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Metal-Free Oxidative Coupling Reactions via σ-Iodonium Intermediates: The Efficient Synthesis of Bithiophenes Using Hypervalent Iodine Reagents

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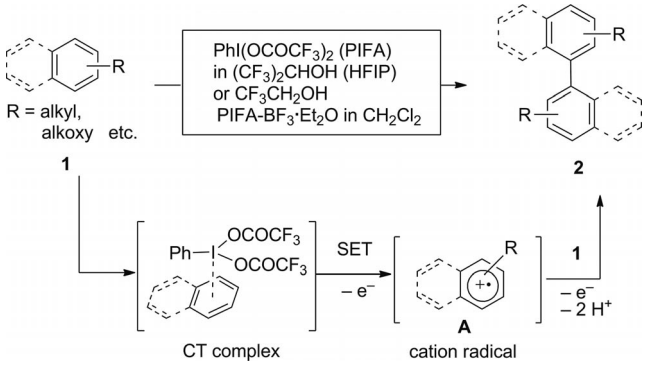
The direct oxidative biaryl coupling reaction is an attractive tool for environmentally benign green chemistry. A novel direct method for the synthesis of bithiophene using a hypervalent iodine reagent has been developed. The reaction mechanism has also been investigated, casting light on the reaction intermediate and revealing the reactivity with iodonium salts.

Introduction

Oligo- and polythiophene derivatives have gained recognition as important materials due to their useful physical properties such as electrical conductivity and electroluminescence.[1] 2,2′-Bithiophenes are one of the most important classes of compounds for synthesizing oligo- and polythiophenes because they polymerize under mild conditions due to their lower oxidation potential relative to thiophene and predominantly yield a higher-quality α-linked polymer compared with that prepared from thiophene.[1b] Therefore there have been a large number of reports on the synthesis of 2,2′-bithiophenes, but these methodologies have been limited to transition-metal-catalyzed coupling reactions, namely carbon–carbon (C–C) coupling reactions performed with Grignard (Kumada–Tamao), boron (Suzuki–Miyaura), and zinc reagents (Negishi).[2,3] On the other hand, the oxidative biaryl coupling reactions of thiophenes is a very attractive and convenient straightforward route to bithiophenes due to its operational simplicity by avoiding the preparation of the corresponding halogenated and metalated thiophenes. However, to the best of our knowledge, there have been no reports on the oxidative dimerization of thiophenes due to the lower oxidation potential of the bithiophenes relative to the corresponding thiophenes. That is, the dimer, which is more easily oxidized than the monomer, usually undergoes further coupling to afford the polythiophene through successive reactions.[4] Therefore typical oxidative coupling methods using electrochemical oxidation or heavy-metal oxidants such as Fe^{III}, Tl^{III}, Ru^{III}, and Mo^{III} have not been utilized for dimerization but for the oligomerization or polymerization of thiophenes.[5] Recently, Mori and co-workers reported the palladium-catalyzed oxidative coupling reaction of 2-substituted thiophenes using stoichiometric silver fluoride as the terminal oxidant.[6]

Hypervalent iodine(III) reagents have received considerable attention as alternatives to toxic heavy-metal reagents due to their mild oxidation abilities, low toxicity, and easy handling.[7] Over the past decades, we have focused our attention on a new, efficient, and mild oxidative transformation of electron-rich aromatic compounds and have developed the phenyliodine(III) bis(trifluoroacetate) (PIFA) induced direct oxidative nucleophilic substitution of phenyl ethers by various nucleophiles such as N_3, OAc, α-dicarbonyl compounds, SAr, and SCN in 1,1,1,3,3,3-hexafluoropropane-2-ol (HFIP).[8]

In addition, we have found that the activated PIFA/BF_3·Et_2O and PIFA/TMSOTf are effective for the intra- and intermolecular biaryl coupling reactions of phenyl ethers and alkylarenes (Scheme 1).[9] These reactions would proceed via the cation radical intermediate **A** and the bond formation could oxidatively occur by the reaction of **A** with



Scheme 1. Biaryl coupling reactions of phenyl ethers and alkylarenes.

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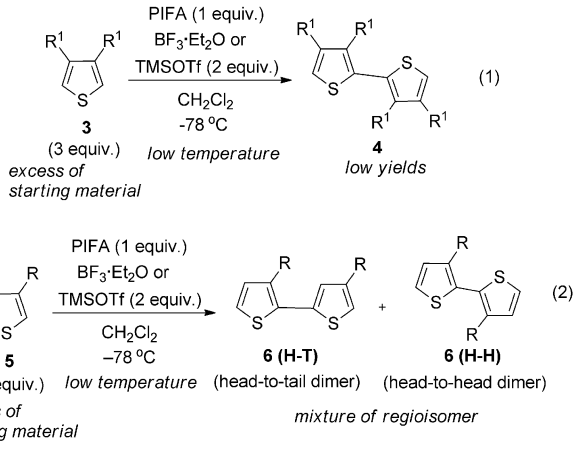
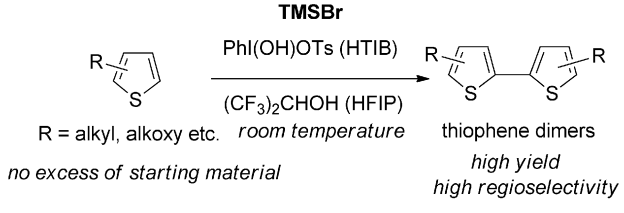
nucleophiles or neutral molecules of the substrate to give the corresponding coupling products. As part of our continued studies on the PIFA-induced biaryl coupling reaction we have developed the biaryl coupling reactions of substituted thiophenes **3** and **5** by using PIFA activated by BF_3·Et_2O or TMSOTf (Scheme 2).[10] However, these reactions required an excessive amount of the starting materials at low temperature, see reaction (1), and the resulting coupling products were obtained as a mixture of regioisomers in low yields, see reaction (2).



Scheme 2. Biaryl coupling reactions of 3-substituted thiophenes using hypervalent iodine reagent.

Recently, our research group has been involved in the development of the hypervalent iodine(III)-induced cross-coupling reactions of heteroaromatic compounds with various arenes.[11] For these processes, the experimental data revealed the involvement of iodonium(III) intermediates. We also reported the regioselective oxidative synthesis of head-to-tail (H-T) bithiophenes **6(H-T)** by using hydroxy(tosyloxy)iodobenzene [PhI(OH)OTs, HTIB].[12]

We now present a detailed study of the oxidative biaryl coupling reaction for the synthesis of substituted bithiophenes (Scheme 3). The reaction conditions permitted the use of electron-rich thiophenes without oligo- or polymerization. We investigated the reaction mechanism and found that the reaction would be mediated by diaryliodonium(III) intermediates generated in situ from thiophenes and HTIB in HFIP. In addition, we also synthesized oligothiophenes with well-defined structures by repeated oxidative coupling reactions.

