68. Palladium-Catalyzed Syntheses of Polyethynyl-Substituted 2,2′-Bithiophenes

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Dedicated to Prof. Dr. *Miha Tišler*, Ljubljana/Slovenia, on the occasion of his 70th birthday

(5.II.96)

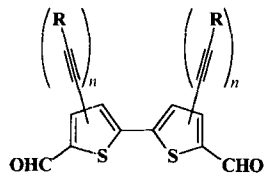
The syntheses of polyethynyl-substituted 2,2′-bithiophenes **2** and related 5,5′-dicarbaldehyde derivatives **1** are described. The treatment of easily available polybrominated 2,2′-bithiophenes **3** and 2,2′-bithiophene-5,5′-dicarbaldehydes **4** with phenyl or (trimethylsilyl)acetylene in the presence of Pd^{II} and Cu^{I} in $(i\text{-Pr})_2NH$ yields substituted polyethynyl-2,2′-bithiophene compounds. The Me_3Si protecting groups can be removed by protodesilylation under basic conditions to give the corresponding terminal ethynyl groups. These polyethynyl-bithiophenes could be interesting precursors for the synthesis of macrocycles with interesting properties.

Introduction. – The development of new synthetic strategies for the syntheses of porphyrins, porphycenes, and related conjugated macrocycles has recently received much attention because of their special aromatic properties as annulene derivatives [1] as well as their potential for use as photosensitizers [2]. There have been a number of investigations in the recent past concerning the use of porphyrins for biomedical applications such as fluorescence detection, viral inhibition [3], and photodynamic tumor therapy (PDT) [4].

Many attempts have been made to modify the porphyrin ring system to create new chromophores. Inverted [5] and expanded porphyrinoides [6] as well as porphycenes, hemiporphycenes, and corrphycenes [7] have been synthesized. Heterocyclic analogs of this class of compounds have also been reported [8].

Prompted by the observation of *Vogel*, *Schaffner* and coworkers [9], which showed the potential of acetylenic and cumulenic porphycene derivatives as PDT agents, we investigated the syntheses of S-containing porphycene analogs, namely 21,23-dithiaporphycene and tetrathiaporphycene [10]. The 2,2′-bithiophenes (= 2,2′-bithienyls), the major component of the thiaporphycene system, have also been reported to possess interesting properties. Naturally occurring bithiophenes, specifically acetylenic derivatives, show nematolocidal, as well as antibiotic, ovicidal, algicidal, larvicidal, and antifeedant properties [11]. These 2,2′-bithiophene compounds have also been shown to inhibit germination and cell growth [12] and are phototoxic to some aquatic organisms [13]. By combining the properties found in porphycenes and those found in alkynyl-substituted bithiophenes, alkynylated thiaporphycenes should produce a group of macrocycles with high biological activity.

Presently, the most efficient route to porphycenes and analogous systems involves the intermolecular dimerization of carbonyl compounds with low-valent titanium, the so-called *McMurry* reaction [7] [10] [14]. We planned to apply this methodology to the



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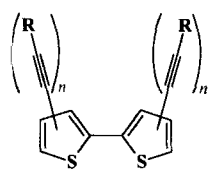


2

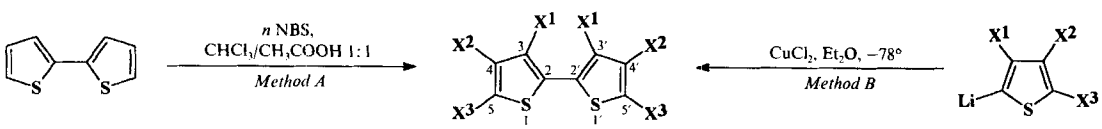
R= H, Ph, $SiMe_3$

synthesis of various alkynylated tetrathiaporphycenes starting from the corresponding 2,2′-bithiophene-5,5′-dicarbaldehydes **1**.

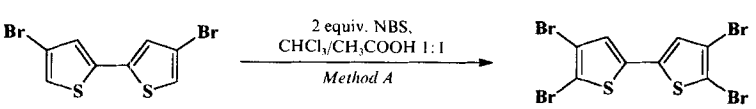
The preparation of ethynyl-substituted bithiophene derivatives has not received much attention. To the best of our knowledge, a synthesis of these compounds, which could also function as building blocks for the construction of heterocyclic carbon-rich materials [15], has not been reported. Thus, our first task was to develop and efficient synthesis of ethynyl-bithiophene derivatives. Given the inherent aromatic character of thiophenes, the Pd^{II}-catalyzed coupling of acetylenes to the readily available halogenated bithiophene derivatives seemed to be the most promising synthetic strategy [16]. Polybrominated bithiophenes **3**, obtained by the bromination of bithiophene or by the oxidative coupling of brominated thienyllithium derivatives, proved to be suitable starting materials for the syntheses of compounds of structure **1** and **2**.

Results and Discussion. – Polybrominated 2,2′-bithiophenes are accessible by two general methods (*Scheme 1*). According to *Töhl* and *Auwers* [17], the treatment of 2,2′-bithiophene with Br_2 in AcOH produces 5,5′-dibromo-2,2′-bithiophene (**3c**) in reasonable yield. However, attempts to introduce additional Br-substituents with a large excess of Br_2 and long reaction times led to unsatisfactory results. Further investigation showed that the bromination of 2,2′-bithiophene is much more efficient and selective, when *N*-bromosuccinimide (NBS) in $CHCl_3$/AcOH is used. It has been reported that

Scheme 1



3a $X^1 = Br, X^2 = X^3 = H$ (76% (*B*))
b $X^1 = X^3 = H, X^2 = Br$ (71% (*B*))
c $X^1 = X^2 = H, X^3 = Br$ (95% (*A*); 86% (*B*))
d $X^1 = X^2 = Br, X^3 = H$ (69% (*B*))
e $X^1 = X^3 = Br, X^2 = H$ (90% (*A*); 81% (*B*))
f $X^1 = X^2 = X^3 = Br$ (61% (*A*); 84% (*B*))



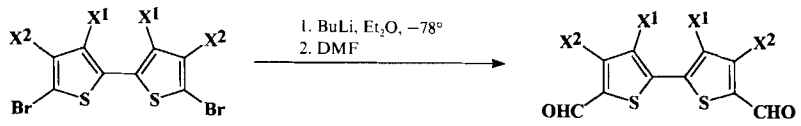
3b **3g** (94%)

5,5′-dibromo-2,2′-bithiophene (**3c**) [18] is prepared in quantitative yield using this method. Under these reaction conditions (*Method A*), the synthesis of **3c** was reproduced and extended to 3,3′,5,5′-tetrabromo-2,2′-bithiophene (**3c**) and the hexabrominated derivative **3f** (*Scheme 1*).

Gronowitz [19] reported the synthesis of 3,3′-dibromo-2,2′-bithiophene (**3a**) by oxidative coupling of regioselectively α-lithiated bromothiophene derivatives [20] with $CuCl_2$ in Et_2O at −78° (*Method B*; *Scheme 1*). In addition to the polybromo-2,2′-bithiophenes **3c, e, f** (independently prepared by *Method A*), 4,4′-dibromo-2,2′-bithiophene (**3b**) and 3,3′,4,4′-tetrabromo-2,2′-bithiophene (**3d**) were readily obtained in high yields by the *Gronowitz* approach. The 4,4′,5,5′-tetrabromo-2,2′-bithiophene (**3g**) could only be obtained using a combination of *Methods A* and *B*: 4,4′-dibromo derivative **3b**, prepared by *Method B*, was treated with NBS according to *Method A* to give **3g** in excellent yield (*Scheme 1*).

The introduction of two formyl substituents in the 5,5′-positions of bromobithiophenes can be accomplished by direct bromination of 2,2′-bithiophene-5,5′-dicarbaldehyde, but this reaction proceeds only in low yields [21]. However, starting from the above described polybromo-2,2′-bithiophenes **3e–g**, we could obtain the brominated 2,2′-bithiophene-5,5′-dicarbaldehydes **4a–c** in good yields by regioselective α-lithiation with 2 equiv. of BuLi in Et_2O followed by treatment with dimethylformamide (DMF) at −78° (*Scheme 2*).

Scheme 2



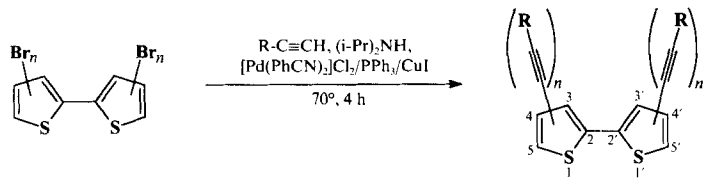
3e X^1 = Br, X^2 = H
f $X^1 = X^2$ = Br
g X^1 = H, X^2 = Br

4a X^1 = Br, X^2 = H (72%)
b X^1 = H, X^2 = Br (69%)
c $X^1 = X^2$ = Br (65%)

Functionalized 2,2′-bithiophene derivatives provided excellent starting materials for the preparation of polyethynyl-2,2′-bithiophenes of structures **1** and **2**. First attempts at the alkynylation of the brominated 2,2′-bithiophenes **3a–g** involved the modified *Heck*-coupling reaction with catalytic amounts of dichlorobis(triphenylphosphine)-palladium(II) as published by *Hagihara* and coworkers [22]. Using these conditions, however, the desired products were obtained in low yields. We, therefore, turned our attention to a method developed by *Neenan* and *Whitesides* [23] who prepared polyethynylthiophenes using a dichlorobis(benzonitrile)palladium(II)CuI/PPh_3 catalyst system in $(i\text{-}Pr)_2NH$. In our studies, when phenylacetylene and (trimethylsilyl)acetylene were used as alkynylation partners for the brominated 2,2′-bithiophenes **3a–g**, compounds **2a–o** were obtained in very good yields (*Scheme 3*).

