_2); 1.50 (s, 9 H, Me_3C); 1.46 (s, 9 H, Me_3C); 1.38 (s, 9 H, Me_3C). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 155.5, 149.3, 143.8, 140.5, 134.4, 128.0, 130.4, 126.3, 126.2, 125.6, 124.9, 123.3, 122.1, 79.8, 79.6, 77.1, 53.3, 50.2, 47.1, 46.6, 28.5, 28.5, 28.4, 25.9. Found (%): C, 62.99; H, 7.44; N, 13.06. $C_{39}H_{56}N_4O_6S_2$. Calculated (%): C, 63.21; H, 7.62; N, 12.95.

***N*,*N*-Bis(2-aminoethyl)-*N*′-[2,5-di(2-thienyl)phenyl]ethane-1,2-diamine 3d.** Yield 80% (*A*), oil. ^{1}H NMR (250 MHz, $CDCl_3$), δ: 7.30—7.39 (m, 2 H, Ph); 6.99—7.03 (m, 1 H, Ph); 7.24—7.28 (m, 2 H, $CH_{thiophene}$); 7.19—7.20 (m, 1 H, $CH_{thiophene}$); 7.13—7.16 (m, 1 H, $CH_{thiophene}$); 7.09—7.11 (m, 1 H, $CH_{thiophene}$); 6.90 (br.s, 1 H, $CH_{thiophene}$); 3.25 (t, 2 H, CH_2, J = 6.0 Hz); 2.76 (t, 2 H, CH_2, J = 6.0 Hz); 2.48 (t, 4 H, 2 CH_2, J = 6.0 Hz); 2.48 (t, 4 H, 2 CH_2, J = 6.0 Hz); 1.17 (br.s, 4 H, 2 NH_2). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 146.1, 144.8, 140.6, 135.4, 131.4, 127.8, 127.5, 126.2, 125.6, 124.6, 123.1, 119.2, 114.7, 108.2, 57.0, 53.5, 41.3, 39.9. Found (%): C, 61.86; H, 7.02; N, 14.44. $C_{20}H_{26}N_4S_2$. Calculated (%): C, 62.14; H, 6.78; N, 14.49.

3′,6′-Di(2-thienyl)-9,10-dihydro-9,10[1′,2′]-benzenoanthracene (4). Potassium *tert*-butoxide (1.12 g, 10 mmol) and anthracene (1.0 g, 5.60 mmol) were added under argon to a solution of compound **1** (X = I, Br, or Cl) (0.5 mmol) in dry toluene (30 mL). The reaction mixture was stirred at 140 °C for 22 h and diluted with water (10 mL). The product was extracted from the organic layer with ethyl acetate (3×10 mL). The combined extracts were washed with water (2×10 mL) and brine (10 mL), dried over $CaCl_2$, filtered, and evaporated to dryness under reduced pressure. The product was separated as a colorless precipitate by column chromatography on silica gel with 10% acetone in hexane as an eluent. Yield 32%, m.p. >250 °C. ^{1}H NMR (250 MHz, $CDCl_3$), δ: 7.48—7.50 (m, 2 H, Ph); 7.39—7.42 (m, 4 H, C_6H_4), 7.24—7.26 (m, 2 H, $CH_{thiophene}$); 7.19—7.21 (m, 2 H, $CH_{thiophene}$); 7.05 (m, 2 H, $CH_{thiophene}$); 7.02—7.05 (m, 4 H, C_6H_4); 6.03 (s, 2 H, CH). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 145.2, 144.1, 141.6, 130.0, 127.5, 126.8, 126.8, 125.8, 125.3, 123.8, 50.8. Found (%): C, 80.59; H, 4.24. $C_{28}H_{18}S_2$. Calculated (%): C, 80.34; H, 4.33.

1-[2,5-Bis(5-bromo-2-thienyl)phenyl]piperidine 5. A solution of freshly recrystallized 1-bromosuccinimide (0.400 g, 2.27 mmol) in dry DMF (5 mL) was added dropwise under argon at −20 °C to a solution of compound **3a** (0.325 g, 1 mmol) in dry DMF (10 mL). The reaction mixture was stirred at −20 °C for 1 h and at room temperature for 12 h and poured into cooled water (50 mL). The product was extracted with ethyl acetate (2×30 mL). The combined extracts were dried with Na_2SO_4 and concentrated on a rotary evaporator. The residue was purified by column chromatography on silica gel with 10% ethyl acetate in hexane as an eluent. Compound **5** was isolated as a colorless crystalline powder, m.p. 112 °C (decomp.). ^{1}H NMR (250 MHz, tetrachloroethane-d_2), δ: 7.41—7.44 (m, 2 H, Ph); 7.30 (s, 1 H, Ph); 7.17 (d, 2 H, $CH_{thiophene}$, J = 4.0 Hz); 6.99 (d, 2 H, $CH_{thiophene}$, J = 3.9 Hz); 2.85 (t, 4 H, 2 CH_2, J = 5.0 Hz); 1.60—1.65 (m, 4 H, 2 CH_2); 1.45—1.53 (m, 2 H, CH_2). Found (%): C, 46.99; H, 3.22; N, 3.05. $C_{19}H_{17}Br_2NS_2$. Calculated (%): C, 47.22; H, 3.55; N, 2.90.

Poly[(2,2′-bithiophene-5,5′-diyl)(2-piperidino-1,4-phenylene)] (6). Cycloocta-1,5-diene (0.5 mL), 2,2′-bipyridine (0.156 g, 1 mmol), and freshly prepared $Ni(COD)_2$[25] (1 mmol) were added under argon to a solution of compound **5** (0.483 g, 1 mmol) in a mixture of dry DMF (5 mL) and toluene (30 mL). The resulting solution was heated at 90 °C for 72 h. The resulting suspension was filtered and the mother liquor was evaporated to dryness *in vacuo*. The solid residue was dissolved in dry THF (20 mL) and reprecipitated with MeOH (5—10 mL). The precipitate of the polymer was filtered off and washed with MeOH. This procedure was repeated several times for better purification of the product. The yield of polymer **6** was 0.250 g, violet-brown fibers.

^{1}H NMR (250 MHz, tetrachloroethane-d_2), δ: 7.38—7.44 (m, 2 H, Ph); 7.30—7.32 (br.s, 1 H, Ph); 7.12—7.20 (m, 2 H, $CH_{thiophene}$); 6.95—7.10 (m, 2 H, $CH_{thiophene}$); 2.80—2.85 (m, 4 H, 2 CH_2); 1.61—1.66 (m, 4 H, 2 CH_2); 1.43—1.52 (m, 2 H, CH_2). ESI MS, *m/z* (%): $[M + H]^+$ 7757.24 (100%). $C_{456}H_{411}N_{24}S_{48}$. Calculated for $C_{456}H_{411}N_{24}S_{48}$: M^+ = 7756.95 (24 monomer units).

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