

STUDIES TOWARDS DIBENZOTHIOPHENE-S-OXIDE ARRAYS AND THEIR PHOTOCHEMICAL REACTIVITY

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STUDIES TOWARDS DIBENZOTHIOPHENE-S-OXIDE ARRAYS AND THEIR PHOTOCHEMICAL REACTIVITY

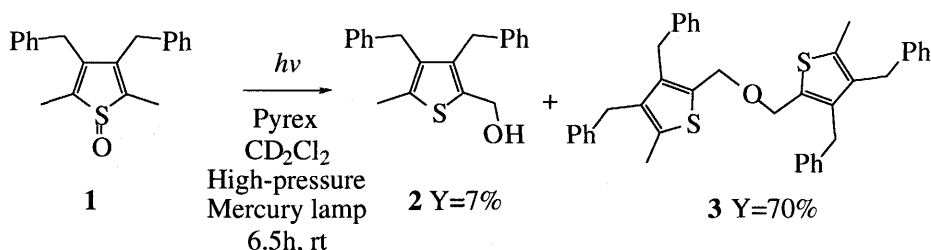
Thies THIEMANN, Kazuya KUMAZOE,^a Kazuya ARIMA,^a Shuntaro MATAKA

A novel access to oligo(dibenzothiophenes) is described. Here, the trimethylsilyl-group is used both as positional protective group and as a directive group which can be exchanged. The reagents benzyltrimethylammonium tribromide (BTMABr₃) and benzyltrimethylammonium iododichloride (BTMAICl₂) are used for the first time in silyl-halo exchange reactions. The dimeric, trimeric and tetrameric dibenzothiophene building blocks are prepared by Suzuki-Kumada C-C coupling reactions. Exemplary oxygenations of these building blocks to the corresponding dibenzothiophene-S-oxides is shown.

Introduction

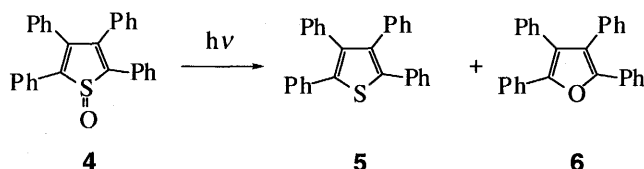
Thiophene-S-oxides have been known to have cytotoxic activity.¹ It is believed that gradual loss of oxygen in these molecules may contribute to their biochemical activity.² On the other hand it has been found

S-oxides may be of value as these molecules themselves have been forwarded as subunits in organic oligomers and polymers with low optical energy gaps.⁵ Foremost, the mechanisms operating in the different photochemical transformations of the thiophene-S-oxides need clarification. Two possible mechanisms for the



Scheme 1

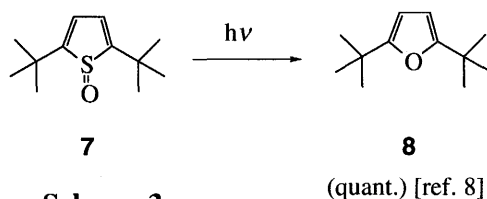
that the deoxygenation of thiophene-S-oxides can be accelerated by photoirradiation of the molecules.² Depending on the substitution pattern of the thiophene-S-oxides, photoirradiation can also lead to hydroxylation



Scheme 2

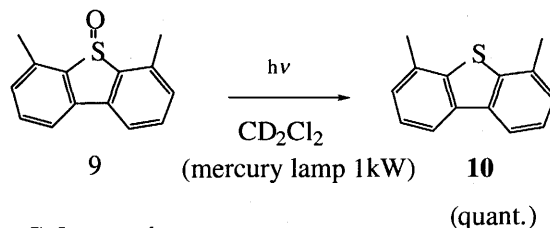
of alkyl (*i.e.*, methyl) groups in positions C-2 or C-5 of the thiophene-unit (Scheme 1).^{2,3} In the case of substituents at C-2 and/or C-5 that possess a proton at the carbon α to the linkage with the thiophene-unit, *e.g.* as in the case of a *tert*-butyl group, the oxygen is included into the heterocyclic ring system and thiophene-S-oxides are transformed into furans (Schemes 2 and 3).⁴ A good knowledge of the photochemical stability of thiophene-

deoxygenation of the thiophene-S-oxides would involve



Scheme 3

a.) an oxenoid species in a monomolecular reaction or b.)



Scheme 4

the evolution of oxygen, either in the singlet or triplet

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Dedicated to Professor Yukio Nishimura on the occasion of his retirement

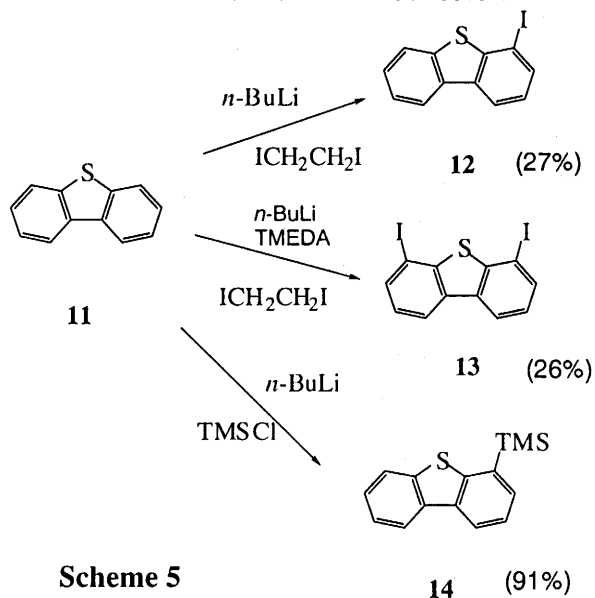
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state, from an excited thiophene-*S*-oxide dimer.^{6,7} While the hydroxyl-ation of the methyl group of methyl substituted thiophene-*S*-oxides indicated that either an oxenoid species or singlet oxygen might be involved, the inability of the liberated oxygen species to hydroxylate one of the methyl groups in the 4,6-dimethyl-dibenzothiophene-*S*-oxide (**9**)⁸ seemed to exclude the involvement of atomic oxygen at least in the case of the irradiation of **9** (Scheme 4).