In spite of using a large excess of phenylacetylene (12 equiv.) and a reaction time of 4 h at 70° in the synthesis of 3,3′,4,4′,5,5′-hexakis(phenylethynyl)-2,2′-bithiophene (**2o**), we isolated the desired product in only 46% yield, besides 27% of incompletely alkynylated 4-bromo-pentakis(phenylethynyl)-2,2′-bithiophene **2p** as major by-product (*Scheme 3*).

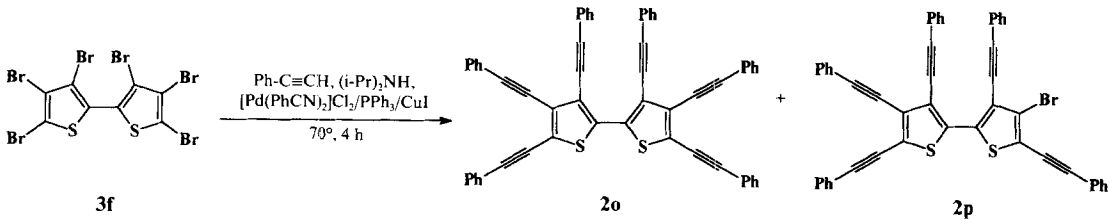
Scheme 3



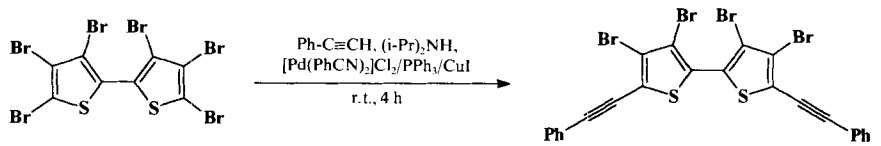
3a–g

2a R = Me_3Si, 3,3′-disubst.
b R = Me_3Si, 4,4′-disubst.
c R = Me_3Si, 5,5′-disubst.
d R = Me_3Si, 3,3′,4,4′-tetrasubst.
e R = Me_2Si, 3,3′,5,5′-tetrasubst.
f R = Me_3Si, 4,4′,5,5′-tetrasubst.
g R = Me_3Si, 3,3′,4,4′,5,5′-hexasubst.

2h R = Ph, 3,3′-disubst.
i R = Ph, 4,4′-disubst.
k R = Ph, 5,5′-disubst.
l R = Ph, 3,3′,4,4′-tetrasubst.
m R = Ph, 3,3′,5,5′-tetrasubst.
n R = Ph, 4,4′,5,5′-tetrasubst.
o R = Ph, 3,3′,4,4′,5,5′-hexasubst.



3f **2o** **2p**

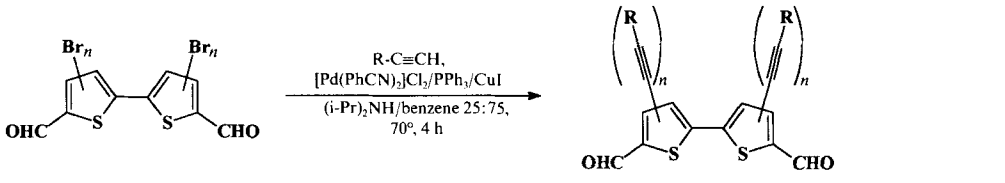


3f **2r**

The substitution pattern of **2p** could not be conclusively explained by spectroscopic methods. Based on the comparison of its ^{13}C-NMR data with those of other phenylethynylated 2,2′-bithiophenes described here and the known differences in reactivity between the 3-, 4-, and 5-positions, and symmetry-related positions of the bithiophene system [24], it can be suggested that the structure of **2p** is as shown. Complete conversion of **3f** to the hexaethynyl derivative **2o** was achieved using a large excess (30 equiv.) of phenylacetylene and heating under reflux for 24 h. The observed reactivity leads to the conclusion that the level of alkynylation can be controlled through variations in temperature. *E.g.*, when a large excess of phenylacetylene was used, but the reaction was conducted at room temperature, only the dialkynylated product 3,3′,4,4′-tetrabromo-5,5′-bis(phenylethynyl)-2,2′-bithiophene (**2r**) was obtained from **3f** (*Scheme 3*).

The syntheses of the polyethynyl-2,2′-bithiophenes **2a–r** with the $[Pd(PhCN)_2Cl_2]$/PPh_3/CuI catalyst system in $(i\text{-}Pr)_2NH$ suggest that this system is well suited for the alkynylation of thiophene analogs. However, application of these conditions to the alkynylation of the polybromo-2,2′-bithiophene-5,5′-dicarbaldehydes **4a–c** gave poor

Scheme 4



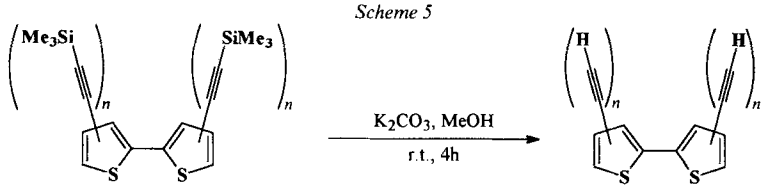
4a–c

1a R = Me_3Si, 3,3′-disubst. **1d** R = Ph, 3,3′-disubst.
b R = Me_3Si, 4,4′-disubst. **e** R = Ph, 4,4′-disubst.
c R = Me_3Si, 3,3′,4,4′-tetrasubst. **f** R = Ph, 3,3′,4,4′-tetrasubst.

results, due to the low solubility of these compounds in $(i\text{-}Pr)_2NH$. By replacing $(i\text{-}Pr)_2NH$ with benzene/$(i\text{-}Pr)_2NH$ 3:1 (*v*/*v*), the (trimethylsilyl)ethynyl and phenylethynyl derivatives **1a–f** were obtained in moderate-to-good yields (*Scheme 4*).

The terminally unprotected ethynylbithiophenes could be easily prepared by protodesilylation with K_2CO_3 in degassed MeOH (*Scheme 5*). Because of the instability of the polyethynylated 2,2′-bithiophenes **5a–e**, isolation and complete characterization was extremely difficult. In the case of the 5,5′-dicarbaldehydes **1a–c**, protodesilylation was not successful.

Scheme 5



2a–c,e,f

5a 3,3′-disubst.
b 4,4′-disubst.
c 5,5′-disubst.
d 3,3′,5,5′-tetrasubst.
e 4,4′,5,5′-tetrasubst.

In conclusion, we have shown that the easily obtained brominated 2,2′-bithiophenes **3a–f** and 2,2′-bithiophene-5,5′-dicarbaldehydes **4a–c** can be converted to the polyethynylbithiophene derivatives **1a–f** and **2a–r** by Pd^{II}-catalyzed coupling reactions. The alkynyl-substitued 5,5′-dicarbaldehydes **1a–f** are potential intermediates in the synthesis of alkynylated tetrathiaporphycenes. Derivatives such as **1a,d**, **2a,f,h,n**, and **5a,e**, which may adopt a conformation that allows for the reaction of the acetylenic moieties with transition-metal complexes, could provide a route to thia derivatives of polycyclic aromatic hydrocarbons [25]. Work in this direction is in progress.

We thank *BASF AG*, *Bayer AG*, and *Hoechst AG*, the *Verband der Chemischen Industrie*, *Fonds der Chemie*, as well as the *Deutsche Forschungsgemeinschaft* for support of this work. Thanks go to *Hewlett Packard* and *Varian* for providing UV/VIS spectrometers and Dr. *J. Fröhlich*, Vienna, for providing samples of 2,2′-bithiophene derivatives. We would also like to thank Ms. *U. Hertle* and Dr. *W. Kramer* for NMR spectra, Mr. *H. Rudy* and Mr. *P. Weyrich* for elemental analysis and mass spectra, Dr. *R. Faust* for many helpful discussions, and Mrs. *A. Bryant-Friedrich*, M.Sc., for help with the manuscript.

Experimental Part

General. All reactions were carried out under Ar in flame-dried glassware. $(i\text{-Pr})_2NH$ was freshly distilled from KOH, Et_2O and benzene were distilled from sodiumbenzophenone before use. Column chromatography (CC): silica gel (60–200 mesh) from *ICN-Biomedicals*. M.p.: *Reichert* melting-point microscope; uncorrected. UV/VIS Spectra: *Hewlett Packard HP 8453 UV-Vis ChemStation* and *Varian CARY 2200* spectrophotometer; CH_2Cl_2 solns.; in nm (lg ε). IR Spectra: *Perkin-Elmer PE-1600-FT-IR* spectrophotometer; KBr pellets; $\tilde{\nu}$ in cm^{-1}. ^{1}H-NMR Spectra: *Bruker-WM-250* spectrometer (at 250.13 MHz) and *Varian-XL-300* spectrometer (at 299.95 MHz), δ in ppm rel. to Me_4Si, J in Hz. ^{13}C-NMR Spectra: at 62.89 and 75.43 MHz on the same spectrometers. MS: *Varian-MAT-311-A* mass spectrometer at 70 eV; *m/z* (rel. %). Elemental analyses: *Foss-Heraeus Vario EL.*

Brominated 2,2′-Bithiophenes **3** *Starting from 2,2′-Bithiophene* (*Method A*): *General Procedure.* To a soln. of 2,2′-bithiophene (0.01 mol, 1.66 g) in $CHCl_3$/AcOH 1:1 (*v/v*; 100 ml) was added NBS (1.05 *n* mol-equiv.) in one portion. The reaction started instantly at r.t. The mixture was then warmed to 70° and, after stirring under reflux for 4 h, allowed to cool to r.t., diluted with $CHCl_3$ (**3a–c**) or CS_2 (**3d–g**), and washed with KOH soln. until basic and then with H_2O. The org. layer was dried ($MgSO_4$) and evaporated.