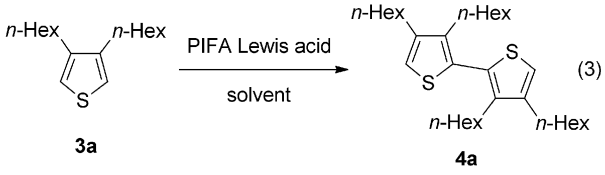


Scheme 3. Biaryl coupling reactions of various substituted thiophenes.

Results and Discussion

Based on our previous results concerning the oxidative biaryl coupling reactions of phenyl ethers and alkylarenes, we first examined the coupling reaction of 3,4-dihexylthiophene (**3a**) with PIFA and a Lewis acid such as BF_3·Et_2O or TMSOTf in dichloromethane at a low temperature (Table 1, entries 1 and 2).[8] However, both BF_3·Et_2O and TMSOTf were ineffective, producing only trace amounts of the coupling product **4a**, which was detected by TLC and GC along with unreacted starting material **3a**. On the other hand, the use of bromotrimethylsilane (TMSBr) produced a small amount of the coupling product **4a**, whereas the previously reported coupling reaction of pyrroles[13] smoothly proceeded under the same reaction conditions (entry 3). To improve the yield of the desired coupling product **4a**, a variety of solvents and temperatures were evaluated. An earlier study by our group has shown that a fluoro alcohol can enhance the reactivity of the hypervalent iodine reagent towards thiophenes.[8b,14] Based on these studies, we attempted the coupling reaction in a fluoro alcohol and found that the use of TMSBr in HFIP increased the reactivity, producing the coupling product **4a** in good yield (entry 6). Other ordinary organic solvents, such as toluene, diethyl ether, DME, dioxane, dichloromethane, and another fluoro alcohol CF_3CH_2OH, were less effective than HFIP.

Table 1. Screening of Lewis acids and solvents in the coupling reaction, see reaction (3).[a]



Entry	Lewis acid	Solvent	Temp. [°C]	Time [h]	Yield [%]
1	BF_3·Et_2O	CH_2Cl_2	–78	6	trace
2	TMSOTf	CH_2Cl_2	–78	6	trace
3	TMSBr	CH_2Cl_2	–78	24	15
4	BF_3·Et_2O	HFIP	r.t.	24	n.d.
5	TMSOTf	HFIP	r.t.	24	n.d.
6	TMSBr	HFIP	r.t.	6	65

[a] Performed by using **3a** (2 equiv.), PIFA (1 equiv.), and Lewis acid (2 equiv.) in solvent.

Further screening of the iodine(III) reagent was carried out by using HFIP as the solvent in conjunction with 2 equiv. of TMSBr (Table 2). The use of phenyliodine diacetate (PIDA) decreased the yield of the reaction product (entry 1). However, HTIB gave a better result than PIFA (entry 2). Interestingly, we noticed the importance of premixing thiophene **3a** and HTIB for the yield of the coupling product. Thus, TMSBr was added to a stirred solution of **3a** and HTIB, and the reaction was completed at this stage, giving a higher yield of the coupling product **4a** (entry 3). Other iodine reagents with an electron-withdrawing group,

such as trifluoromethyl or fluoride, were less efficient for this coupling reaction (entries 4 and 5). After the optimization process, the biaryl coupling of various thiophenes was carried out under our standard conditions: 2 equiv. of TMSBr, 1 equiv. of HTIB as the oxidant, and HFIP as the solvent.

Table 2. Screening of iodine(III) reagents in the coupling reaction, see reaction (3).[a]

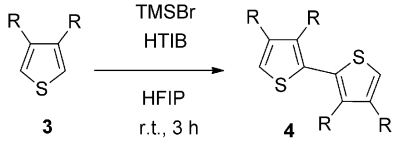
Entry	Iodine(III) reagent	Temp. [°C]	Time [h]	Yield [%]
1	$PhI(OCOCH_3)_2$ (PIDA)	r.t.	6	32
2	PhI(OH)OTs (HTIB)	r.t.	6	76
3[b]	PhI(OH)OTs (HTIB)	r.t.	6	83
4	$C_6F_5I(OH)OTs$	r.t.	24	trace
5	$4\text{-}CF_3C_6H_4I(OH)OTs$	r.t.	6	67

[a] Performed by using **3a** (2 equiv.), I^{III} (1 equiv.), and TMSBr (2 equiv.) in HFIP at room temperature. [b] TMSBr was added after thiophene **3a** had reacted with HTIB in HFIP.

Scope of the Reaction

The optimized conditions were then applied to examine the scope and limitations of the reaction. The reaction was found to be compatible with a wide range of substituted thiophenes and the results are summarized in Table 3. The alkylthiophenes **3a**–**c**, with a small or large alkyl substituent, gave the desired coupling products in excellent yields (entries 1–3). The bulkier substituent in **3d** did not affect the product yield (entry 4). In general, electron-rich alkoxy-substituted bithiophenes, such as **3e** and **3f**,[15] have problems under acidic and oxidative conditions due to their low oxidation potentials. When we attempted the coupling reactions of **3e** and **3f**, the coupling products **4e** and **4f** were obtained in 83 and 89% yields under the same reaction conditions (entries 5 and 6). The 3,4-(diethylenedioxy)thiophene (EDOT) dimer **4g**, which has a very low oxidation potential and is a precursor for electropolymerization, giving a polymer with excellent conductivities and stable doped states,[16] was produced in 61% yield (entry 7).

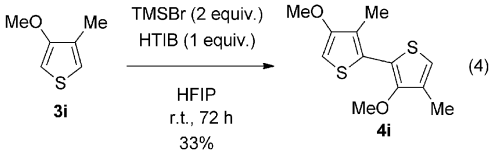
Table 3. Scope of the coupling reaction.[a]



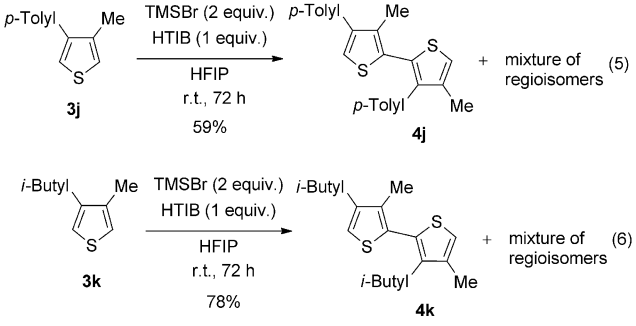
Entry	R	Time [h]	Yield [%]
1	*n*Hex (**3a**)	3	83
2	Me (**3b**)	3	73
3	*n*Oct (**3c**)	3	74
4	isobutyl (**3d**)	3	78
5	OMe (**3e**)	3	83
6	OBu (**3f**)	3	89
7	$-O(CH_2)_2O-$ (**3g**)	6	61
8	*p*-tolyl (**3h**)	6	56

[a] Performed by using **3** (2 equiv.), HTIB (1 equiv.), and TMSBr (2 equiv.) in HFIP at room temperature.