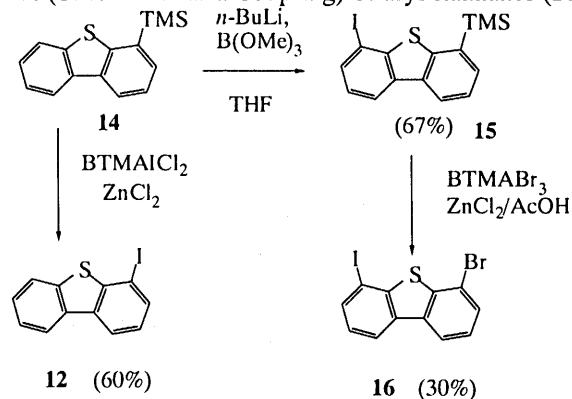
Thus, it is of interest to suppress the dimer formation of the thiophene-*S*-oxides by steric hinderance either by placing a sterically demanding substituent at the C2 and/or C5-position(s) or by enlargening the molecule as such. This way it would be possible to assess whether dimer-formation is necessary for the progression of the simple deoxygenation process. That thiophene-*S*-oxides which cannot readily form dimers may follow other pathways in the photochemical transformation can be seen in the photoradiation of 2,5-diphenylthiophene-*S*-oxide (**4**), where a mixture of 2,5-diphenylthiophene (**5**) and 2,5-diphenylfuran (**6**) is produced (Scheme 2).^{2,8} The sterically more congested 2,5-*tert*-butylthiophene-*S*-oxide (**7**) gives the corresponding furan **8** even exclusively (Scheme 3).^{2,8}

In the following, the preparation of dibenzothiophene-dimers, trimers and tetramers as a starting point for arrays of dibenzothiophene-*S*-oxides and an exemplary study of the photochemical behaviour of a bis(dibenzothiophene-*S*-oxide) are presented. The arrays have been prepared to more closely study the photochemistry, *i.e.*, the photodeoxygenation of dibenzothiophene-*S*-oxides. The results may be helpful to acquire additional insights in the mechanisms governing the photochemical behaviour of thiophene-*S*-oxides themselves. Furthermore, oligodibenzothiophene-*S*-oxides may provide materials with interesting electro-optical properties.

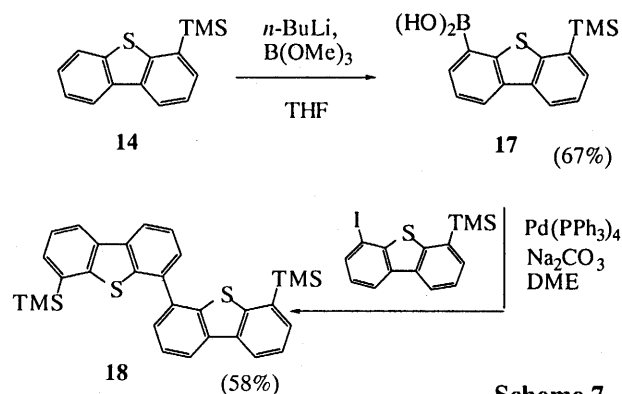
Results and Discussion



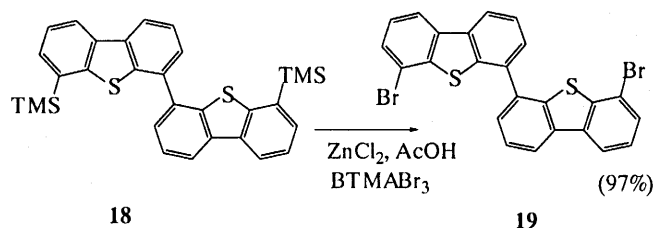
The preparation of arrays of dibenzothiophenes necessitates C-C coupling between dibenzothiophenes. As there are a number of C-C bond forming (cross-coupling) reactions known involving aryl halides and aryl boronic acids (Suzuki-Kumada Coupling) or aryl stannanes (Stille



coupling), a versatile access to halogenated dibenzothiophenes was needed. Lithiation of dibenzothiophene with *n*-BuLi in THF proceeds at C-4. Reaction of the lithiated species with 1,2-diiodoethane leads to 4-iodo-

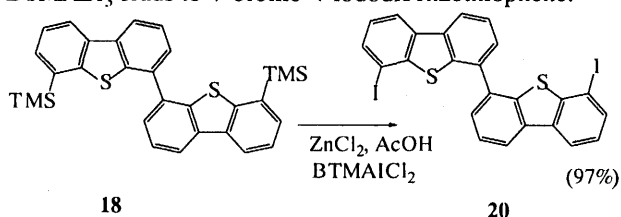


dibenzothiophene (**12**) (Scheme 5). A lithiation of dibenzothiophene can be achieved selectively at C-4 and C-6 with an excess of *n*-BuLi/TMEDA in THF. Reaction of this dilithiated species with 1,2-diiodoethane yields 4,6-diiododibenzo-thiophene (**13**), albeit in very moderate yield (Scheme 5). The mono-lithiated product can also be reacted with chlorotrimethylsilane to yield 4-trimethylsilyldibenzothiophene (**14**) (Scheme 5).⁹ This is



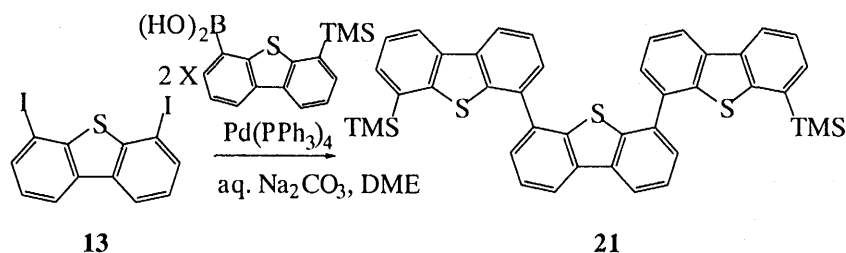
of interest as the trimethylsilyl group at C-4 can serve either as a positional protective group or as a directive, exchangeable functionality. Thus, as an example of the first case, 4-trimethylsilyldibenzothiophene (**14**) itself

can be lithiated at C-6 and easily reacted with 1,2-diiodoethane to yield 4-iodo-6-trimethyl-silyldibenzothiophene (**15**) (Scheme 6). As an example of the second case, 4-trimethylsilyldibenzothiophene (**14**) can be reacted with benzyl trimethylammonium iododichloride (BTMAICl₂)¹⁰ in an iodo-silyl exchange to give the 4-iododibenzothiophene (**12**) (Scheme 6). Alternatively, the same reaction with benzyltrimethylammonium tribromide gives the analogous 4-bromo-derivative. Interestingly, the direct bromination of a (substituted) dibenzothiophene with benzyltrimethylammonium tribromide leads to a different regioisomer, namely to the corresponding 3-bromo derivative. Thus, it is also possible to selectively produce different regioisomers of 'mixed' dihalogenated dibenzothiophenes. Reaction of 4-iodo-6-trimethylsilyldibenzothiophene (**15**) with benzyltrimethylammonium tribromide (BTMABr₃) leads via iodo-trimethylsilyl exchange to the 6-bromo-4-iododibenzothiophene, while the reaction of 4-iododibenzothiophene (**12**) with BTMABr₃ leads to 7-bromo-4-iododibenzothiophene.¹¹