Brominated 2,2′-Bithiophenes **3** *Starting from Bromothiophene Derivatives* (*Method B*): *General Procedure.* Anh. $CuCl_2$ (4 g, 0.03 mol) was added to a soln. of brominated 2-thienyllithium in abs. Et_2O (150 ml) at −78° (the 2-thienyllithium was prepared in the usual way by treating 0.02 mol of the corresponding 2- bromothiophene and 8.4 ml (0.021 mol) of 2.5M BuLi in hexane at −78°). After stirring at −78° for 2 h, the mixture was allowed to warm to r.t. overnight and then treated with 5N HCl at 0°. The Et_2O phase was diluted with $CHCl_3$ (**3a–c**) or CS_2 (**3d–g**), extracted with 5N HCl to remove residual $CuCl_2$, washed with H_2O, dried ($MgSO_4$), and evaporated.

3,3′-Dibromo-2,2′-bithiophene (**3a**) [19] (*Method B*): Pure **3a** was obtained by bulb-to-bulb distillation (b.p. 100–120°/6·10^{-3}mbar) and recrystallization from petroleum ether (90–110): 2.47 g (76.2%). Colorless crystals. M.p. 98–100°. IR (KBr): 3104*m*, 3083*w*, 1553*w*, 1487*s*, 1444*s*, 1401*w*, 1340*s*, 1132*m*, 1077*m*, 1071*w*, 926*m*, 857*s*, 805*m*, 794*m*, 720*s*, 706*s*, 672*m*, 640*m*, 596*s*, 512*w*, 487*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.39 (*d*, ^3J = 5.4, 2 H); 7.07 (*d*, ^3J = 5.4, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 130.58; 128.50; 127.28; 112.45. EI-MS: 324 (100, M^+), 243 (20, $[M-Br]^+$), 164 (70, $[M-2\ Br]^+$). HR-MS: 321.8121 ($C_8H_4{}^{79}Br_2S_2^+$; calc. 321.8121). Anal. calc. for $C_8H_4Br_2S_2$: C 29.65, H 1.24, Br 49.32, S 19.79; found: C 29.63, H 1.26, Br 49.02, S 20.09.

4,4′-Dibromo-2,2′-bithiophene (**3b**; *Method B*): Recrystallization from EtOH or benzene gave pure **3b**: 2.29 g (70.7%). Colorless flakes. M.p. 131°. IR (KBr): 3108*s*, 3077*w*, 1490*s*, 1295*m*, 1177*w*, 910*s*, 840*m*, 812*s*, 795*m*, 733*s*, 580*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.13 (*d*, ^4J = 1.3, 2 H); 7.06 (*d*, ^4J = 1.3, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 136.82; 126.48; 122.06; 110.34. EI-MS: 324 (100, M^+), 243 (15, $[M-Br]^+$), 164 (30, $[M-2\ Br]^+$), 162 (10, $M^+/2$). HR-MS: 323.8101 ($C_8H_4{}^{79}Br^{81}BrS_2^+$; calc. 323.8101). Anal. calc. for $C_8H_4Br_2S_2$: C 29.65, H 1.24, Br 49.32, S 19.79; found: C 29.56, H 1.25, Br 49.62, S 19.57.

5,5′-Dibromo-2,2′bithiophene (**3c**) [17] [18] (*Method A* and *B*): Recrystallization from EtOH or benzene gave pure **3c**: 3.08 g (95.1%; *Method A*) and 2.79 g (86.1%; *Method B*). Colorless flakes. M.p. 149°. IR (KBr): 3092*w*, 3068*w*, 3038*w*, 1505*m*, 1417*s*, 1198*m*, 1058*m*, 970*m*, 867*m*, 794*s*, 627*m*, 457*s*. ^{1}H-NMR (250 MHz, $CDCl_3$): 6.96 (*d*, ^3J = 3.8, 2 H); 6.84 (*d*, ^3J = 3.8, 2 H). ^{13}C-NMR (63 MHz, $CDCl_3$): 137.78; 130.64; 124.13; 111.52. EI-MS: 324 (100, M^+), 243 (40, $[M-Br]^+$), 164 (50, $[M-2\ Br]^+$), 82 (70, $[M-2\ Br-C_4H_2S]^+$). HR-MS: 321.8121 ($C_8H_4{}^{79}Br_2S_2^+$; calc. 321.8121). Anal. calc. for $C_8H_4Br_2S_2$: C 29.65, H 1.24, Br 49.32, S 19.79; found: C 29.70, H 1.35, Br 49.24, S 19.71.

3,3′,4,4′-Tetrabromo-2,2′-bithiophene (**3d**, *Method B*): Recrystallization from EtOH or benzene gave pure **3d**: 3.33 g (69.1%). Colorless needles. M.p. 108–109°. IR (KBr): 3100*m*, 1465*s*, 1319*w*, 1303*s*, 1251*w*, 930*m*, 882*w*, 849*m*, 787*w*, 743*s*, 664*m*, 619*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.51 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 129.58; 124.96; 116.58; 114.41. EI-MS: 482 (100, M^+), 401 (5, $[M-Br]^+$), 322 (55, $[M-2\ Br]^+$), 241 (15, $[M-3\ Br]^+$), 162 (25, $[M-4\ Br]^+$). HR-MS: 481.6290 ($C_8H_2{}^{79}Br_2{}^{81}Br_2S_2^+$; calc. 481.6290). Anal. calc. for $C_8H_2Br_4S_2$: C 19.94, H 0.42, Br 66.33, S 13.31; found: C 20.17, H 0.49, Br 65.82, S 13.52.

3,3′,5,5′-Tetrabromo-2,2′-bithiophene (**3e**) [17] (*Method A* and *B*): Pure **3e** was obtained by sublimation at 105–110°/8·10^{-3} mbar and recrystallization from EtOH or benzene: 4.34 g (90.0%; *Method A*) and 3.88 g (80.5%; *Method B*). Colorless crystals. M.p. 137–138°. IR (KBr): 3100*w*, 1483*m*, 1395*w*, 1292*w*, 1130*w*, 982*m*, 830*w*, 804*s*, 668*w*, 587*w*, 472*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.04 (*s*, 2 H). ^{13}C-NMR (63 MHz, $CDCl_3$): 132.99; 129.56; 114.81; 112.11. ^{13}C-NMR (63 MHz, CS_2/(D_6)aceton 2:1, gated decoupling): 133.57 (^1J(C(3),H) = 180.4); 130.03 (^3J(C(2),H) = 9.18); 115.73 (^2J(C(4),H) = 0.89); 112.97 (^2J(C(2),H) = 1.78). EI-MS: 482 (100, M^+), 401 (20, $[M-Br]^+$), 322 (70, $[M-2\ Br]^+$), 241 (30, $[M-3\ Br]^+$), 162 (95, $[M-4\ Br]^+$). HR-MS: 481.6290 ($C_8H_2{}^{79}Br_2{}^{81}Br_2S_2^+$; calc. 481.6290). Anal. calc. for $C_8H_2Br_4S_2$: C 19.94, H 0.42, Br 66.33, S 13.31; found: C 19.71, H 0.56, Br 66.26, S 13.47.

3,3',4,4',5,5'-Hexabromo-2,2'-bithiophene (**3f**) [17] (*Method A* and *B*): Recrystallization of the residue from benzene gave pure **3f**: 3.89 g (60.8%; *Method A*) and 4.10 g (83.6%; *Method B*). Colorless needles. M.p. 254–256°. IR (KBr): 1468*s*, 1388*m*, 1290*m*, 1275*s*, 1249*w*, 1099*w*, 901*w*, 840*m*, 793*w*, 713*m*, 499*w*. ^{13}C-NMR (75 MHz, CS_2/$CDCl_3$ 1:1): 140.45; 118.54; 115.98; 113.51. EI-MS: 640 (100, M^+), 559 (20, $[M - Br]^+$), 480 (5, $[M - 2\ Br]^+$), 399 (5, $[M - 3\ Br]^+$), 320 (5, $[M - 4\ Br]^+$), 239 (5, $[M - 5\ Br]^+$), 160 (5, $[M - 6\ Br]^+$). HR-MS: 639.4481 ($C_8{}^{79}Br_3{}^{81}Br_3S_2^+$; calc. 639.4480). Anal. calc. for $C_8Br_6S_2$: C 15.02, Br 74.96, S 10.02; found: C 15.22, Br 74.78, S 10.00.