Next we performed the coupling reaction with unsymmetrical 3,4-disubstituted thiophenes. In the case of 3-methyl-4-methoxythiophene (**3i**), the coupling product **4i** was obtained as a single regioisomer, albeit in a low yield, see reaction (4).



On the other hand, 3-methyl-4-(*p*-tolyl)thiophene (**3j**) and 3-isobutyl-4-methylthiophene (**3k**) are good substrates for this reaction, providing the coupling products **4j** and **4k**, respectively, see reactions (5) and (6). However, the resulting coupling products **4j** and **4k** are produced together with a mixture of other regioisomers that are inseparable by column chromatography.

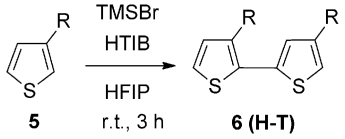


Highly Regioselective Oxidative Coupling Reactions of Thiophenes

We were also interested in the regioselective coupling reactions of 3-monosubstituted thiophenes. For the coupling reactions of β-substituted thiophenes, the resulting coupling products were thought to be a mixture of three regioisomers: head-to-head (H-H) coupled between the 2- and 2′-positions of the thiophene ring, tail-to-tail (T-T) coupled between the 5- and 5′-positions of the thiophene ring, and head-to-tail (H-T) coupled between the 2- and 5′-positions of the thiophene ring. However, we extended our coupling reaction to various 3-monosubstituted thiophenes **5a**–**g** with electron-donating groups, such as alkyl and alkoxy, and the H-T dimers were obtained as single isomers (Table 4). The head-to-tail (H-T) dimers[3] are useful precursors for high quality, well-defined regioregular oligo- and polythiophenes and their derivatives.[17] The regiochemistries of the products were determined by measurement of their ^1H NMR spectra or by comparing them with authentic samples. Alkylthiophenes **5a**–**d** gave the desired products in excellent yields and with high regioselectivities (entries 1–4). The coupling reactions of sterically hindered substrates **5e** and **5f** also proceeded smoothly to give the desired H-T coupling products (entries 5 and 6). The bromo group of **5g**

is tolerated under the reaction conditions (entry 7). In each case, the resulting coupling product contained less than 1% or no other regioisomers.

Table 4. Regioselective coupling reactions of 3-alkylthiophenes.[a]



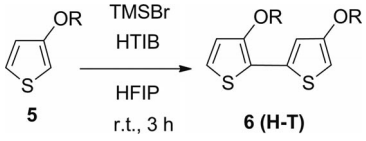
Entry	R	Yield [%]
1	*n*Hex (**5a**)	78
2	Me (**5b**)	87
3	*n*Bu (**5c**)	88
4	*n*Oct (**5d**)	75
5	isobutyl (**5e**)	74
6	*c*Hex (**5f**)	75
7	$-(CH_2)_6-Br$ (**5g**)	72

[a] Performed by using **5** (2 equiv.), HTIB (1 equiv.), and TMSBr (2 equiv.) in HFIP at room temperature.

Alkoxythiophenes

We examined various 3-alkoxy-substituted thiophenes **5h**–**o** to explore the substrate scope under our reaction conditions (Table 5). The reactions proceeded smoothly and gave the corresponding H-T bithiophenes **5h**–**o(H-T)** in high yields as a single isomer. The bithiophenes **6i(H-T)** and **6j(H-T)** should be useful precursors for high-conducting polymers (entries 2 and 3) as poly(3-butoxythiophene)s and poly(3-hexyloxythiophene)s are frequently used as soluble, conjugated polymers with excellent stability in air.[1] Steric effects affected neither the reactivity nor selectivity of the reactions with **5k** and **5l**, giving the coupling products **6k(H-T)** and **6l(H-T)** in high yields. The fluoroalkyl-substituted thiophene **5m** also provided **6m(H-T)** as a single isomer in 75% yield. The presence of protecting groups such as 2-(2-methoxyethoxy)ethyl (MEET) and benzyl were well tolerated, affording the corresponding coupling products **6n(H-T)** and **6o(H-T)** in good yields.

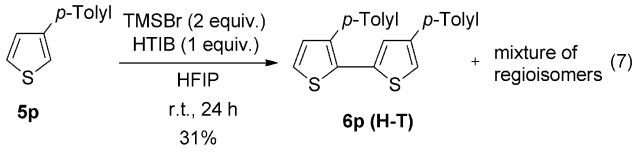
Table 5. Regioselective coupling reactions of 3-alkoxythiophenes.[a]



Entry	R	Yield [%]
1	Me (**5h**)	85
2	*n*Hex (**5i**)	84
3	*n*Bu (**5j**)	75
4	isobutyl (**5k**)	73
5	*c*Hex (**5l**)	70
6	$-CH_2(CF_2)_5CF_3$ (**5m**)	75
7	$(CH_2)_2O(CH_2)_2OCH_3$ (**5n**)	72
8	Bn (**5o**)	61

[a] Performed by using **5** (2 equiv.), HTIB (1 equiv.), and TMSBr (2 equiv.) in HFIP at room temperature.

On the other hand, in the reaction of the 3-arylthiophene **5p**, the yield of the coupling product was lower and the starting materials remained almost unchanged, see reaction (7). Moreover, the coupling products were obtained as a mixture of regioisomers.

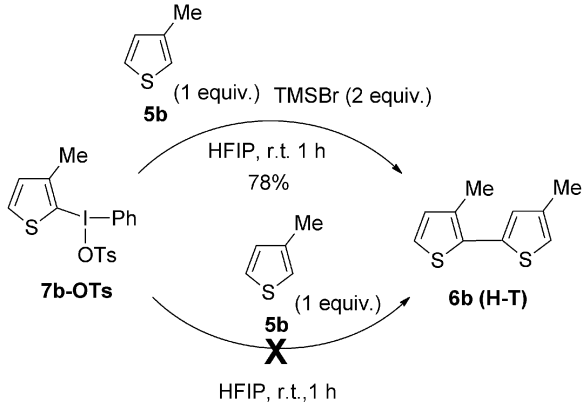


Thiophenes bearing strongly electron-withdrawing groups, such as acetyl, cyano, and chloro, did not react at all and the starting materials were recovered unchanged under the present oxidative reaction conditions. These results indicate that the electronic effects of the substituent on the thiophene ring[18] are important if this coupling reaction is to proceed.