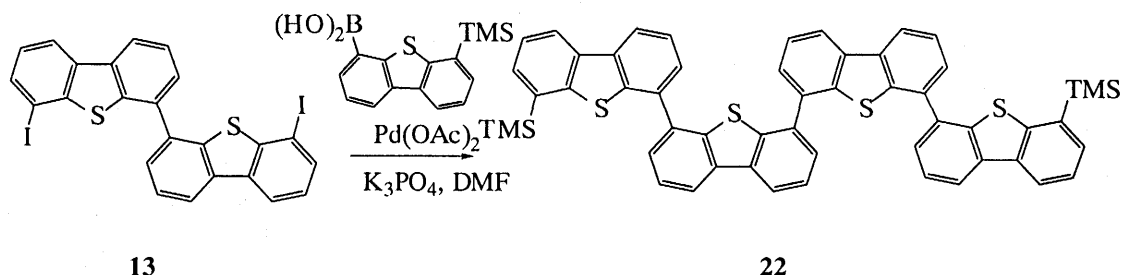
Scheme 9

When 4-trimethylsilyldibenzothiophene (**14**) is lithiated (*n*-BuLi, THF) it can be reacted with trimethylborate to give upon acidic work-up 4-trimethylsilyldibenzothiophene 6-boronic acid (**17**) (Scheme 7). **17** can



Scheme 10

be reacted with 4-iodo-6-trimethylsilyldibenzothiophene (**15**) under normal Suzuki-Kumada conditions [2M aq.

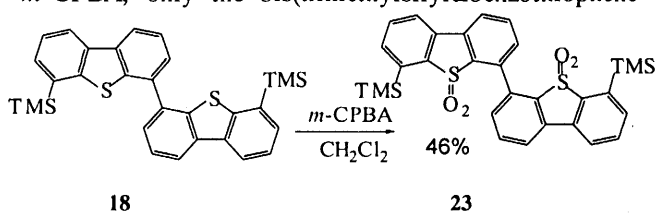


Scheme 11

Na₂CO₃, DME, Pd(PPh₃)₄]^{12,13} to furnish 6,6'-bis(trimethylsilyl)-4,4'-bis(dibenzothiophene) (**18**) (Scheme

7). This, in turn, can undergo silyl-halo exchange with either BTMABr₃ to yield the brominated dimer **19** or with BTMAICl₂ to give the iodinated dimer **20**. Further coupling reactions of these dihalogenated bis(dibenzothiophenes) to higher homologues is hindered by the low solubility of the starting material in the reaction solvent. Here, the use of DMF as the solvent is beneficial and other reaction conditions [K₃PO₄, Pd(OAc)₂]¹⁴ provide better results and the tetramer **22** could be prepared (Scheme 11). In an analogous way the trimer **21** was prepared from 4,6-diiododibenzothiophene (**13**) (Scheme 10). Here, however, the 4,6-diiododibenzothiophene (**13**) (as opposed to the diiodinated dimer **20**) showed sufficient solubility in DME for the reaction to proceed under the normal Suzuki-Kumada conditions [2M aq. Na₂CO₃, DME, Pd(PPh₃)₄] (Scheme 10).

A number of methods are known for the oxidation of dibenzothiophenes to the corresponding sulfoxides. When bis(trimethylsilyldibenzothiophene) **18** was treated with *m*-CPBA, only the bis(trimethylsilyldibenzothiophene-



Scheme 12

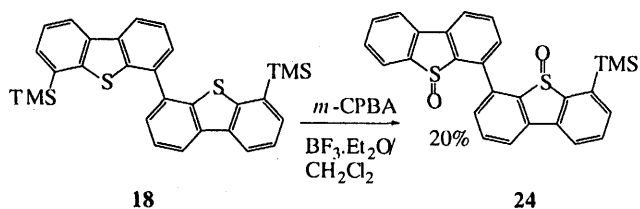
S,S-dioxide) (**23**) could be isolated (Scheme 12). On the other hand the use of *m*-CPBA in the presence of the Lewis acid BF₃·Et₂O yields the mono-silylated bis(dibenzothiophene *S*-oxide) **24** (Scheme 13). This

partial desilylation of the starting material is very likely due to the presence of BF₄⁻ and F⁻ in the reaction

mixture.¹⁵

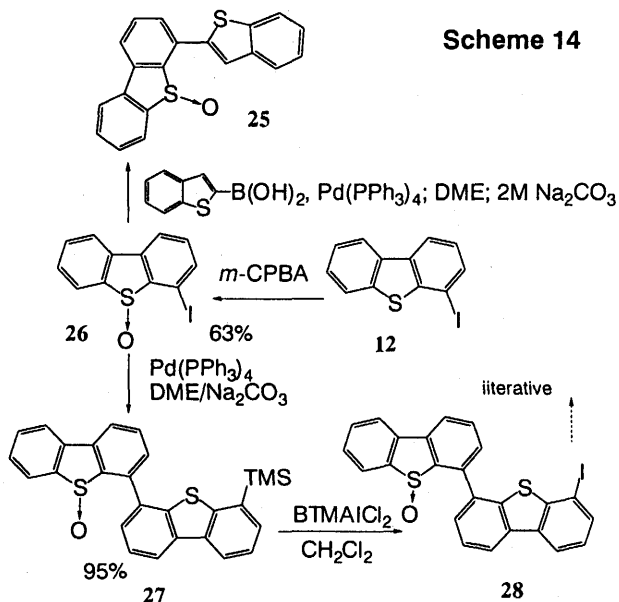
The authors feel that the problems in the coupling of

larger dibenzothiophene-arrays due to the low solubility of the starting material and the problems encountered in the selective oxidation of individual dibenzothiophene-units in the arrays can be circumvented by following an



Scheme 13

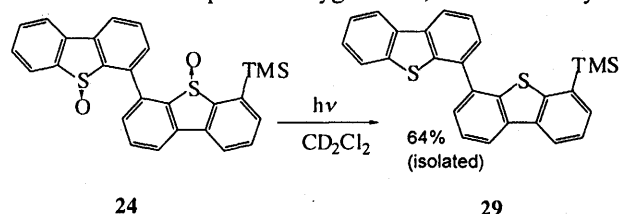
alternative approach. Here, the dibenzothiophene-*S*-oxide (i.e., **26**) itself as a mono-subunit is subjected to a coupling reaction with the trimethylsilyl substituted dibenzothiopheneboronic acid **17**. Facultatively, after halo-silyl exchange this process can be repeated (Scheme 14). Potentially, other types of silyl substituted aryl/hetarylboronic acids can be used in these reactions. This leads to the possibility of preparing both arrays with neighboring dibenzothiophene-*S*-oxide units and arrays with alternating units of dibenzothiophene and dibenzothiophene-*S*-oxide. The Suzuki-Kumada coupling of dibenzothiophene-*S*-oxides is a general reaction as evidenced by a second coupling with a benzothiopheneboronic acid (i.e., to **25**) (Scheme 14). The dibenzothiophene-*S*-oxide is not deoxygenated by the process. This is similar to the C-C-coupling via Stille-reaction that has been carried out on a bromobenzothiophene-*S*-oxide – in



that case, however, the halo-aryl exchange was accompanied by a 1,2-transposition.¹⁶