4,4',5,5'-Tetrabromo-2,2'-bithiophene (**3g**; *Method A*, from **3b**): Recrystallization from EtOH or benzene gave pure **3g**: 4.53 g (94.0%). Colorless needles. M.p. 179–180°. IR (KBr): 3077*w*, 1496*s*, 1413*m*, 1270*m*, 995*m*, 886*m*, 806*s*, 574*w*, 467*m*. ^{1}H-NMR (300 MHz, $CDCl_3$/CS_2 1:2): 6.91 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$/CS_2 1:2): 136.15; 126.55; 114.77; 111.12. EI-MS: 482 (100, M^+), 401 (15, $[M - Br]^+$), 322 (45, $[M - 2\ Br]^+$), 241 (20, $[M - 3\ Br]^+$), 162 (40, $[M - 4\ Br]^+$). HR-MS: 481.6290 ($C_8H_2{}^{79}Br_2{}^{81}Br_2S_2^+$; calc. 481.6290). Anal. calc. for $C_8H_2Br_4S_2$: C 19.94, H 0.42, Br 66.33, S 13.31; found: C 19.93, H 0.44, Br 66.10, S 13.53.

Brominated 2,2'-Bithiophene-5,5'-dicarbaldehydes **4a–c**: *General Procedure*. To a soln. of **3e–g** (5 mmol) in abs. Et_2O (150 ml) were added dropwise 2.5M BuLi in hexane (4.4 ml, 11 mmol) within 30 min at −78°. After stirring for 1 h at −78°, DMF (11 mmol, 0.9 ml) was added in one portion. After stirring for an additional 2 h at −78°, the mixture was allowed to warm to r.t. overnight, then hydrolyzed with 5N HCl with ice cooling, and diluted with $CHCl_3$. The aq. phase was extracted with $CHCl_3$ and the combined org. phase washed with H_2O, dried ($MgSO_4$), and evaporated, and the remaining solid recrystallized from benzene.

3,3'-Dibromo-2,2'-bithiophene-5,5'-dicarbaldehyde (**4a**): 1.36 g (71.6%). M.p. 234–235°. UV/VIS (CH_2Cl_2): 256 (4.03), 325 (4.05), 350 (sh, 4.02), 368 (sh, 3.93), 389 (sh, 3.68). IR (KBr): 3077*m*, 2839*m*, 1654*s*, 1508*m*, 1362*s*, 1292*m*, 1215*s*, 1124*m*, 1115*s*, 869*w*, 812*m*, 715*w*, 669*m*, 598*w*, 479*w*. ^{1}H-NMR (300 MHz, $CDCl_3$/CS_2 1:2): 9.90 (*s*, 2 H); 7.71 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$/CS_2 1:2): 180.07; 140.00; 137.76; 136.09; 113.79. EI-MS: 380 (100, M^+), 351 (10, $[M - CHO]^+$), 270 (30, $[M - CHO - Br]^+$), 241 (10, $[M - 2\ CHO - Br]^+$), 162 (40, $[M - 2\ CHO - 2\ Br]^+$). HR-MS: 377.8018 ($C_{10}H_4{}^{79}Br_2S_2O_2^+$; calc. 377.8019). Anal. calc. for $C_{10}H_4Br_2S_2O_2$: C 31.76, H 1.06, Br 41.78, S 16.93; found: C 31.51, H 1.20, Br 41.62, S 17.16.

4,4'-Dibromo-2,2'-bithiophene-5,5'-dicarbaldehyde (**4b**) [26]: 1.31 g (68.9%). M.p. 252–254°. UV/VIS (CH_2Cl_2): 242 (sh, 4.00), 285 (3.96), 313 (3.92), 356 (sh, 4.33), 370 (4.38), 386 (sh, 4.25). IR (KBr): 3079*w*, 2844*w*, 1654*s*, 1492*m*, 1433*s*, 1367*w*, 1281*w*, 1204*s*, 1159*m*, 920*m*, 848*m*, 686*w*, 660*w*, 599*w*, 477*w*. ^{1}H-NMR (300 MHz, $CDCl_3$/CS_2 1:2): 9.97 (*s*, 2 H); 7.36 (*s*, 2 H). ^{1}H-NMR (63 MHz, $CDCl_3$/CS_2 1:2): 181.70; 142.96; 137.71; 129.98; 120.59. EI-MS: 380 (100, M^+), 351 (10, $[M - CHO]^+$), 299 (20, $[M - Br]^+$), 270 (20, $[M - CHO - Br]^+$), 241 (20, $[M - 2\ CHO - Br]^+$), 162 (20, $[M - 2\ CHO - 2\ Br]^+$). HR-MS: 377.8018 ($C_{10}H_4{}^{79}Br_2S_2O_2^+$; calc. 377.8019). Anal. calc. for $C_{10}H_4Br_2O_2S_2$: C 31.76, H 1.06, Br 41.78, S 16.93; found: C 31.64, H 1.06, Br 41.96, S 16.89.

3,3',4,4'-Tetrabromo-2,2'-bithiophene-5,5'-dicarbaldehyde (**4c**) [21]: 1.76 g (65.4%). M.p. 266–267°. UV/VIS (CH_2Cl_2): 242 (sh, 3.89), 387 (sh, 4.03), 322 (4.14), 374 (sh, 3.83), 395 (sh, 3.56). IR (KBr): 2865*w*, 1659*s*, 1481*w*, 1458*w*, 1382*w*, 1351*m*, 1298*w*, 1276*w*, 1200*s*, 813*w*, 768*w*, 676*m*, 653*w*. ^{1}H-NMR (300 MHz, $CDCl_3$/CS_2 1:2): 10.02 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$/CS_2 1:2): 182.07; 138.49; 135.99; 123.84; 118.66. EI-MS: 538 (100, M^+), 480 (20, $[M - 2\ CHO]^+$), 457 (20, $[M - Br]^+$), 399 (20, $[M - 2\ CHO - Br]^+$), 349 (30, $[M - CHO - 2\ Br]^+$), 320 (20, $[M - 2\ CHO - 2\ Br]^+$), 268 (20, $[M - CHO - 3\ Br]^+$), 239 (20, $[M - 2\ CHO - 3\ Br]^+$), 160 (40, $[M - 2\ CHO - 4\ Br]^+$). HR-MS: 537.6189 ($C_{10}H_2{}^{79}Br_2{}^{81}Br_2O_2S_2^+$; calc. 537.6190). Anal. calc. for $C_{10}H_2Br_4O_2S_2$: C 22.33, H 0.37, Br 59.42, S 11.92; found: C 22.32, H 0.56, Br 59.31, S 12.08.

Polyethynyl-2,2'-bithiophenes **2a–r**: *General Procedure*. Brominated 2,2'-bithiophene **3a–g** (0.5 mmol) was dissolved in freshly distilled $(i\text{-}Pr)_2NH$ (80 ml). To this clear soln. were added dichlorobis(benzonitrile)palladium(II) (78 mg, 0.2 mmol), PPh_3 (106 mg, 0.4 mmol), and CuI (38 mg, 0.2 mmol). The soln. was degassed by passing a rapid stream of Ar through it. An excess of the corresponding acetylene (2 equiv. of phenylacetylene or (trimethylsilyl)acetylene per Br-atom) was then added at r.t. After stirring for 30 min, the soln. was heated at 70° for 4 h. During this time, the soln. rapidly turned bright yellow, then yellow brown, and finally dark brown, with the formation of a heavy precipitate. The soln. was allowed to cool to r.t. and was then filtered. The filtrate was evaporated and the residue chromatographed (silica gel column).

3,3'-Bis[(trimethylsilyl)ethynyl]-2,2'-bithiophene (**2a**): CC (petroleum ether 40–60)) and recrystallization from MeOH gave pure **2a**: 150 mg (83.8%). Colorless needles. M.p. 74–75°. IR (KBr): 3087*w*, 2954*m*, 2148*m*, 1494*w*, 1361*w*, 1252*m*, 1239*m*, 1082*w*, 950*s*, 886*s*, 843*s*, 824*s*, 755*s*, 712*s*, 636*s*, 435*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.16 (*d*, ^3J = 5.2, 2 H); 7.05 (*d*, ^3J = 5.2, 2 H); 0.26 (*s*, 18 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 139.02; 130.67; 123.82; 119.39; 101.56; 100.78; −0.13. EI-MS: 358 (30, M^+), 343 (25, $[M - Me]^+$), 328 (10, $[M - 2\ Me]^+$), 285 (10,

$[M - SiMe_3]^+$); 97 (10, $C_2SiMe_3^+$), 73 (100, $SiMe_3^+$). HR-MS: 358.0700 ($C_{18}H_{22}S_2Si_2^+$; calc. 358.0702). Anal. calc. for $C_{18}H_{22}S_2Si_2$: C 60.32, H 6.19, S 17.86; found: C 60.36, H 6.30, S 18.00.