Mechanistic Considerations

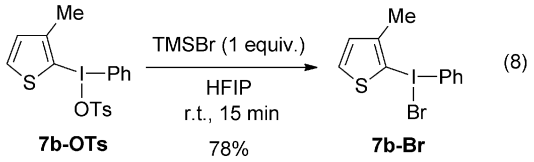
The reason for the H-T product selectivity is the focus of continuing investigation. We assumed that the intermediate of this coupling reaction is different to that of the coupling reactions of phenyl ethers and alkylarenes, which proceed via cation radical intermediates.[8] When we carried out the reaction in the absence of TMSBr, stable diaryliodonium salts of the thiophenes were obtained in high yields. Therefore we presumed from this result that the coupling reactions of thiophenes proceed via the diaryliodonium salts. To clarify the precise reaction mechanism for this oxidative biaryl coupling reaction, we examined the reactivity of the diaryliodonium salts.

First, 3-methylthiophene (**5b**) was treated with the HTIB in HFIP to form the stable iodonium salt **7b-OTs** in 98% yield.[13] The iodonium salt **7b-OTs** was then treated with thiophene **5b** in the presence of TMSBr to produce the coupling product in comparable yield under the same reaction conditions. However, **7b-OTs** did not react with **5b** in the absence of TMSBr (Scheme 4).

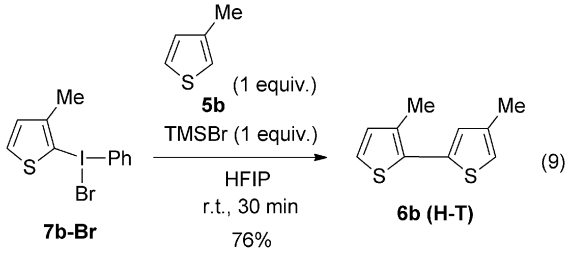


Scheme 4. Reactivity of iodonium salt **7b-OTs**.

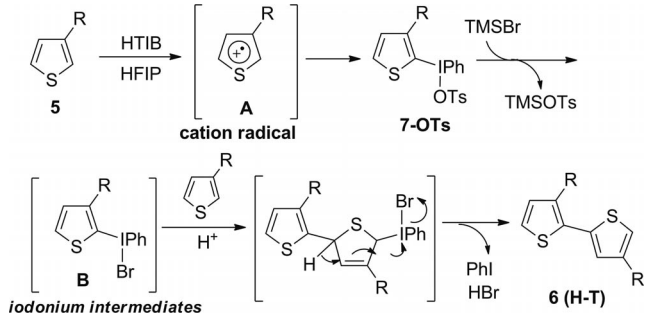
We next examined the role of TMSBr in the reaction. When iodonium tosylate **7b-OTs** was treated with 1 equiv. of TMSBr in HFIP, the iodonium bromide was obtained in 78% yield. From this result, it is clear that one of the important steps is the generation of the iodonium bromide intermediate **7b-Br**, see reaction (8).



The isolated iodonium bromide **7b-Br** reacted with the 3-methylthiophene (**5b**) in the presence of 1 equiv. of TMSBr to give the coupling product **6b(H-T)** in 76% yield, see reaction (9). In this case, no transfer of the phenyl group from the salts was observed.



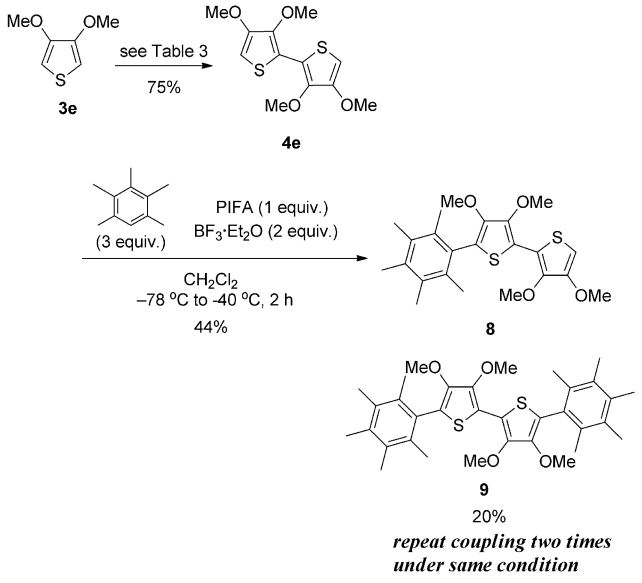
A plausible reaction mechanism for the present oxidative coupling of thiophenes is illustrated in Scheme 5. As presumed from our experimental results, first, HTIB induces the SET oxidation of thiophenes to produce the cation radical via the CT complex in HFIP. The formation of the cation radical **A** is sufficiently confirmed by the UV spectra.[14] The cation radical can selectively react at the 2-position with the iodine oxidant to form the stable iodonium-OTs **7-OTs**. This process occurs rapidly with the aid of the fluoro alcohol solvent. From this experiment, it is clear that **7-OTs** reacts with TMSBr and the resulting iodonium bromide **B** is activated by the added TMSBr in HFIP to induce further reactions and provide the bithiophenes **6(H-T)**.



Scheme 5. Plausible mechanism for the coupling reaction.

Convenient Synthesis of Substituted Thiophene Oligomer

Poly- and oligoaryl compounds involving thiophenes have been used to prepare electronic and electro-optical devices.[19] Therefore the synthesis of oligothiophenes with well-defined structures is highly important. We envisaged a facile synthesis of extended oligomers by repeating the oxidative coupling and thus they have been synthesized by utilizing our coupling method (Scheme 6). As a result, 5-arylated 2,2′-bithiophene **8** was obtained in 44% yield when the activated PIFA/BF_3·Et_2O-induced cross-coupling of **4e** was carried out with 3 equiv. of pentamethylbenzene. Repeated oxidative cross-coupling led to 5,5′-diaryl-2,2′-bithiophene **9** in 20% yield under the same conditions. 5,5′-Diaryl-2,2′-bithiophenes have been shown to be useful as organic semiconductors and fluorescent materials.[19c,19d] Our method has a significant advantage as it does not require stoichiometric metalation or halogenation of the aromatics.



Scheme 6. Short-step synthesis of oligoaryls from the dimer **4e**.

Conclusions

We have described herein the oxidative biaryl coupling reaction of substituted thiophenes using a combination of a hypervalent iodine(III) reagent with TMSBr in HFIP at room temperature. Our novel biaryl coupling reaction has some characteristic features: 1) Direct and regioselective coupling of substituted thiophenes without the use of transition-metal catalysts or heavy-metal oxidants and 2) the coupling reaction proceeds via the stable iodonium intermediate generated in situ from thiophenes and the iodine(III) reagent. The high regioselectivities might be attributed to this thiophene intermediate.

Experimental Section

General: ^1H and ^{13}C NMR spectra were recorded with a JEOL JMN-300 spectrometer operating at 300 MHz in $CDCl_3$ and CD_3OD at 25 °C with tetramethylsilane as the internal standard.