If it is true that one main pathway of the deoxygenation process of dibenzothiophene-*S*-oxides proceeds via the formation of an excited dimer species (of dibenzothiophene-*S*-oxides), it may be possible to control the release of oxygen by the number of adjacent dibenzothiophene-*S*-oxide units in an array. To better understand

the possible contribution of adjacent dibenzothiophene-*S*-oxide units to the photodeoxygenation, an exact analysis



Scheme 15

of the distribution of different conformers in such arrays still needs to be carried out. It is supposed that the intermolecular dimer formation in larger arrays becomes increasingly difficult with the size and the complexity of these molecules, especially when these molecules themselves are included within polymeric material. The possibility of using monomeric dibenzothiophene-*S*-oxide in the photochemical hydroxylation of side chains in 'finished' polymers has already been demonstrated recently.¹⁷ The inclusion of dibenzothiophene-*S*-oxide arrays in such polymeric material may lead to a better control of the oxygen release and to a better control of the hydroxylation of such materials.

The photoirradiation itself of the dimers, such as **24**, leads to the deoxygenated product after 19 h (completion of the reaction). No dibenzofuran could be observed. After 1h the turnover of the reaction was minimal (Scheme 15). Thus, viewed in a qualitative manner, the photodeoxygenation of this dibenzothiophene-*S*-oxide is slower than the photodeoxygenation of the monomeric dibenzothiophene-*S*-oxide. The study of the kinetics of this reaction is underway. Moreover, the use of dibenzothiophene-*S*-oxides and thiophene-*S*-oxides – either as single molecules or in arrays – as photochemical oxidants in the preparation of conducting polymers is under development.¹⁸

Experimental

General. IR spectra were recorded on a JASCO IR-700 spectrometer (KBr pellets or NaCl plates [designated as *neat*]). ¹H NMR spectra were measured on a JEOL EX-270 (270 MHz), a JEOL JNM-LA 395 (400 MHz), and a JEOL JNM-LA 600 (600 MHz) spectrometer. ¹³C NMR spectra were measured on a JEOL EX-270 (67.9 MHz), a JEOL 395 (100.4 MHz) and a JEOL JNM-LA 600 (150.8 MHz) spectrometer. Assignments of ¹³C signals were aided by DEPT (= Distortionless Enhancement by Polarisation Transfer) measurements; (+) denotes primary and tertiary, (-) secondary, and (C_{quat}) quaternary carbon atoms; Mass spectra were taken on a JEOL-01-SG-2 machine at 70 eV using a direct inlet system. Wakogel C-300 was used as silica gel in all column chromatographic separations. Analytical thin layer chromatography (TLC) was carried out on TLC aluminum sheets (silica gel 60 F₂₅₄, Merck). Dibenzothiophene (Acros), 1,2-diodomethane (TCI),

trimethylborate (Kishida), chlorotrimethylsilane (Aldrich), *n*-BuLi (Kanto Chemicals) and *tert*-BuLi (Kanto Chemicals) were commercially available. Benzyltrimethylammonium tribromide (BTMABr₃) and benzyl trimethylammonium iododichloride (BTMAICl₂) were prepared according to literature procedures.

4-Iododibenzothiophene (12). - *Route A.* To dibenzothiophene (**11**) (4.5 g, 24.4 mmol) in THF, cooled to -78°C, was added gradually *n*-BuLi (2.6M, 10.3 mL, 26.8 mmol). Thereafter, the solution was warmed to rt and stirred for 3h. Later the reaction mixture was cooled again to -78°C and 1,2-diiodoethane (8.25 g, 29.3 mmol) was added slowly. The reaction was warmed to rt and stirred for 14h at rt. The reaction mixture was poured into sat. aq. Na₂S₂O₃ (10 mL) and the product was extracted with CH₂Cl₂ (10 mL). The organic phase was dried over anhydrous MgSO₄ and subsequently the solvent was evaporated *in vacuo* to give 4-iododibenzothiophene (**12**) (2.05 g, 27%) as a colorless powder; mp 102°C; IR (KBr) ν 1540, 1432, 1381, 1099, 1021, 784, 746 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.20 (dd, 1H, ³J 8.0, ³J 8.2 Hz), 7.45 (d, 2H, *J* 1.3 Hz), 7.81 (m, 2H), 8.04 (m, 2H). *Route B.* In an inert atmosphere ZnCl₂ (69 mg, 0.48 mmol) was added to a mixture of 4-trimethylsilyldibenzothiophene (**14**) (for preparation, see below) (100 mg, 0.4 mmol) and benzyltrimethylammonium iododichloride (135 mg, 0.4 mmol) in acetic acid (2 mL). The resulting mixture was stirred at 80°C for 22h. Thereafter, the mixture was poured into water (10 mL) and the product was extracted with CH₂Cl₂ (10 mL). The organic phase was washed with water (10 mL) and dried over MgSO₄. Then the solvent was distilled off and the residue was washed with ether. The product was dried *in vacuo* to give **12** (72 mg, 0.38 mmol, 60%).

4,6-Diiododibenzothiophene (13). - To a mixture of dibenzothiophene (**11**) (4.0 g, 22.0 mmol) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (5 mL) in THF (10 mL), cooled to -78°C, was added gradually *tert*-BuLi (2.6 M, 20 mL, 24 mmol). The resulting solution was warmed to rt and stirred for 2h. Thereafter, it was cooled to -78°C and 1,2-diiodoethane (14.0 g, 32.0 mmol) was slowly added. The solution was warmed to rt and stirred at rt for 17h. Then the reaction mixture was poured into sat. aq. Na₂S₂O₃ (10 mL) and the organic material was extracted with CH₂Cl₂ (2X10 mL). The organic phase was dried over MgSO₄ and evaporated to give 4,6-diiododibenzo-thiophene (**13**) (2.46 g, 11.7 mmol, 26%) as a pale yellow solid; mp 140.5 - 143.9°C; IR (KBr) ν 1536, 1407, 1367, 1315, 1014, 809, 762 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.51 (dd, 2H, ³J 7.6, ³J 7.3 Hz), 7.84 (d, 2H, ³J 7.6 Hz), 8.08 (d, 2H, ³J 7.3 Hz); MS (70 eV) *m/z* 435 (M⁺-1, 100). HRMS Found: 435.8273. Calcd.: 435.8280.