4,4'-Bis[(trimethyl)ethynylsilyl]-2,2'-bithiophene (**2b**): CC (petroleum ether (40–60)) and recrystallization from MeCN gave pure **2b**. 132 mg (73.7%). Light-yellow crystals. M.p. 123–124°. UV/VIS (CH_2Cl_2): 239 (sh, 4.61), 247 (4.75), 257 (sh, 4.47), 318 (3.97). IR (KBr): 3102*m*, 3062*w*, 2958*m*, 2898*w*, 2156*s*, 1521*m*, 1481*w*, 1407*w*, 1326*m*, 1255*s*, 1245*s*, 1185*m*, 1153*w*, 978*s*, 867*s*, 848*s*, 827*s*, 758*s*, 739*s*, 702*s*, 631*m*, 617*s*, 478*w*, 422*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.35 (*d*, ^4J = 1.2, 2 H); 7.17 (*d*, ^4J = 1.2, 2 H); 0.25 (*s*, 18 H). ^{13}C-NMR (63 MHz, $CDCl_3$): 136.12; 128.78; 126.78; 123.06; 99.38; 94.28; –0.09. EI-MS: 358 (100, M^+), 343 (85, $[M - Me]^+$), 313 (5, $[M - 3\ Me]^+$), 164 (30, $[M - 2\ C_2SiMe_3]^+$). HR-MS: 358.0703 ($C_{18}H_{22}S_2Si_2^+$; calc. 358.0702). Anal. calc. for $C_{18}H_{22}S_2Si_2$: C 60.32, H 6.19, S 17.86; found: C 60.12, H 6.14, S 17.60.

5,5'-Bis[(trimethylsilyl)ethynyl]-2,2'-bithiophene (**2c**): CC (petroleum ether (40–60)) and recrystallization from MeCN gave pure **2c**: 166 mg (92.7%). Light-yellow flakes. M.p. 172°. UV/VIS (CH_2Cl_2): 261 (3.72), 357 (sh, 4.39), 371 (4.42), 387 (sh, 4.27). IR (KBr): 3089*w*, 3078*w*, 2957*w*, 2898*w*, 2143*s*, 1503*w*, 1255*m*, 1245*m*, 1162*w*, 1155*w*, 1054*w*, 841*s*, 797*s*, 757*m*, 637*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.11 (*d*, ^3J = 3.9, 2 H); 6.99 (*d*, ^3J = 3.9, 2 H); 0.27 (*s*, 18 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 137.84; 133.35; 123.66; 122.45; 100.45; 97.15; –0.07. EI-MS: 358 (30, M^+), 343 (70, $[M - Me]^+$), 313 (5, $[M - 3\ Me]^+$), 164 (25, $[M - 2\ C_2SiMe_3]^+$). HR-MS: 358.0703 ($C_{18}H_{22}S_2Si_2^+$; calc. 358.0702). Anal. calc. for $C_{18}H_{22}S_2Si_2$: C 60.32, H 6.19, S 17.86; found: C 60.01, H 6.14, S 17.78.

3,3',4,4'-Tetrakis[(trimethylsilyl)ethynyl]-2,2'-bithiophene (**2d**): CC (hexane) and recrystallization from MeOH gave pure **2d**: 123 mg (54.7%). Light-yellow crystals. M.p. 169–171° (dec.). UV/VIS (CH_2Cl_2): 253 (4.64), 259 (sh, 4.63), 308 (sh, 3.96), 321 (4.05), 336 (4.10), 360 (4.17), 375 (4.09). IR (KBr): 3111*w*, 2959*m*, 2898*w*, 2163*m*, 2150*m*, 1501*w*, 1405*w*, 1341*w*, 1248*s*, 1134*w*, 893*s*, 875*s*, 843*s*, 756*s*, 700*m*, 642*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.37 (*s*, 2 H); 0.28 (*s*, 18 H); 0.26 (*s*, 18 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 137.72; 127.73; 125.08; 121.91; 105.21; 98.75; 98.16; 96.86; 0.11; –0.25. EI-MS: 550 (20, M^+), 535 (5, $[M - Me]^+$), 477 (5, $[M - SiMe_3]^+$), 462 (5, $[M - SiMe_3 - Me]^+$), 447 (5, $[M - SiMe_3 - 2\ Me]^+$), 73 (100, $SiMe_3^+$). HR-MS: 550.1491 ($C_{28}H_{38}S_2Si_4^+$; calc. 550.1492). Anal. calc. for $C_{28}H_{38}S_2Si_4$: C 61.08, H 6.96, S 11.62; found: C 60.72, H 6.87, S 11.62.

3,3',5,5'-Tetrakis[(trimethylsilyl)ethynyl]-2,2'-bithiophene (**2e**): CC (petroleum ether (40–60)/$CHCl_3$ 5:1) and recrystallization from MeCN or pentane gave pure **2e**: 204 mg (90.7%). Yellow crystals. M.p. 153–154° (dec.). UV/VIS (CH_2Cl_2): 266 (sh, 4.65), 270 (4.66), 379 (4.30), 400 (4.46), 423 (4.40). IR (KBr): 3092*w*, 2955*m*, 2146*s*, 1510*m*, 1248*s*, 1139*w*, 976*m*, 892*m*, 845*s*, 758*s*, 699*w*, 642*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.14 (*s*, 2 H); 0.30 (*s*, 18 H); 0.24 (*s*, 18 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 139.14; 134.78; 121.33; 118.23; 103.27; 101.21; 100.05; 96.52; –0.16; –0.52. EI-MS: 550 (50, M^+), 535 (10, $[M - Me]^+$), 477 (5, $[M - SiMe_3]^+$), 462 (5, $[M - SiMe_3 - Me]^+$), 447 (5, $[M - SiMe_3 - 2\ Me]^+$), 73 (100, $SiMe_3^+$). HR-MS: 550.1492 ($C_{28}H_{38}S_2Si_4^+$; calc. 550.1493). Anal. calc. for $C_{28}H_{38}S_2Si_4$: C 61.08, H 6.96, S 11.62; found: C 61.08, H 7.04, S 11.30.

4,4',5,5'-Tetrakis[(trimethylsilyl)ethynyl]-2,2'-bithiophene (**2f**): CC (petroleum ether (40–60)/$CHCl_3$ 5:1) and recrystallization from MeCN gave pure **2f**: 193 mg (85.8%). Yellow-orange crystals. M.p. 208–209°. UV/VIS (CH_2Cl_2): 257 (sh, 4.49), 267 (4.66), 294 (4.21), 305 (4.22), 365 (sh, 4.41), 379 (4.47), 393 (sh, 4.35). IR (KBr): 3089*w*, 2959*m*, 2898*w*, 2142*s*, 1505*m*, 1414*w*, 1332*w*, 1248*s*, 1199*m*, 994*s*, 842*s*, 759*s*, 703*m*, 643*w*, 623*w*, 512*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.01 (*s*, 2 H); 0.27 (*s*, 18 H); 0.26 (*s*, 18 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 135.24; 128.13; 126.33; 126.01; 105.42; 99.35; 98.04; 95.85; 0.04; –0.05. EI-MS: 550 (80, M^+), 535 (5, $[M - Me]^+$), 477 (5, $[M - SiMe_3]^+$), 73 (100, $SiMe_3^+$). HR-MS: 550.1491 ($C_{28}H_{38}S_2Si_4^+$; calc. 550.1492). Anal. calc. for $C_{28}H_{38}S_2Si_4$: C 61.08, H 6.96, S 11.62; found: C 61.03, H 6.99, S 11.22.

3,3',4,4',5,5'-Hexakis[(trimethylsilyl)ethynyl]-2,2'-bithiophene (**2g**): CC (petroleum ether (40–60)/$CHCl_3$ 5:1) and recrystallization from MeCN gave pure **2g**: 271 mg (73.0%). Orange crystals. M.p. 237–241° (dec.). UV/VIS (CH_2Cl_2): 265 (4.61), 276 (4.72), 295 (4.67), 385 (sh, 4.28), 405 (4.47), 431 (4.45). IR (KBr): 2960*s*, 2899*m*, 2146*s*, 1487*m*, 1407*m*, 1366*w*, 1249*s*, 1084*m*, 934*s*, 846*s*, 759*s*, 745*m*, 699*m*, 647*s*, 632*m*, 578*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.31 (*s*, 18 H); 0.27 (*s*, 36 H, overlapped). ^{13}C-NMR (75 MHz, $CDCl_3$): 136.75; 129.55; 124.75; 121.40; 106.64; 105.61; 101.61; 98.69; 97.14; 95.72; 0.09; –0.12; –0.45. EI-MS: 742 (55, M^+), 727 (5, $[M - Me]^+$), 669 (5, $[M - SiMe_3]^+$), 371 (5, ½ M^+), 73 (100, $SiMe_3^+$). HR-MS: 742.2283 ($C_{38}H_{54}S_2Si_6^+$; calc. 742.2283). Anal. calc. for $C_{38}H_{54}S_2Si_6$: C 61.43, H 7.33, S 8.62; found: C 61.45, H 7.15, S 8.64.

3,3'-Bis(phenylethynyl)-2,2'-bithiophene (**2h**): CC (petroleum ether (40–60)/$CHCl_3$ 5:1) and recrystallization from petroleum ether (40–60)/$CHCl_3$ 9:1 or benzene gave pure **2h**: 165 mg (90.2%). Yellow cubes. M.p. 162–164°. UV/VIS (CH_2Cl_2): 251 (4.42), 266 (4.44), 285 (sh, 4.36), 339 (4.29). IR (KBr): 3105*w*, 3076*w*, 3038*w*, 2199*w*, 1594*w*, 1506*m*, 1486*m*, 1439*m*, 1363*w*, 1160*w*, 1070*w*, 1029*w*, 942*w*, 913*w*, 876*w*, 828*m*, 759*m*, 753*s*, 711*s*, 690*s*, 632*s*, 549*w*, 537*w*, 521*w*, 477*w*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.60–7.56 (*m*, 4 H); 7.37–7.33 (*m*, 6 H); 7.24 (*d*, ^3J = 5.3, 2 H); 7.16 (*d*, ^3J = 5.3, 2 H). ^{13}C-NMR (63 MHz, $CDCl_3$): 138.27; 131.40; 130.40; 128.43; 124.25; 123.42; 119.34; 95.47;

85.84. EI-MS: 366 (100, M^+), 183 (20, ½ M^+). HR-MS: 366.0535 ($C_{24}H_{14}S_2^+$; calc. 366.0537). Anal. calc. for $C_{24}H_{14}S_2$: C 78.68, H 3.85, S 17.47; found: C 78.70, H 3.97, S 17.33.