The data are reported as follows: Chemical shifts (δ) in ppm, multiplicity (s singlet, d doublet, t triplet, q quartet, quint quintet, br. broad, m multiplet), coupling constant in Hz, integration, and interpretation. IR spectra were recorded by using a Hitachi 270-50 spectrometer; intensities of absorptions are reported in reciprocal centimeters. Mass spectra were obtained by using a Shimadzu GC–MS QP 5000 spectrometer with ionization voltages of 70 eV. High-resolution mass spectra were recorded by the Elemental Analysis Section of Osaka University. Column chromatography and TLC were carried out on Merck silica gel 60 (230–400 mesh) and Merck silica gel F_{254} plates (0.25 mm), respectively.

Representative Procedure for the Direct Oxidative Biaryl Coupling Reaction of Thiophenes: HTIB (0.3 mmol) and then TMSBr (0.08 mL, 0.6 mmol) were added to a stirred solution of 3,4-dihexylthiophene (**3a**; 151 mg, 0.6 mmol) in HFIP (6 mL) at room temperature and the color of the solution immediately changed to brown. After stirring for 3 h, CH_2Cl_2 and saturated aq. $NaHCO_3$ were successively added to the reaction mixture with stirring. The organic layer was then separated and the solvents evaporated to dryness. The residue was evaporated and subjected to column chromatography (SiO_2, hexane) to give 3,3′,4,4′-tetrahexyl-2,2′-bithiophene (**4a**; 125 mg, 83%) as a pale-yellow oil. The regiochemistry of the product **4a** was determined by comparing it with an authentic sample.

3,3′,4,4′-Tetrahexyl-2,2′-bithiophene (4a): A pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81–0.91 (m, 12 H), 1.19–1.39 (m, 28 H), 1.61–1.67 (m, 4 H), 2.42 (t, J = 8.0 Hz, 4 H), 2.52 (t, J = 7.7 Hz, 4 H), 6.92 (s, 2 H) ppm. ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 14.1, 14.1, 22.5, 22.6, 27.6, 29.3, 29.3, 29.4, 29.7, 30.4, 31.5, 31.8, 120.0, 129.8, 141.4, 142.3 ppm. IR (KBr): $\tilde{\nu}$ = 2926, 2855, 2340, 1462, 1377, 1261, 1171, 1016, 874, 797, 743 cm^{-1}. HRMS (FAB): calcd. for $C_{32}H_{54}S_2$ [M]$^+$ 502.3667; found 502.3667.

3,3′,4,4′-Tetramethyl-2,2′-bithiophene (4b):[20] A colorless crystal; m.p. 87–88 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.01 (s, 6 H), 2.16 (s, 6 H), 6.88 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.4, 15.4, 120.6, 131.1, 136.9, 178.4 ppm. IR (KBr): $\tilde{\nu}$ = 2922, 2253, 1445, 1385, 1261, 1096, 988, 912, 860, 787, 743, 650, 623 cm^{-1}.

3,3′,4,4′-Tetraoctyl-2,2′-bithiophene (4c):[21] A pale-yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83–0.89 (m, 12 H), 1.24–1.39 (m, 44 H), 1.53–1.68 (m, 4 H), 2.43 (t, J = 8.1 Hz, 4 H), 2.52 (t, J = 8.1 Hz, 4 H), 6.91 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.7, 27.5, 29.2, 29.2, 29.3, 29.3, 29.5, 29.5, 29.6, 29.7, 29.7, 30.5, 31.9, 31.9, 31.9, 120.0, 129.8, 141.3, 142.3 ppm. IR (KBr): $\tilde{\nu}$ = 3051, 2955, 2924, 2855, 1728, 1464, 1377, 1263, 1121, 895, 874, 789, 746, 706 cm^{-1}.

3,3′,4,4′-Tetraisobutyl-2,2′-bithiophene (4d): A pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.72 (d, J = 6.8 Hz, 12 H), 0.92 (d, J = 6.4 Hz, 12 H), 1.62–1.72 (m, 2 H), 1.83–1.93 (m, 2 H), 2.30 (d, J = 7.2 Hz, 4 H), 2.40 (d, J = 7.2 Hz, 4 H), 6.90 (s, 2 H) ppm. ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 22.5, 22.6, 28.8, 29.1, 36.7, 38.7, 121.0, 130.9, 140.1, 141.4 ppm. IR (KBr): $\tilde{\nu}$ = 3051, 2955, 2928, 2868, 1726, 1464, 1433, 1383, 1366, 1337, 1275, 1263, 1207, 1167, 1124, 1076, 1040, 895, 881, 862, 802, 748, 706, 665 cm^{-1}. HRMS (FAB): calcd. for $C_{24}H_{38}S_2$ [M]$^+$ 390.2415; found 390.2419.

3,3′,4,4′-Tetramethoxy-2,2′-bithiophene (4e): A white solid; m.p. 195–196 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 6 H), 3.88 (s, 6 H), 6.10 (s, 2 H) ppm. ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 57.2, 60.0, 94.6, 117.8, 142.9, 150.3 ppm. IR (KBr): $\tilde{\nu}$ = 3942, 3105, 3058, 2986, 2936, 2685, 2305, 1552, 1475, 1447, 1435, 1421, 1402, 1261, 1203, 1151, 1028, 993, 897, 864, 764, 748, 704 cm^{-1}. HRMS (FAB): calcd. for $C_{12}H_{14}O_4S_2$ [M]$^+$ 286.0334; found 286.0334.

3,3′,4,4′-Tetrabutoxy-2,2′-bithiophene (4f): A brown solid; m.p. 132–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, J = 7.4 Hz, 12 H), 1.42–1.53 (m, 8 H), 1.72–1.83 (m, 8 H), 3.94 (t, J = 6.3 Hz, 4 H), 4.07 (t, J = 6.7 Hz, 4 H), 6.03 (s, 2 H) ppm. ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 14.6, 14.7, 19.9, 20.1, 32.1, 33.0, 70.4, 73.2, 95.3, 118.7, 142.9, 150.4 ppm. IR (KBr): $\tilde{\nu}$ = 3113, 2957, 2933, 1548, 1458, 1376, 1261, 1229, 1194, 1172, 1145, 1068, 1025, 958, 902, 849, 750, 724, 688 cm^{-1}. HRMS (FAB): calcd. for $C_{24}H_{38}O_4S_2$ [M]$^+$ 454.2212; found 454.2219.

3,4:3′,4′-Bis(ethylenedioxy)-2,2′-bithiophene(4g):[22] A white solid; m.p. 205–207 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.24 (m, 4 H), 4.36 (m, 4 H), 6.27 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 64.6, 65.0, 97.5, 109.9, 137.0, 141.2 ppm. IR (KBr): $\tilde{\nu}$ = 2924, 2868, 2361, 2341, 1566, 1468, 1439, 1364, 1244, 1173, 1144, 1057, 1024, 951, 897, 866, 745, 700, 652 cm^{-1}. HRMS (FAB): calcd. for $C_{12}H_{14}O_4S_2$ [M]$^+$ 282.0021; found 283.0076.