4-Trimethylsilyldibenzothiophene (14). - To a

solution of dibenzothiophene (**11**) (21.9 g, 116 mmol) in THF (5 mL), cooled to 78°C, was added *n*-BuLi (2.6M, 16.7 mL, 127 mmol). Thereafter, the mixture was warmed to rt and stirred for 3h. Then, the solution was cooled to -78°C and chlorotrimethylsilane (16.7 mL, 139 mmol) was added dropwise and the solution was warmed to rt and stirred for additional 5h at rt. The reaction was poured into a sat. aq. NaHCO₃ solution (5 mL) and the product was extracted with CH₂Cl₂ (10 mL). The organic phase was dried over anhydrous MgSO₄ and the solvent was evaporated *in vacuo* to give **14** (27.1 g, 91%) as a yellow oil, which upon standing crystallizes very slowly; IR (neat) ν 3058, 2954, 2894, 1439, 1427, 1366, 1250, 856, 838, 747 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 0.46 (s, 9H, SiMe₃), 7.37 - 8.11 (m, 7H); ¹³C NMR (67.8 MHz, CDCl₃) δ 0.02, 122.85, 124.56, 125.08, 125.26, 128.89, 135.72, 136.56, 136.60, 136.67, 136.75, 140.82, 146.38.

4-Bromodibenzothiophene. - In an inert atmosphere ZnCl₂ (690 mg, 0.48 mmol) was added to a mixture of 4-trimethylsilyldibenzothiophene (**14**) (1.0 g, 3.9 mmol) and benzyltrimethylammonium tribromide (1.53 g, 3.9 mmol) in acetic acid (15 mL). The resulting mixture was stirred at 80°C for 5h. Thereafter, the mixture was poured into water (20 mL) and the product was extracted with CH₂Cl₂ (20 mL). The organic phase was washed with water (20 mL) and dried over MgSO₄. Then the solvent was distilled off and the residue was washed with ether. The product was dried *in vacuo* to give 4-bromodibenzothiophene (667 mg, 2.38 mmol, 61%) as a yellowish powder; mp 54.5 - 58.9°C; ¹H NMR (270 MHz, CDCl₃) δ 7.33 - 8.12 (m, 7H); MS (70 eV) 280 (⁸¹BrM⁺, 36), 278 (⁷⁹BrM⁺, 35).

4-Iodo-6-trimethylsilyldibenzothiophene (15).

- To 4-trimethylsilyldibenzothiophene (**14**) (1.0 g, 3.9 mmol) in dry THF (5 mL) was added gradually at -78°C *tert*-BuLi (2.6 M, 2.3 mL, 4.7 mmol). Thereafter, the solution was warmed to rt and stirred for 2h. Then the solution was cooled to -78°C and diiodoethane (1.32 mL, 5.6 mmol) was added slowly. The resulting solution was warmed to rt and stirred at rt for 17h. Then the reaction mixture was poured into sat. aq. Na₂S₂O₃ (20 mL) and the product was extracted with CH₂Cl₂ (50 mL). The organic phase was dried over anhydrous MgSO₄ and the solvent was evaporated *in vacuo* to give **15** (1.0 g, 67%) as colorless crystals; IR (KBr) ν 3048, 2952, 1401, 1242, 1109, 861, 750 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 0.46 (s, 9H, SiMe₃), 6.85 (dd, 1H, ³J 5.7, ³J 5.4 Hz), 7.05 (dd, 1H, ³J 5.6, ³J 5.4 Hz), 7.22 (d, 1H, ³J 5.5 Hz), 7.45 (d, 1H, ³J 5.5 Hz), 8.77 (m, 2H); MS (70 eV) *m/z* (%) 382 (M⁺, 100). HRMS Found: 381.9704. Calcd. for C₁₅H₁₅ISi: 381.9708.

4-Bromo-6-iododibenzothiophene (16). - In an inert atmosphere ZnCl₂ (43 mg, 0.3 mmol) was added to a

mixture of 4-iodo-6-trimethylsilyldibenzothiophene (**15**) (100 mg, 0.26 mmol) and benzyltrimethylammonium tribromide (102 mg, 0.26 mmol) in acetic acid (4 mL). The resulting mixture was stirred at 80°C for 5h. Thereafter, the mixture was poured into water (10 mL) and the product was extracted with CH₂Cl₂ (10 mL). The organic phase was washed with water (10 mL) and dried over MgSO₄. Then the solvent was distilled off and the residue was washed with ether. The product was dried *in vacuo* to give **16** (98 mg, 2.52 mmol, 97%) as a colorless powder; mp 60.4 – 62.4°C; ¹H NMR (270 MHz, CDCl₃) δ 7.30 – 8.20 (m, 6H); MS (70 eV) *m/z* (%) 389 (⁸¹BrM⁺, 16), 387 (⁷⁹BrM⁺, 16). HRMS Found: 387.8419. Calcd. for C₁₂H₆⁷⁹BrIS: 387.8418.

7-Bromo-4-iododibenzothiophene. - In an inert atmosphere ZnCl₂ (408 mg, 2.6 mmol) was added to a mixture of 4-iododibenzothiophene (**12**) (700 mg, 2.34 mmol) and benzyltrimethylammonium tribromide (897 mg, 2.3 mmol) in acetic acid (10 mL). The resulting mixture was stirred at rt for 5h. Thereafter, the mixture was poured into water (20 mL) and the product was extracted with CH₂Cl₂ (20 mL). The organic phase was washed with water (20 mL) and dried over MgSO₄. Then the solvent was distilled off and the residue was washed with ether. The product was dried *in vacuo* to give 7-bromo-4-iododibenzothiophene (667 mg, 1.7 mmol, 74%) as yellow crystals; mp 147 – 149°C; ¹H NMR (270 MHz, CDCl₃) δ 7.45 (m, 2H), 7.80 (m, 2H), 8.01 (m, 2H); MS (70 eV) *m/z* (%) 389 (⁸¹BrM⁺, 21), 387 (⁷⁹BrM⁺, 21). HRMS Found: 387.8418. Calcd. for C₁₂H₆⁷⁹BrIS: 387.8418.

4-Trimethylsilyldibenzothiophene-6-boronic acid (17). - To a cooled solution of 4-trimethylsilyldibenzothiophene (**14**) (1.0 g, 3.9 mmol) in THF (5 mL) was added at -78°C *n*-BuLi (2.6 M, 1 mL, 3.9 mmol). Thereafter, the solution was warmed to rt and stirred for 3h. Then, the solution was cooled to -78°C and trimethylborate (269 mg, 3.9 mmol) was added slowly. The resulting mixture was warmed to rt and stirred for 16 h at rt. Then, the reaction mixture was poured into 10w% aq. HCl (10 mL) and the product was extracted with CH₂Cl₂. The organic phase was dried over anhydrous MgSO₄ and concentrated *in vacuo*. The residue was washed with hexane. The product was dried *in vacuo* to give **17** (96.7 mg, 2.6 mmol, 67%) as a colorless solid; mp 399°C; IR (KBr) ν 3052, 2952, 1565, 1339, 1273, 1246, 1133, 1096, 1037, 838, 730, 698 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 0.46 (s, 9H, SiMe₃), 3.51 (br.s, 2H), 7.64 (m, 3H), 8.12 (m, 1H), 8.46 (m, 2H); ¹³C NMR (67.8 MHz, CDCl₃) δ 1.38, 121.90, 122.64, 122.91, 123.65, 124.20, 124.60, 124.94, 126.93, 132.64, 133.24, 134.66, 138.07.