4,4'-Bis(phenylethynyl)-2,2'-bithiophene (**2i**): CC (petroleum ether (40–60)/$CHCl_3$ 5:1) and recrystallization from petroleum ether (40–60)/$CHCl_3$ 1:1 or benzene gave pure **2i**: 147 mg (80.3%). Yellow crystals. M.p. 171–172°. UV/VIS (CH_2Cl_2): 283 (4.88), 297 (sh, 4.76), 325 (sh, 4.11). IR (KBr): 3110*m*, 3054*m*, 2215*w*, 1593*m*, 1528*m*, 1485*m*, 1442*m*, 1344*m*, 1182*m*, 1071*m*, 1026*m*, 972*m*, 921*m*, 864*m*, 841*s*, 829*s*, 758*s*, 693*s*, 618*s*, 552*m*, 530*s*, 462*w*. ^{1}H-NMR (300 MHz, $CDCl_3/CS_2$ 1:2): 7.45–7.39 (*m*, 4 H); 7.32 (*d*, ^4J = 1.3, 2 H); 7.30–7.25 (*m*, 6 H); 7.18 (*d*, ^4J = 1.3, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3/CS_2$ 1:2): 136.07; 131.26; 128.02; 127.94; 127.56; 126.35; 123.10; 122.84; 89.48; 84.47. EI-MS: 366 (100, M^+), 182 (20, ½ M^+). HR-MS: 366.0538 ($C_{24}H_{14}S_2^+$; calc. 366.0537). Anal. calc. for $C_{24}H_{14}S_2$: C 78.68, H 3.85, S 17.47; found: C 79.06, H 3.81, S 17.13.

5,5'-Bis(phenylethynyl)-2,2'-bithiophene (**2k**): CC (petroleum ether (40–60)/$CHCl_3$ 5:1) and recrystallization from benzene gave pure **2k**: 175 mg (95.6%). Yellow crystals. M.p. 173–175°. UV/VIS (CH_2Cl_2): 385 (4.70). IR (KBr): 3047*w*, 2195*w*, 1597*w*, 1514*m*, 1483*w*, 1441*m*, 1070*w*, 1046*w*, 1024*w*, 912*w*, 876*w*, 804*s*, 756*s*, 691*s*, 499*m*. ^{1}H-NMR (250 MHz, $CDCl_3$, T = 323 K): 7.53–7.46 (*m*, 4 H); 7.36–7.26 (*m*, 6 H); 7.15 (*d*, ^3J = 4.0, 2 H); 7.32 (*d*, ^3J = 4.0, 2 H). ^{13}C-NMR (63 MHz, $CDCl_3$, T = 323 K): 138.15; 132.79; 131.46; 128.55; 128.41; 124.02; 122.90; 122.85; 94.63; 82.57. EI-MS: 366 (100, M^+), 183 (35, ½ M^+). HR-MS: 366.0535 ($C_{24}H_{14}S_2^+$; calc. 366.0537). Anal. calc. for $C_{24}H_{14}S_2$: C 78.68, H 3.85, S 17.47; found: C 78.39, H 3.90, S 17.71.

3,3',4,4'-Tetrakis(phenylethynyl)-2,2'-bithiophene (**2l**): CC (petroleum ether (40–60)/$CHCl_3$ 5:1) and recrystallization from benzene gave pure **2l**: 220 mg (77.7%). Yellow needles. M.p. 182–183°. UV/VIS (CH_2Cl_2): 290 (4.86), 307 (4.77), 377 (4.36). IR (KBr): 3094*w*, 2207*w*, 1594*w*, 1507*w*, 1495*m*, 1477*m*, 1440*m*, 1070*w*, 1029*w*, 915*w*, 753*s*, 689*s*, 680*m*, 551*w*, 532*w*, 508*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.64–7.61 (*m*, 4 H); 7.59–7.54 (*m*, 4 H); 7.49 (*s*, 2 H); 7.39–7.32 (*m*, 12 H). ^{13}C-NMR (63 MHz, $CDCl_3$): 137.25; 131.67; 131.46; 128.69; 128.49; 128.40; 127.16; 125.14; 123.23; 123.11; 121.70; 99.28; 91.93; 84.68; 83.50. EI-MS: 566 (100, M^+). HR-MS: 566.1163 ($C_{40}H_{22}S_2^+$; calc. 566.1163). Anal. calc. for $C_{40}H_{22}S_2$: C 84.78, H 3.92, S 11.30; found: C 85.12, H 3.92, S 10.96.

3,3',5,5'-Tetrakis(phenylethynyl)-2,2'-bithiophene (**2m**): CC (petroleum ether (40–60)/$CHCl_3$ 1:1) and recrystallization from benzene gave pure **2m**: 264 mg (93.3%). Orange needles. M.p. 239–241°. UV/VIS (CH_2Cl_2): 242 (4.58), 310 (4.76), 321 (4.75), 425 (4.38), 447 (sh, 4.33). IR (KBr): 3051*w*, 2201*w*, 1596*m*, 1522*m*, 1481*m*, 1441*m*, 1068*w*, 1021*w*, 913*w*, 828*m*, 755*s*, 691*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.65–7.61 (*m*, 4 H); 7.54–7.50 (*m*, 4 H); 7.42–7.34 (*m*, 12 H); 7.32 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 137.98; 134.54; 131.18; 128.42; 128.41; 128.18; 128.11; 128.09; 122.63; 122.23; 121.68; 119.5; 96.15; 95.00; 84.93; 81.75. EI-MS: 566 (100, M^+), 283 (20, ½ M^+). HR-MS: 566.1163 ($C_{40}H_{22}S_2^+$; calc. 566.1163). Anal. calc. for $C_{40}H_{22}S_2$: C 84.78, H 3.92, S 11.30; found: C 85.03, H 3.67, S 11.30.

4,4',5,5'-Tetrakis(phenylethynyl)-2,2'-bithiophene (**2n**): CC (petroleum ether (40–60)/$CHCl_3$ 1:1) and recrystallization from benzene gave pure **2n**: 244 mg (86.2%). Orange crystals. M.p. 256–257° (dec.). UV/VIS (CH_2Cl_2): 238 (4.54), 292 (sh, 4.65), 306 (4.76), 404 (4.59). IR (KBr): 3077*w*, 3054*w*, 3031*w*, 2207*w*, 2192*w*, 1592*m*, 1521*m*, 1491*m*, 1441*m*, 1069*w*, 1024*w*, 915*w*, 816*m*, 752*s*, 690*s*, 678*m*, 524*w*, 499*m*. ^{1}H-NMR (300 MHz, $CDCl_3/CS_2$ 1:2): 7.52–7.49 (*m*, 8 H); 7.34–7.31 (*m*, 12 H); 7.12 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3/CS_2$ 1:2): 135.77; 131.64; 131.46; 128.70; 128.40; 128.35; 128.26; 127.55; 126.25; 125.66; 122.98; 122.73; 99.54; 94.19; 84.00; 82.44. EI-MS: 566 (100, M^+), 283 (25, ½ M^+). HR-MS: 566.1163 ($C_{40}H_{22}S_2$; calc. 566.1163). Anal. calc. for $C_{40}H_{22}S_2$: C 84.78, H 3.92, S 11.30; found: C 85.13, H 3.91, S 10.96.

3,3',4,4',5,5'-Hexakis(phenylethynyl)-2,2'-bithiophene (**2o**): To achieve complete conversion, **3f** was treated with a large excess of phenylacetylene (15 mmol) for 24 h. Without preceding filtration, the mixture was purified by CC ($CHCl_3$). Recrystallization from chlorobenzene gave **2o**: 288 mg (75.2%). Orange needles. M.p. 298° (dec.). UV/VIS (CH_2Cl_2): 245 (sh, 4.46), 290 (sh, 4.43), 327 (4.59), 438 (4.20), 456 (4.18). IR (KBr): 3069*w*, 3050*w*, 3034*w*, 2202*w*, 2192*w*, 1597*m*, 1516*w*, 1495*m*, 1441*m*, 1068*w*, 910*m*, 751*s*, 687*s*. ^{1}H-NMR (250 MHz, $CS_2/(D_6)$aceton 3:1): 7.64–7.59 (*m*, 6 H); 7.53–7.47 (*m*, 6 H); 7.41–7.31 (*m*, 18 H). EI-MS: 766 (100, M^+). HR-MS: 766.1791 ($C_{56}H_{30}S_2^+$; calc. 766.1788). Anal. calc. for $C_{56}H_{30}S_2$: C 87.70, H 3.94, S 8.36; found: C 87.73, H 3.92, S 8.35.