3,3′,4,4′-Tetra(*p*-tolyl)-2,2′-bithiophene (4h): A pale-yellow solid; m.p. 201–204 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.24 (s, 6 H), 2.26 (s, 6 H), 6.69 (d, J = 7.8 Hz, 4 H), 6.85 (d, J = 7.8 Hz, 4 H), 6.91–6.99 (m, 8 H), 7.17 (s, 2 H) ppm. ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 21.1, 21.3, 123.2, 128.4, 128.6, 128.7, 128.8, 130.3, 132.6, 133.9, 136.0, 136.2, 140.0, 142.4 ppm. IR (KBr): $\tilde{\nu}$ = 3022, 2921, 2859, 1523, 1492, 1449, 1378, 1345, 1261, 1184, 1125, 1109, 1021, 911, 870, 818, 737, 700, 651 cm^{-1}. HRMS (FAB): calcd. for $C_{36}H_{30}S_2$ [M]$^+$ 526.1789; found 526.1801.

3,4′-Dimethoxy-3′,4-dimethyl-2,2′-bithiophene (4i):[23] A brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.10 (s, 3 H), 2.13 (s, 3 H), 3.65 (s, 3 H), 3.82 (s, 3 H), 6.19 (s, 1 H), 6.82 (s, 1 H) ppm. ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 11.9, 13.3, 57.0, 60.1, 95.6, 117.6, 119.3, 127.4, 127.7, 131.7, 153.4, 156.4 ppm. IR (KBr): $\tilde{\nu}$ = 2925, 2853, 1726, 1551, 1497, 1454, 1380, 1261, 1203, 1150, 1100, 1021, 876, 854, 822, 768, 750, 660, 612 cm^{-1}.

3,4′-Dihexyl-2,2′-bithiophene [6a(H-T)]:[24] A pale-yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84–0.92 (m, 6 H), 1.20–1.35 (m, 12 H), 1.52–1.70 (m, 4 H), 2.63 (t, J = 8.4 Hz, 2 H), 2.74 (t, J = 8.4 Hz, 2 H), 6.89–6.92 (m, 2 H), 7.03 (s, 1 H), 7.12 (d, J = 5.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.6, 29.0, 29.1, 29.2, 29.7, 30.4, 30.5, 30.7, 31.6, 31.7, 119.9, 123.4, 124.8, 127.3, 129.9, 130.9, 135.8, 139.3, 143.5 ppm. HRMS (FAB): calcd for $C_{20}H_{30}S_2$ [M]$^+$ 334.1789; found 334.1784.

3,4′-Dimethyl-2,2′-bithiophene [6b(H-T)]:[25] A pale-yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.28 (s, 3 H), 2.38 (s, 3 H), 6.86–6.87 (m, 2 H), 6.94 (s, 1 H), 7.11 (d, J = 5.1 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.3, 15.7, 120.4, 123.0, 127.7, 131.3, 133.7, 136.3, 138.0, 141.3 ppm. HRMS (FAB): calcd. for $C_{20}H_{26}O_2S_2$ [M]$^+$ 362.1374; found 362.1371.

3,4′-Dibutyl-2,2′-bithiophene [6c(H-T)]:[26] A pale-yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83–0.96 (m, 6 H), 1.29–1.42 (m, 4 H), 1.58–1.67 (m, 4 H), 2.61 (t, J = 7.5 Hz, 2 H), 2.75 (t, J = 7.5 Hz, 2 H), 6.87–6.96 (m, 3 H), 7.13 (d, J = 5.1 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9, 22.4, 22.6, 28.9, 30.2 (×2), 32.6, 32.9, 119.9, 123.4, 127.3, 129.9, 130.9, 134.1, 139.3, 143.5 ppm. IR (KBr): $\tilde{\nu}$ = 3051, 2930, 2858, 1732, 1456, 1377, 1263, 1088, 831, 748, 652 cm^{-1}. HRMS (FAB): calcd. for $C_{18}H_{22}S_2$ [M]$^+$ 278.1163; found 278.1162. $C_{16}H_{22}S_2$ (278.48): C 69.01, H 7.96, S 23.03; found C 69.01, H 7.93, S 22.74.

3,4′-Dioctyl-2,2′-bithiophene [6d(H-T)]:[27] A pale-yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86–0.88 (m, 6 H), 1.20–1.30 (m, 20 H), 1.56–1.63 (m, 4 H), 2.60 (t, J = 7.5 Hz, 2 H), 2.74 (t, J = 7.5 Hz, 2 H), 6.88–6.93 (m, 3 H), 7.14 (d, J = 5.1 Hz, 1 H) ppm. ^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 14.12, 15.28, 22.68, 29.14,

29.27, 29.36, 29.42, 29.44, 29.55, 30.43, 30.51, 30.73, 31.89, 119.87, 123.38, 127.30, 129.89, 130.97, 135.83, 139.36, 143.54 ppm. IR (KBr): $\tilde{\nu}$ = 2953, 2924, 2853, 2359, 2341, 1556, 1529, 1464, 1412, 1303, 1200, 1086, 864, 831, 721, 687, 669, 652 cm^{-1}. $C_{24}H_{38}S_2$ (390.68): calcd. C 73.78, H 9.80, S 16.42; found C 73.83, H 9.82, S 16.13.

3,4′-Bis(2-methylpropyl)-2,2′-bithiophene [6e(H-T)]:[28] A pale-yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.90–0.94 (m, 12 H), 1.83–1.96 (m, 2 H), 2.46 (d, J = 7.2 Hz, 2 H), 2.61 (d, J = 7.2 Hz, 2 H), 6.85 (d, J = 1.2 Hz, 1 H), 6.89 (d, J = 5.1 Hz, 1 H), 6.90 (d, J = 1.2 Hz, 1 H), 7.13 (d, J = 5.1 Hz, 1 H) ppm. ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 22.4, 22.5, 29.6, 29.7, 38.1, 39.8, 120.8, 123.1, 128.0, 130.5, 131.5, 135.7, 138.4, 142.2 ppm. HRMS (FAB): calcd. for $C_{16}H_{22}S_2$ $[M]^+$ 278.1163; found 278.1152.

3,4′-Dicyclohexyl-2,2′-bithiophene [6f(H-T)]: A pale-yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.26–1.56 (m, 12 H), 1.72–1.87 (m, 6 H), 1.99–2.02 (m, 2 H), 2.57–2.59 (m, 1 H), 2.96–3.01 (m, 1 H), 6.91 (s, 1 H), 6.97–7.03 (m, 2 H), 7.15 (d, J = 5.4 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.1 (×2), 26.6, 26.7, 34.1, 34.4, 38.2, 39.6, 118.5, 123.8, 126.4, 127.3, 130.1, 135.5, 144.8, 149.3 ppm. IR (KBr): $\tilde{\nu}$ = 2923, 2851, 1728, 1448, 1263, 1124, 943, 833, 731, 708, 650 cm^{-1}. HRMS (FAB): calcd. for $C_{20}H_{26}S_2$ $[M]^+$ 330.1476; found 330.1470. $C_{20}H_{26}S_2$ (330.55): C 72.67, H 7.93, S 19.40; found C 72.66, H 7.86, S 19.09.