6,6'-Bis(trimethylsilyl)-4,4'-bis(dibenzothiophene) (18). - Under an inert atmosphere, a mixture of

4-trimethylsilyldibenzothiophene (**14**) (26 mg, 0.067 mmol) and 4-trimethylsilyldibenzothiophene 6-boronic acid (**17**) (20 mg, 0.067 mmol), Pd(PPh₃)₄ (2.0 mg, 1.10⁻³ mmol) and aq. 2.3 M Na₂CO₃ (0.2 mL) in DME (1 mL) was heated under reflux for 24 h. Thereafter, the solution was poured into water (5 mL) and extracted with CH₂Cl₂ (10 mL). The resulting organic phase was dried over anhydrous MgSO₄ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (eluant: hexane) to give **18** (20 mg, 0.04 mmol, 58%) as colorless crystals; mp 100.2 – 102.0°C; IR (KBr) ν 3052, 2950, 1566, 1248, 1037, 838, 750, 618 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 0.38 (s, 18H, 2 SiMe₃), 7.60 – 7.86 (m, 8H), 8.31 – 8.45 (m, 4H); ¹³C NMR (67.8 MHz, CDCl₃) δ 122.19, 122.92, 123.09, 124.38, 125.25, 125.44, 127.32, 127.43, 133.30, 134.57, 135.31, 136.70; MS (70 eV) *m/z* 510 (M⁺, 100). HRMS Found: 510.1328. Calcd. for C₃₀H₃₀Si₂S₂: 510.1327.

6,6'-Dibromo-4,4'-bis(dibenzothiophene) (19). - To a mixture of 6,6'-bis(trimethylsilyl)-4,4'-bis(dibenzothiophene) (**18**) (73.0 mg, 0.14 mmol) and BTMABr₃ (134 mg, 0.28 mmol) in acetic acid (6 mL) was added in an inert atmosphere ZnCl₂ (23 mg, 0.34 mmol) and the resulting reaction mixture was stirred at 80°C for 13 h. Thereafter, the reaction mixture was poured into water (20 mL) and extracted with CH₂Cl₂ (20 mL). The organic phase was washed with water (20 mL), dried over anhydrous MgSO₄ and concentrated *in vacuo*. The residue was washed with ether (10 mL). The product was dried *in vacuo* to give **19** (72 mg, 0.14 mmol, 97%) as a brownish powder; mp 119 – 120°C; IR (KBr) ν 3054, 1545, 1436, 1025, 774, 701 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.33 – 8.12 (m, 6H), 8.52 – 8.82 (m, 6H); ¹³C NMR (67.9 MHz, CDCl₃) δ 117.54, 121.47, 124.01, 125.93, 127.34, 128.46, 129.65, 131.14, 133.26, 137.16, 138.02, 140.61; MS (70 eV) *m/z* (%) 523 (35). HRMS Found: 523.8726. Calcd. for C₂₄H₁₂⁷⁹Br⁸¹BrS₂: 523.8727.

6,6'-Diiodo-4,4'-bis(dibenzothiophene) (20). - To a mixture of 6,6'-bis(trimethylsilyl)-4,4'-(dibenzothiophene) (**18**) (50 mg, 0.1 mmol) and BTMAICl₂ (68 mg, 0.2 mmol) in acetic acid (2 mL) was added ZnCl₂ (27 mg, 0.24 mmol) and the resulting mixture was stirred at 80°C for 22h. Thereafter, the mixture was poured into water (10 mL) and extracted with CH₂Cl₂ (20 mL). The organic phase was washed with water (10 mL), dried over anhydrous MgSO₄ and concentrated *in vacuo*. The residue was washed with diethylether (10 mL). The product was dried *in vacuo* to afford **20** (85 mg, 0.38 mmol, 98%) as a brownish powder; mp 64.2 – 68.2°C; IR (KBr) ν 2960, 1541, 1438, 1260, 1098, 1022, 743 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.16 (dd, 1H, ³J 5.2, ³J 5.0 Hz), 7.42 – 7.56 (m, 2H), 7.70 – 7.86 (m, 2H), 8.04 – 8.11 (m, 2H); ¹³C NMR (67.9 MHz, CDCl₃) δ 121.94, 122.03, 122.86, 125.67, 127.65, 128.74, 129.87, 131.93, 133.40; MS (70 eV) *m/z* (%) 618 (100). HRMS Found: 617.8749;

Calcd. for $C_{24}H_{12}S_2I_2$: 617.8470.

6,6'-Bis(trimethylsilyl)-4,4'-bis(dibenzothiophene-*S,S*-dioxide) (23). – To a solution of bis(4-trimethylsilyldibenzothiophene) (**18**) (50 mg, 0.098 mmol) in CH_2Cl_2 (2 mL) was given at rt *m*-CPBA (80 mg, 0.47 mmol). The reaction mixture was stirred at rt for 2h. Then it was poured into sat. aq. $NaHCO_3$ (20 mL) and the organic material was extracted with CH_2Cl_2 (10 mL). The organic phase was washed with water (2 X 20 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was subjected to column chromatography on silica gel (ether/hexane 1:1) to give **23** (26 mg, 0.045 mmol, 46%) as a colorless powder; 1H NMR (600 MHz, $CDCl_3$) δ 0.05 (s, 18H, 2 $SiMe_3$), 6.99 – 7.35 (m, 12H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 0.62, 122.14, 122.44, 131.59, 132.51, 132.81, 132.88, 133.24, 133.66, 135.99, 137.98, 143.68; MS (FAB, 3-nitrobenzyl alcohol) m/z 575 (MH^+). HRMS Found: 575.1204. Calcd. for $C_{30}H_{31}O_4Si_2S_2$ (MH^+ , FAB).

Oxidation of 6,6'-Bis(trimethylsilyl)-4,4'-bis(dibenzothiophene) with *m*-CPBA/ $BF_3 \cdot Et_2O$ (24). – To a solution of **18** (50 mg, 0.098 mmol) in CH_2Cl_2 (2 mL), cooled to 0°C, was added $BF_3 \cdot Et_2O$ (0.04 mL, 0.39 mmol) and subsequently in *m*-CPBA (40 mg, 0.22 mmol) in CH_2Cl_2 (4 mL). The reaction mixture was stirred for 2h. Then the mixture was given into conc. aq. $NaHCO_3$ (20 mL). The organic material was extracted with CH_2Cl_2 (2 X 10 mL). The organic phase was washed with water (10 mL) and dried over anhydrous $MgSO_4$. Thereafter, the solvent was evaporated *in vacuo* and the residue was subjected to column chromatography on silica gel (ethyl acetate / hexane = 1 : 1) give **24** (9.0 mg, 0.019 mmol, 20%) as colorless crystals; 1H NMR (270 MHz, $CDCl_3$) δ 0.32 (s, 9H, $SiMe_3$), 7.44 – 7.91 (m, 13H); MS (70 eV) m/z (%) 470 (M^+ , 18), 454 ($M^+ - [O]$, 41), 438 ($M^+ - [2O]$, 100), 423 (438- CH_3 , 89). HRMS Found: 470.0829. Calcd. for $C_{27}H_{22}O_2Si_2$: 470.0831.