4-Bromo-3,3',4',5,5'-pentakis(phenylethynyl)-2,2'-bithiophene (**2p**): Pure **2p** was obtained as a by-product in the synthesis of **2o** (yield: 45.5%) from **3f** after a reaction time of 4 h. Workup as described for **2o** and recrystallization from benzene gave **2p**: 101 mg (27.2%). Orange needles. M.p. 225–227°. UV/VIS (CH_2Cl_2): 243 (sh, 4.70), 317 (4.81), 328 (4.81), 350 (4.49), 437 (4.47), 455 (sh, 4.43). IR (KBr): 3049*w*, 2202*w*, 1598*w*, 1514*w*, 1497*w*, 1440*w*, 1069*w*, 1022*w*, 752*s*, 684*s*, 669*m*. ^{1}H-NMR (300 MHz, $CS_2/(D_6)$aceton 3:1): 7.72–7.65 (*m*, 4 H); 7.61–7.54 (*m*, 6 H); 7.48–7.37 (*m*, 15 H). ^{13}C-NMR (75 MHz, $CS_2/(D_6)$aceton 3:1): 138.10; 136.98; 132.90; 132.83; 132.73; 130.53; 130.43; 130.37; 130.04; 129.95; 129.93; 129.90; 129.88; 129.82; 129.81; 129.79; 129.76; 125.88; 124.06; 123.84; 123.68; 123.63; 123.57; 123.42; 122.72; 122.56; 121.68; 121.10; 105.29; 102.27; 102.12; 101.70; 100.94; 98.26; 85.88; 84.68; 83.38; 82.75. EI-MS: 746 (100, M^+), 666 (10, $[M - Br]^+$). HR-MS: 744.0578

($C_{48}H_{25}{}^{79}BrS_2^+$; calc. 744.0581). Anal. calc. for $C_{48}H_{25}BrS_2$: C 77.41, H 3.39, Br 10.61; S 8.59; found: C 77.14, H 3.42, Br 10.65, S 8.79.

3,3',4,4'-Tetrabromo-5,5'-bis(phenylethynyl)-2,2'-bithiophene (**2r**): Pure **2r** was obtained under the same conditions as described for **2o**, but after 4 h at r.t. CC ($CHCl_3$) and recrystallization from benzene gave **2r**: 276 mg (80.9%). Yellow needles. M.p. 229–230°. UV/VIS (CH_2Cl_2): 273 (4.27), 321 (sh, 4.34), 345 (4.46). IR (KBr): 3052*w*, 2200*w*, 1508*m*, 1440*w*, 1298*m*, 1253*w*, 905*m*, 748*s*, 721*w*, 682*s*, 516*m*. ^{1}H-NMR (250 MHz, CS_2/(D_6)aceton 3:1): 7.53–7.47 (*m*, 4 H); 7.40–7.32 (*m*, 6 H). ^{13}C-NMR (63 MHz, CS_2/(D_6)aceton 3:1): 132.29; 130.06; 129.67; 129.21; 123.80; 122.44; 120.93; 117.30; 100.95; 81.53. EI-MS: 682 (100, M^+), 601 (30, $[M - Br]^+$), 522 (20, $[M - 2\ Br]^+$), 441 (5, $[M - 3\ Br]^+$), 362 (10, $[M - 4\ Br]^+$), 341 (15, ½ M^+). HR-MS: 681.6917 ($C_{24}H_{10}{}^{79}Br_2{}^{81}Br_2S_2^+$; calc. 681.6917). Anal. calc. for $C_{24}H_{10}Br_4S_2$: C 42.26, H 1.48, Br 46.86, S 9.40; found: C 42.41, H 1.30, Br 46.90, S 9.39.

Polyethynyl-2,2'-bithiophene-5,5'-dicarbaldehydes **1a–f**: *General Procedure*. 2,2'-Bithiophene-5,5'-dicarbaldehyde **4a–c** (0.5 mmol) was dissolved in abs. benzene/freshly distilled (i-Pr)$_2$NH 3:1 (*v*/*v*; 150 ml) at 70°. To this clear soln. was added dichlorobis(benzonitrile)palladium(II) (78 mg, 0.2 mmol), PPh_3 (106 mg, 0.4 mmol), and CuI (38 mg, 0.2 mmol). The soln. was degassed by passing a rapid stream of Ar through it. An excess of the corresponding acetylene (2 equiv. of phenylacetylene or (trimethylsilyl)acetylene per Br-atom) was added, and the soln. was then stirred at 70° for 4 h. During this time, the soln. rapidly turned bright yellow, then yellow brown, and finally dark brown, with the formation of a heavy precipitate. The mixture was allowed to cool to r.t. and evaporated. The yellow brown precipitate was chromatographed (silica-gel column).

3,3'-Bis[(trimethylsilyl)ethynyl]-2,2'-bithiophene-5,5'-dicarbaldehyde (**1a**): CC (petroleum ether (40–60)/$CHCl_3$ 1:1) and recrystallization from petroleum ether (40–60)/$CHCl_3$ 9:1 gave pure **1a**: 169 mg (81.6%). Yellow needles. M.p. 203–205°. UV/VIS (CH_2Cl_2): 268 (sh, 4.59), 273 (4.61), 318 (sh, 3.78), 331 (3.88), 346 (3.86), 384 (sh, 4.15), 402 (4.33), 426 (4.25). IR (KBr): 3090*w*, 2960*w*, 2817*w*, 2152*w*, 1679*s*, 1402*w*, 1361*w*, 1246*m*, 1231*m*, 1142*m*, 975*w*, 892*w*, 857*m*, 746*w*, 675*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 9.89 (*s*, 2 H); 7.74 (*s*, 2 H); 0.32 (*s*, 18 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 182.40; 144.73; 141.27; 138.69; 122.04; 106.47; 98.84; –0.53. EI-MS: 414 (20, M^+), 399 (10, $[M - Me]^+$), 341 (5, $[M - SiMe_3]^+$), 73 (100, $SiMe_3^+$). HR-MS: 414.0600 ($C_{20}H_{22}O_2S_2Si_2^+$; calc. 414.0600). Anal. calc. for $C_{20}H_{22}O_2S_2Si_2$: C 57.96, H 5.35, S 15.45; found: C 57.46, H 5.35, S 15.26.

4,4'-Bis[(trimethylsilyl)ethynyl]-2,2'-bithiophene-5,5'-dicarbaldehyde (**1b**): CC (petroleum ether (40–60)/$CHCl_3$ 1:1) and recrystallization from benzene gave pure **33**: 101 mg (48.9%). Yellow needles. M.p. 225–226°. UV/VIS (CH_2Cl_2): 262 (sh, 4.37), 270 (4.42), 303 (sh, 4.12), 313 (4.26), 330 (4.17), 364 (sh, 4.26), 377 (4.33), 391 (sh, 4.24). IR (KBr): 3067*w*, 2961*w*, 2844*w*, 2153*w*, 1670*s*, 1427*m*, 1253*w*, 1230*w*, 1213*m*, 1203*m*, 1031*w*, 867*m*, 847*m*, 764*w*, 703*w*, 668*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.09 (*s*, 2 H); 7.36 (*s*, 2 H); 0.29 (*s*, 18 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 182.47; 144.19; 142.33; 131.27; 129.58; 103.54; 95.46; –0.25. EI-MS: 414 (100, M^+), 399 (80, $[M - Me]^+$), 341 (15, $[M - SiMe_3]^+$), 73 (70, $SiMe_3^+$). HR-MS: 414.0601 ($C_{20}H_{22}O_2S_2Si_2^+$; calc. 414.0600). Anal. calc. for $C_{20}H_{22}O_2S_2Si_2$: C 57.96, H 5.35, S 15.45; found: C 57.81, H 5.45, S 15.16.

3,3',4,4'-Tetrakis[(trimethylsilyl)ethynyl]-2,2'-bithiophene-5,5'-dicarbaldehyde (**1c**): CC (petroleum ether (40–60)/$CHCl_3$ 5:1) and recrystallization from pentane gave pure **1c**: 225 mg (74.3%). Yellow needles. M.p. 235–237° (dec.). UV/VIS (CH_2Cl_2): 285 (4.71), 293 (4.70), 368 (sh, 4.07), 386 (4.21), 407 (4.34), 433 (4.34). IR (KBr): 2962*s*, 2900*s*, 2841*m*, 2147*w*, 1666*s*, 1404*w*, 1375*m*, 1347*s*, 1249*s*, 1234*s*, 927*s*, 847*s*, 763*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.14 (*s*, 2 H); 0.35 (*s*, 18 H); 0.30 (*s*, 18 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 182.89; 142.85; 141.81; 132.71; 125.08; 110.34; 105.83; 97.38; 94.75; –0.12; –0.46. EI-MS: 606 (20, M^+), 591 (5, $[M - Me]^+$), 533 (10, $[M - SiMe_3]^+$), 460 (5, $[M - 2\ SiMe_3]^+$), 431 (5, $[M - SiMe_3 - CHO]^+$), 73 (100, $SiMe_3^+$). HR-MS: 606.1390 ($C_{30}H_{38}O_2S_2Si_4^+$; calc. 606.1390). Anal. calc. for $C_{30}H_{38}O_2S_2Si_4$: C 59.39, H 6.32, S 10.55; found: C 59.49, H 6.40, S 10.27.