3,4′-Bis(6-bromohexyl)-2,2′-bithiophene [6g(H-T)]:[29] A pale-yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.30–1.51 (m, 8 H), 1.59–1.71 (m, 4 H), 1.80–1.92 (m, 4 H), 2.61 (t, J = 7.5 Hz, 2 H), 2.75 (t, J = 7.5 Hz, 2 H), 3.40 (q, J = 7.5 Hz, 4 H), 6.89–6.92 (m, 3 H), 7.20 (d, J = 5.1 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.9, 28.4, 28.5, 28.9, 30.1, 30.2, 30.3, 30.4, 32.7, 33.9 (×2), 120.0, 123.6, 127.3, 129.8, 131.0, 135.8, 139.0, 143.2 ppm. HRMS (FAB): calcd. for $C_{20}H_{28}Br_2S_2$ $[M]^+$ 489.9999; found 489.9988.

3,4′-Dimethoxy-2,2′-bithiophene [6h(H-T)]:[30] A pale-yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 3 H), 3.92 (s, 3 H), 6.11 (d, J = 1.6 Hz, 1 H), 6.84 (d, J = 5.6 Hz, 1 H), 6.88 (d, J = 1.6 Hz, 1 H), 7.05 (d, J = 5.6 Hz, 1 H) ppm. ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 57.1, 58.8, 95.0, 114.7, 115.1, 116.8, 121.7, 133.9, 153.7, 157.9 ppm. IR (KBr): $\tilde{\nu}$ = 3113, 3002, 2935, 2852, 1568, 1540, 1433, 1369, 1257, 1204, 1155, 1103, 1070, 1036, 962, 926, 914, 867, 824, 692, 645, 620 cm^{-1}. HRMS (FAB): calcd. for $C_{10}H_{10}O_2S_2$ $[M]^+$ 226.0122; found 226.0123.

3,4′-Bis(hexyloxy)-2,2′-bithiophene [6i(H-T)]: A pale-yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.87–0.92 (m, 6 H), 1.31–1.35 (m, 8 H), 1.41–1.55 (m, 4 H), 1.72–1.85 (m, 4 H), 3.93 (t, J = 6.4 Hz, 2 H), 4.07 (t, J = 6.4 Hz, 2 H), 6.08 (d, J = 1.6 Hz, 1 H), 6.81 (d, J = 5.6 Hz, 1 H), 6.89 (d, J = 1.6 Hz, 1 H), 7.01 (d, J = 5.6 Hz, 1 H) ppm. ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 14.0, 22.5, 22.6, 25.6, 25.7, 29.2, 29.6, 31.5, 31.6, 70.0, 71.8, 95.3, 114.5, 115.3, 117.3, 121.4, 133.9, 152.9, 157.1 ppm. IR (KBr): $\tilde{\nu}$ = 3114, 2932, 2856, 1567, 1538, 1463, 1359, 1259, 1172, 1067, 1030, 912, 867, 826, 807, 713, 682, 639, 617 cm^{-1}. HRMS (FAB): calcd. for $C_{20}H_{30}O_2S_2$ $[M]^+$ 366.1687; found 366.1683.

3,4′-Dibutoxy-2,2′-bithiophene [6j(H-T)]:[31] A pale-yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.93–0.98 (m, 6 H), 1.45–1.52 (m, 4 H), 1.72–1.81 (m, 4 H), 3.93 (t, J = 6.4 Hz, 2 H), 4.08 (t, J = 6.4 Hz, 2 H), 6.08 (d, J = 1.6 Hz, 1 H), 6.80 (d, J = 5.6 Hz, 1 H), 6.87 (d, J = 1.6 Hz, 1 H), 7.02 (d, J = 5.6 Hz, 1 H) ppm. ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 13.8, 19.2, 31.3, 31.7, 69.7, 71.5, 95.4, 114.5, 115.3, 117.3, 121.4, 133.9, 152.9, 157.1 ppm. IR (KBr): $\tilde{\nu}$ = 3114, 2957, 2871, 1567, 1538, 1463, 1399, 1360, 1260, 1173, 1072, 1040, 867, 844, 824, 742, 714, 684, 639, 618 cm^{-1}. HRMS (FAB): calcd. for $C_{16}H_{22}O_2S_2$ $[M]^+$ 310.1061; found 310.1063.

3,4′-Bis(2-methylpropyloxy)-2,2′-bithiophene [6k(H-T)]: A pale-yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.00 (d, J = 6.8 Hz, 6 H), 1.07 (d, J = 6.8 Hz, 6 H), 2.04–2.15 (m, 2 H), 3.69 (d, J = 6.4 Hz, 2 H), 3.86 (d, J = 6.4 Hz, 2 H), 6.08 (d, J = 1.6 Hz, 1 H), 6.79 (d, J = 5.6 Hz, 1 H), 6.88 (d, J = 1.6 Hz, 1 H), 7.01 (d, J = 5.6 Hz, 1 H) ppm. ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 19.2, 19.3, 28.2, 28.7, 76.4, 78.1, 95.4, 114.5, 115.0, 117.1, 121.4, 133.9, 153.0, 157.2 ppm. IR (KBr): $\tilde{\nu}$ = 3114, 2958, 2929, 2871, 1567, 1538, 1466, 1385, 1358, 1261, 1169, 1100, 1065, 1035, 1016, 982, 916, 866, 825, 806, 687, 640, 617 cm^{-1}. HRMS (FAB): calcd. for $C_{16}H_{22}O_2S_2$ $[M]^+$ 310.1061; found 310.1045.

3,4′-Bis(cyclohexyloxy)-2,2′-bithiophene [6l(H-T)]: A pale-yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.26–1.39 (m, 6 H), 1.45–1.57 (m, 4 H), 1.60–1.69 (m, 2 H), 1.78–1.81 (m, 4 H), 1.92–2.03 (m, 4 H), 4.08 (quint, J = 4.0 Hz, 1 H), 4.22 (quint, J = 4.0 Hz, 1 H), 6.11 (d, J = 1.6 Hz, 1 H), 6.78 (d, J = 5.6 Hz, 1 H), 6.88 (d, J = 1.6 Hz, 1 H), 7.01 (d, J = 5.6 Hz, 1 H) ppm. ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 23.4, 23.8, 25.5, 25.6, 31.8, 32.0, 76.7, 79.2, 97.1, 115.2, 116.6, 118.3, 121.3, 133.8, 151.5, 155.4 ppm. IR (KBr): $\tilde{\nu}$ = 3111, 2934, 2856, 1563, 1534, 1465, 1387, 1360, 1261, 1166, 1126, 1044, 1023, 993, 951, 915, 889, 865, 822, 808, 741, 687, 645, 622 cm^{-1}. HRMS (FAB): calcd. for $C_{20}H_{26}O_2S_2$ $[M]^+$ 362.1374; found 362.1371.