Trimer 21. – Under an inert atmosphere, a mixture of 4,6-diiodobenzothiophene (**13**) (100 mg, 0.23 mmol), 4-trimethylsilyldibenzothiopheneboronic acid (**17**) (83 mg, 0.023 mmol), $Pd(PPh_3)_4$ (5.0 mg, $1.10 \cdot 10^{-6}$ mol) and aq. Na_2CO_3 (63 mg) in DME (6 mL) was heated under reflux at 60°C for 6d. Thereafter, the solution was poured into water (5 mL) and extracted with CH_2Cl_2 (10 mL). The organic phase was dried over anhydrous $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was purified by column chromatography on silica gel (eluant: hexane) to give **21** (20 mg, 0.03 mmol, 13%) as colorless plates, mp 98.2° - 99.2°C; 1H NMR (270 MHz, $CDCl_3$) δ 0.05 (s, 18H, 2 $SiMe_3$), 7.38 – 7.44 (m, 12H), 7.87 – 7.89 (m, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 1.30, 121.09, 121.37, 122.44, 124.73, 124.99, 126.82, 127.09, 134.04, 134.91, 135.32, 136.22, 136.78, 148.30, 148.51, 149.86; MS (70 eV) m/z (%) 692 (21). HRMS Found:

692.1512. Calcd. for $C_{42}H_{36}Si_2S_3$; 692.1518.

Tetramer 22. – Under an inert atmosphere, a mixture of bis(iodobenzothiophene) (**20**) 55 mg, 0.089 mmol), 4-trimethylsilyldibenzothiopheneboronic acid (**17**), $Pd(PPh_3)_4$ (2 mg, $2 \cdot 10^{-3}$ mmol) and aq. Na_2CO_3 (48 mg) in DME (4 mL) was heated under reflux at 60°C for 4d. Thereafter, the reaction mixture was poured into water (5 mL) and the organic material was extracted with CH_2Cl_2 (10 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (eluant: hexane:ether 4:1) to give **22** (6 mg, $6.9 \cdot 10^{-3}$ mmol, 8%) as a colorless powder; mp 80.2 – 81.0°C; 1H NMR (270 MHz, $CDCl_3$) δ 0.66 (s, 18H, 2 $SiMe_3$), 7.12 – 7.39 (m, 16H), 7.82 – 7.88 (m, 8H); MS (70 eV) m/z (%) 874 (6). HRMS Found: 874.1700. Calcd. for $C_{54}H_{42}Si_2S_4$: 874.1708.

4-Iodobenzothiophene-*S*-oxide (26). – To 4-iodobenzothiophene (**12**) (1.0 g, 3.2 mmol) in CH_2Cl_2 (10 mL) was added solid *m*-CPBA (580 mg, 3.4 mmol) at rt and in 15 portions over a time period of 1.5h. The reaction mixture was stirred at rt for 2h. Thereafter, the mixture was poured into water (20 mL) and extracted with chloroform. The organic phase was dried over anhydrous $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was subjected to column chromatography on silica gel (eluant: chloroform) to give **26** (618 mg, 63%) as a colorless solid; mp 183.7 – 185.0°C; 1H NMR (270 MHz, $CDCl_3$) δ 7.25 (dd, 1H, 3J 9.0, 3J 8.0 Hz), 7.52 (m, 2H), 7.68 – 7.81 (m, 3H), 7.99 (d, 1H, J 6.0 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 94.63, 121.49, 122.26, 127.51, 130.08, 132.63, 133.69, 136.76, 138.94, 139.21, 144.40, 148.27; MS (70 eV) m/z (%) 325 (45, $M^+ - 1$).

Suzuki-Kumada Coupling Reactions with 26. – Example 1: A mixture of **26** (72 mg, 0.22 mmol), benzo[*b*]thiopheneboronic acid (99 mg, 0.55 mmol), $Pd(PPh_3)_4$ (20 mg, $17.3 \cdot 10^{-3}$ mmol) in a solvent mixture of DME (3.5 mL) and 2M aq. Na_2CO_3 solution (1.5 mL) was heated at reflux for 9h. Thereafter, the mixture was poured into water (20 mL) and extracted with chloroform (2 X 15 mL). The organic phase was dried over anhydrous $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was subjected to column chromatography on silica gel (eluant: ether/hexane 5:1) to give **25** (72 mg, 0.21 mmol, 98%) as an off-white solid; mp 177.9 – 181.6°C (ether); IR (KBr) ν 1447, 1022, 764 cm^{-1} ; 1H NMR (270 MHz, $CDCl_3$) δ 7.32 – 8.01 (m, 11H), 8.26 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$, DEPT) δ 121.29 (+, CH), 121.98 (+, CH), 122.07 (+, CH), 124.74 (+, CH),

124.83 (+, CH), 125.21 (+, CH), 127.06 (+, CH), 127.33 (+, CH), 130.01 (+, CH), 130.78 (+, CH), 132.54 (+, CH), 133.19 (+, CH), 136.57 (C_{quat}), 136.93 (C_{quat})*; MS (FAB, 3-nitrobenzyl alcohol) (%) 333 (MH⁺, 18), 316 (M⁺-[O]), 307 (27), 289 (12), 154 (100). HRMS Found: 333.0410. Calcd. for C₂₀H₁₃OS₂: 333.0408 (MH⁺, FAB); *not all of the quaternary carbons are listed.