3,3'-Bis(phenylethynyl)-2,2'-bithiophene-5,5'-dicarbaldehyde (**1d**): CC ($CHCl_3$) and recrystallization from petroleum ether (40–60)/$CHCl_3$ 1:1 gave pure **1d**: 190 mg (90.0%). Yellow needles. M.p. 235–236°. UV/VIS (CH_2Cl_2): 295 (sh, 4.74), 300 (4.75), 423 (4.24), 440 (sh, 4.18). IR (KBr): 3079*w*, 3056*w*, 2829*w*, 2202*w*, 1660*s*, 1520*w*, 1492*m*, 1441*w*, 1414*w*, 1349*w*, 1238*w*, 1205*s*, 1129*s*, 857*m*, 761*s*, 691*m*, 669*w*, 643*w*, 543*w*, 522*w*. ^{1}H-NMR (250 MHz, $CDCl_3$): 9.95 (*s*, 2 H); 7.85 (*s*, 2 H); 7.67–7.59 (*m*, 4 H); 7.44–7.39 (*m*, 6 H). ^{13}C-NMR (63 MHz, $CDCl_3$): 182.65; 143.85; 141.73; 138.88; 135.40; 131.54; 129.39; 128.74; 122.21; 98.89; 84.17. EI-MS: 422 (100, M^+), 393 (15, $[M - CHO]^+$), 364 (20, $[M - 2\ CHO]^+$). HR-MS: 422.0437 ($C_{26}H_{14}O_2S_2^+$; calc. 422.0435). Anal. calc. for $C_{26}H_{14}O_2S_2$: C 73.93, H 3.34, S 15.15; found: C 73.90, H 3.37, S 14.89.

4,4'-Bis(phenylethynyl)-2,2'-bithiophene-5,5'-dicarbaldehyde (**1e**): CC ($CHCl_3$) and recrystallization from chlorobenzene gave pure **1e**: 88 mg (41.7%). Yellow-orange needles. M.p. 217–218°. UV/VIS (CH_2Cl_2): 272 (sh, 4.44), 287 (4.51), 298 (4.55), 333 (4.50), 344 (sh, 4.48), 374 (sh, 4.40), 396 (sh, 4.21). IR (KBr): 3082*w*, 3052*w*, 2835*w*, 2208*w*, 1657*s*, 1521*w*, 1484*w*, 1431*m*, 1349*m*, 1211*s*, 864*m*, 759*m*, 691*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.21 (*s*, 2 H); 7.60–7.55 (*m*, 4 H); 7.46 (*s*, 2 H); 7.44–7.25 (*m*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 182.35; 143.23; 142.57;

131.80; 131.34; 129.56; 129.40; 128.57; 121.48; 96.78; 80.84. EI-MS: 422 (100, M^+), 393 (10, $[M - CHO]^+$), 364 (10, $[M - 2\,CHO]^+$). HR-MS: 422.0437 ($C_{26}H_{14}O_2S_2^+$; calc. 422.0435). Anal. calc. for $C_{26}H_{14}O_2S_2$: C 73.93, H 3.34, S 15.15; found: C 73.45, H 3.40, S 14.81.

3,3',4,4'-Tetrakis(phenylethynyl)-2,2'-bithiophene-5,5'-dicarbaldehyde (**1f**): CC ($CHCl_3$) and recrystallization from benzene gave pure **1f**: 185 mg (59.5%). Yellow needles. M.p. 295° (dec.). UV/VIS (CH_2Cl_2): 256 (4.59), 322 (4.84), 432 (4.23), 455 (sh, 4.19). IR (KBr): 3046*w*, 2821*w*, 2200*m*, 1662*s*, 1495*w*, 1384*m*, 1347*m*, 1280*w*, 1213*m*, 1203*m*, 756*m*, 686*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.30 (*s*, 2 H); 7.71–7.67 (*m*, 4 H); 7.64–7.60 (*m*, 4 H); 7.47–7.41 (*m*, 12 H). EI-MS: 622 (100, M^+), 593 (10, $[M - CHO]^+$), 564 (10, $[M - 2\,CHO]^+$). HR-MS: 622.1063 ($C_{42}H_{22}O_2S_2^+$; calc. 622.1061). Anal. calc. for $C_{42}H_{22}O_2S_2$: C 81.02, H 3.56, S 10.28; found: C 80.69, H 3.41, S 9.92.

Polyethynyl-2,2'-bithiophenes **5a–e**: *General Procedure for the Removal of $SiMe_3$ Protecting Groups.* To a suspension of poly[(trimethylsilyl)ethynyl]-2,2'-bithiophene **2a–c, e, f** (0.2 mmol) in deoxygenated MeOH (50 ml) was added sat. K_2CO_3 soln. (0.5 ml) at r.t. The mixture was stirred for 4 h (→soln.). The soln. was diluted with CH_2Cl_2, washed several times with H_2O, dried ($MgSO_4$), and evaporated: pure product.

3,3'-Diethynyl-2,2'-bithiophene (**5a**): Recrystallization from MeOH: 41 mg (95.8%). Colorless needles. M.p. 94–97° (dec.). IR (KBr): 3261*s*, 3100*w*, 2091*w*, 1086*w*, 930*w*, 882*m*, 819*m*, 718*s*, 678*s*, 615*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.23 (*d*, ^3J = 5.3, 2 H); 7.12 (*d*, ^3J = 5.3, 2 H); 3.36 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.31; 130.86 (^1J = 172.1, ^2J = 4.0); 124.41 (^1J = 188.4, ^2J = 6.3); 118.68; 82.85 (^1J = 253.5); 79.05. EI-MS: 214 (100, M^+). HR-MS: 213.9911 ($C_{12}H_6S_2^+$; calc. 213.9911). Anal. calc. for $C_{12}H_6S_2$: C 67.29, H 2.83, S 29.88; found: C 67.05, H 2.83, S 30.12.

4,4'-Diethynyl-2,2'-bithiophene (**5b**): Recrystallization from MeOH: 40 mg (93.5%). Light-yellow needles. M.p. 119–120°. UV/VIS (CH_2Cl_2): 235 (4.53), 250 (sh, 4.20), 312 (4.00). IR (KBr): 3280*s*, 3104*w*, 3052*w*, 2110*w*, 1517*w*, 1403*w*, 1326*w*, 1185*w*, 1136*w*, 964*w*, 863*m*, 832*w*, 819*s*, 747*m*, 700*m*, 676*m*, 624*w*, 596*s*, 510*w*, 476*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.39 (*d*, ^4J = 1.2, 2 H); 7.18 (*d*, ^4J = 1.2, 2 H); 3.05 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 135.99; 129.14; 126.58; 121.68; 78.21; 77.14. EI-MS: 214 (100, M^+). HR-MS: 213.9911 ($C_{12}H_6S_2^+$; calc. 213.9911). Anal. calc. for $C_{12}H_6S_2$: C 67.29, H 2.83, S 29.88; found: C 67.29, H 3.06, S 29.65.

5,5'-Diethynyl-2,2'-bithiophene (**5c**): Recrystallization from MeOH: 41 mg (95.8%). Light-yellow needles. UV/VIS (CH_2Cl_2): 256 (3.80), 345 (sh, 4.38), 354 (4.40), 371 (sh, 4.24). IR (KBr): 3284*s*, 3089*w*, 3068*w*, 2095*m*, 1436*m*, 1200*m*, 1140*m*, 1051*m*, 881*m*, 800*s*, 694*m*, 589*m*, 561*m*, 515*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.15 (*d*, ^3J = 3.9, 2 H); 7.01 (*d*, ^3J = 3.9, 2 H); 3.41 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 137.85; 133.72; 123.68; 121.23; 82.52; 76.52. EI-MS: 214 (100, M^+). HR-MS: 213.9910 ($C_{12}H_6S_2^+$; calc. 213.9911). Anal. calc. for $C_{12}H_6S_2$: C 67.29, H 2.83, S 29.88; found: C 66.99, H 2.81, S 30.20.

3,3',5,5'-Tetraethynyl-2,2'-bithiophene (**5d**): Recrystallization from MeOH or benzene: 50 mg (95.4%). Colorless needles. IR (KBr): 3281*s*, 3099*w*, 2098*w*, 1512*w*, 847*s*, 664*s*, 605*s*, 535*m*, 449*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.25 (*s*, 2 H); 3.45 (*s*, 2 H); 3.42 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.79; 136.37; 121.10; 118.64; 84.66; 83.46; 78.35; 75.75. EI-MS: 262 (100, M^+), 131 (5, ½ M^+). HR-MS: 261.9910 ($C_{16}H_2S_2^+$; calc. 261.9911). Anal. calc. for $C_{16}H_6S_2$: C 73.28, H 2.31, S 24.41; found: C 73.02, H 2.05, S 24.93.

4,4',5,5'-Tetraethynyl-2,2'-bithiophene (**5e**): Recrystallization from MeOH: 49 mg (93.5%). Light-yellow needles. IR (KBr): 3279*s*, 3077*w*, 3039*w*, 2108*w*, 1511*m*, 1417*w*, 966*m*, 830*s*, 682*s*, 608*s*, 507*m*, 448*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.09 (*s*, 2 H); 3.67 (*s*, 2 H); 3.34 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 135.49; 127.13; 126.51; 125.55; 86.86; 81.58; 81.33; 75.05. EI-MS: 262 (100, M^+), 131 (5, ½ M^+). HR-MS: 261.9911 ($C_{16}H_6S_2^+$; calc. 261.9911). Anal. calc. for $C_{16}H_6S_2$: C 73.28, H 2.31, S 24.41; found: C 73.17, H 2.29, S 24.54.

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