Example 2: A mixture of **26** (500 mg, 1.5 mmol), 4-trimethylsilyldibenzothiophene boronic acid (**17**) (1.2 g, 3.3 mmol), and Pd(PPh₃)₄ (20 mg, 17.3 × 10⁻³ mmol) in a solvent mixture of DME (7.5 mL) and 2M aq. Na₂CO₃ solution (3 mL) was heated at reflux for 19h. Thereafter, the solution was poured into water (20 mL) and extracted with chloroform. The organic phase was dried over anhydrous MgSO₄ and the solvent was evaporated *in vacuo*. The residue was subjected to column chromatography on silica gel (eluant: chloroform) to give **27** (650 mg, 95%) as a colorless oil; IR (neat) ν 3052, 2954, 1572, 1445, 1354, 1249, 1063, 1028 840, 756, 730 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 0.12 (s, 9H, SiMe₃), 6.9 – 8.0 (m, 13H); ¹³C NMR (67.8 MHz, CDCl₃, DEPT) δ -1.2 (+, CH₃, SiMe₃), 121.60 (+, CH), 121.80 (+, CH), 121.92 (+, CH), 122.64 (+, CH), 124.06 (+, CH), 124.75 (+, CH), 127.42 (+, CH), 129.22 (C_{quat}), 129.79 (+, CH), 130.62 (+, CH), 131.95 (C_{quat}), 132.44 (+, CH), 132.78 (+, CH), 133.03 (+, CH), 134.03 (C_{quat}), 134.97 (C_{quat}), 136.12 (C_{quat}), 137.14 (C_{quat}), 138.82 (C_{quat}), 139.01 (C_{quat}), 142.05 (C_{quat}), 143.76 (C_{quat}), 145.14 (C_{quat}); MS (50 eV) *m/z* (%) 454 (M⁺, 26), 438 (M⁺-[O], 26); 423 (438-CH₃, 27), 73(100). HRMS Found: 454.0879. Calcd. for C₂₇H₂₂OSiS₂: 454.0881.

Photoirradiation of 24. – **24** (5 mg) in deaerated CD₂Cl₂ (1 mL) was photoirradiated for 19h at rt. A pyrex tube was used. Thereafter, the solvent was evaporated and the residue was subjected to column chromatography on silica gel (ethyl acetate/hexane 1:3) to give **29** (3 mg, 64%); ¹H NMR (600 MHz, CDCl₃) δ 0.62 (s, 9H, SiMe₃), 7.36 – 7.81 (m, 10H), 8.07 – 8.21 (m, 3H); MS (70 eV) *m/z* (%) 438 (100). HRMS Found: 438.0933. Calcd. for C₂₇H₂₂SiS₂: 438.0932.

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References and Footnotes

- 1) T. Thiemann and National Cancer Institute (NCI); unpublished results. The testing of the thiophene-S-oxides was performed within the Developmental Therapeutics Program, DCTD, NCI in Bethesda, Maryland, USA.
- 2) T. Thiemann, D. Ohira, K. Arima, T. Sawada, S. Mataka, F. Marken, R. G. Compton, S. D. Bull, S. G. Davies, *J. Org. Phys. Chem.* **2000**, *13*, 648.
- 3) D. Ohira, *MSc thesis*, Kyushu University **2000**.
- 4) T. Thiemann, K. Arima, D. Ohira, K. Kumazoe, S. Mataka, *ECSOC 4 2000*; <http://reprints.net/ecsoc-4/a0090/a0090.htm>; *ECSOC-4 Proceedings* (T. Wirth, C. O. Kappe, E. Felder, U. Diedrichsen, S.-K. Lin, eds.) ISBN 3-906980-05-7.
- 5) a.) B. T. Jiang, T. D. Tilley, *J. Am. Chem. Soc.* **1999**, *121*, 9744 – 9745; b.) M. C. Suh, B. Jiang, T. D. Tilley, *Angew. Chem.* **2000**, *112*, 2992; *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 2870 – 2873.
- 6) For a discussion of the two possible mechanisms in the analogous deoxygenation of dibenzothiophene-S-oxides and benzothiophene-S-oxides, see: a.) G. M. Gurria, G. H. Posner, *J. Org. Chem.* **1973**, *38*, 2419; b.) M. E. F. El Amoudi, P. Geneste, J.-L. Olive, *J. Org. Chem.* **1981**, *46*, 4258; c.) Z. Wan, W. S. Jenks, *J. Am. Chem. Soc.* **1995**, *117*, 2667; d.) D. D. Gregory, Z. Wan, W. S. Jenks, *J. Am. Chem. Soc.* **1997**, *119*, 94. Also see ref. 6.
- 7) a.) T. Thiemann, K. Arima, S. Mataka, *Rep. Inst. Adv. Mat. Study, Kyushu Univ.* **2000**, *14*(1), 37; b.) T. Thiemann, K. Arima, K. Kumazoe, S. Mataka, *Rep. Inst. Adv. Mat. Study, Kyushu Univ.* **2000**, *14*(2), 139.
- 8) K. Arima, *MSc-thesis*, Kyushu Univ. **2001**.
- 9) This compound has been prepared by Gilman et al.: H. Gilman, J. F. Nobis, *J. Am. Chem. Soc.* **1950**, *72*, 2629. H. Gilman distills the compound in the purification process and provides a boiling point for the compound.
- 10) For the preparation and the general reactivity of quaternary ammonium polyhalides, see: S. Kajigaeshi, T. Kakinami, T. Okamoto, S. Fujisaki, *Halogenation and Oxidation with Quaternary Ammonium Polyhalides*, Colony Press 1996.
- 11) Silyl-halo exchanges are also known to proceed with the following reagents: (for bromo) Br₂: [ref. 9a] C. Eaborn, A. A. Najam, D. R. M. Walton, *J. Chem. Soc., Perkin Trans. 1* **1972**, 2481; NaBr, NCS: [ref. 9b] D. S. Wilbur, K. W. Anderson, W. E. Stone, H. A. O'Brien, Jr., *J. Label. Cpd. Radiopharm.* **1982**, *19*, 1171; Br /*t*-BuOCl: ref. 9b; NBS; (for iodo) I₂; ICl ref. 9a,b; NaI/NCS: ref. 9b, and D. S. Wilbur, W. E. Stone, K. W. Anderson, *J. Org. Chem.* **1983**, *48*, 1542; NaI/*t*-BuOCl: ref. 9b. The use of BTMABr₃ or BTMAICl₂ in this reaction has not yet been published.
- 12) For similar conditions in Suzuki reactions, see: T. Thiemann, K. Umeno, D. Ohira, E. Inohae, T. Sawada, S. Mataka, *New J. Chem.* **1999**, *23*, 1067 and ref. cited.
- 13) A. Suzuki in *Metal Catalyzed Cross-Coupling*

Reactions (F. Diederich, P. J. Stang, eds.), Wiley-VCH, Weinheim **1998**, pp. 70.

- 14) For the use of Pd(OAc)₂/K₃PO₄/DMF, in cross-coupling reactions utilizing aryl boronic acids, see: S. W. Wright, D. L. Hageman, L. D. McClure, *J. Org. Chem.* **1994**, *59*, 6095.
- 15) P. Dansette et al. have witnessed a similar problem upon treating trimethylsilylbenzothiophene with *m*-CPBA/BF₃·Et₂O: P. Dansette, private communication, Paris/Fukuoka 2001.
- 16) S. Kim, J. Yang, F. DiNanno, *Tetrahedron Lett.* **1999**, *40*, 2909 – 2912.
- 17) C. Wang, R. G. Weiss, *Macromolecules* **1999**, *32*, 7032 – 7039.
- 18) D. J. Walton, I. R. Peterson (U. Cov., UK) and T. Thiemann, RSC-project proposal (Photo-oxidative Route to Conducting Polymers), submitted.