3,4′-Bis(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyloxy)-2,2′-bithiophene [6m(H-T)]: A pale-yellow solid; m.p. 67–68 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.24 (t, J = 12.8 Hz, 2 H), 4.52 (t, J = 12.8 Hz, 2 H), 6.29 (d, J = 1.6 Hz, 1 H), 6.81 (d, J = 5.6 Hz, 1 H), 6.97 (d, J = 1.6 Hz, 1 H), 7.11 (d, J = 5.6 Hz, 1 H) ppm. ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 66.9 (t, J = 27.3 Hz), 68.0 (t, J = 27.3 Hz), 99.0, 110.5 (m), 110.9 (m), 114.7 (m), 115.4, 115.7 (m), 117.2, 118.0, 118.6 (m), 122.7, 133.6, 150.7, 155.2 ppm. IR (KBr): $\tilde{\nu}$ = 3113, 1568, 1535, 1458, 1415, 1360, 1235, 1202, 1146, 1099, 1052, 984, 959, 913, 847, 805, 792, 743, 707, 688, 666, 633, 609, 563, 525 cm^{-1}. HRMS (FAB): calcd. for $C_{22}H_8F_{26}O_2S_2$ $[M]^+$ 861.9551; found 861.9556.

3,4′-Bis[2-(2-methoxyethoxy)ethoxy]-2,2′-bithiophene [6n(H-T)]: A pale-yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.35 (s, 3 H), 3.36 (s, 3 H), 3.54 (m, 4 H), 3.69 (m, 4 H), 3.81 (t, J = 4.8 Hz, 2 H), 3.85 (t, J = 4.8 Hz, 2 H), 4.10 (t, J = 4.8 Hz, 2 H), 4.22 (t, J = 4.8 Hz, 2 H), 6.09 (d, J = 1.6 Hz, 1 H), 6.81 (d, J = 5.6 Hz, 1 H), 6.91 (d, J = 1.6 Hz, 1 H), 7.00 (d, J = 5.6 Hz, 1 H) ppm. ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 59.0, 69.2, 69.6, 69.9, 70.6, 70.8, 71.2, 71.8, 71.9, 95.9, 114.9, 116.1, 117.8, 121.5, 133.7, 152.5, 156.7 ppm. IR (KBr): $\tilde{\nu}$ = 3109, 2925, 2876, 1567, 1538, 1452, 1395, 1350, 1259, 1199, 1176, 1110, 1075, 987, 932, 868, 823, 714, 688, 659, 640, 621 cm^{-1}. HRMS (FAB): calcd. for $C_{18}H_{26}O_6S_2$ $[M]^+$ 402.1171; found 402.1159.

3,4′-Bis(benzyloxy)-2,2′-bithiophene [6o(H-T)]: A pale-yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.42 (s, 2 H), 5.17 (s, 2 H), 6.19 (d, J = 1.6 Hz, 1 H), 6.82 (d, J = 5.6 Hz, 1 H), 6.98 (d, J = 1.6 Hz, 1 H), 7.02 (d, J = 5.6 Hz, 1 H), 7.32–7.48 (m, 10 H) ppm. ^{13}C NMR (100.53 MHz, $CDCl_3$): δ = 72.0, 73.5, 96.6, 115.0, 116.2, 117.8, 121.6, 127.3, 127.6, 128.0, 128.1, 128.5, 133.8, 136.7, 136.8, 152.4, 156.7 ppm. IR (KBr): $\tilde{\nu}$ = 3112, 3031, 2927, 2871, 1566, 1536, 1454, 1353, 1261, 1205, 1166, 1059, 1026, 976, 912, 823, 740, 697, 640, 618 cm^{-1}.

3,4′-Di-*p*-tolyl-2,2′-bithiophene [6p(H-T)]:[32] A pale-yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.32 (s, 3 H), 2.34 (s, 3 H), 7.04 (d, J = 5.1 Hz, 1 H), 7.12–7.15 (m, 4 H), 7.20–7.28 (m, 5 H), 7.37 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 21.3, 120.0, 124.0, 125.6, 126.1, 129.1 129.2, 129.4, 130.6, 131.2, 132.8, 133.2, 136.7, 136.9, 137.2, 139.1, 142.1 ppm.

Phenyl(3-methyl-2-thienyl)iodonium Tosylate (7b-OTs):[33] A white solid; m.p. 165 °C. ^{1}H NMR (300 MHz, CD_3OD): δ = 2.33 (s, 3 H), 2.49 (s, 3 H), 7.03 (d, J = 5.1 Hz, 1 H), 7.19 (d, J = 7.2 Hz, 2 H), 7.46–7.49 (m, 2 H), 7.59–7.67 (m, 3 H), 7.83 (d, J = 5.1 Hz, 1 H), 8.05 (d, J = 7.8 Hz, 2 H) ppm. ^{13}C NMR (75.5 MHz, CD_3OD): δ = 17.5, 21.3, 98.4, 118.4, 126.9, 129.8, 131.0, 133.0, 133.1, 133.4, 135.4, 137.7, 141.6, 150.0 ppm. IR (KBr): $\tilde{\nu}$ = 3051, 1575, 1469, 1440, 1191, 1132, 1045, 1014, 991, 815, 746, 680 cm^{-1}. HRMS (FAB): calcd. for $C_{11}H_{10}IS$ $[M]^+$ 300.9548; found 300.9549.

Phenyl(3-methyl-2-thienyl)iodonium Bromide (7b-Br): A gray solid; m.p. 132 °C. ^{1}H NMR (300 MHz, CD_3OD): δ = 2.54 (s, 3 H), 7.08 (d, J = 5.4 Hz, 1 H), 7.52 (t, J = 6.9 Hz, 2 H), 7.63–7.68 (m, 1 H), 7.86 (d, J = 5.4 Hz, 1 H), 8.08 (d, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (75.5 MHz, CD_3OD): δ = 16.9, 104.2, 121.4, 129.7, 131.3, 131.4, 134.3, 135.5, 146.3 ppm. IR (KBr): $\tilde{\nu}$ = 3051, 2920, 2853, 1562, 1526, 1468, 1439, 1375, 1319, 1263, 1157, 1086, 993, 1009, 824, 748, 727, 679, 675, 650 cm^{-1}. HRMS (FAB): calcd. for $C_{11}H_{10}IS$ $[M]^+$ 300.9548; found 300.9553. $C_{11}H_{10}BrIS$ (381.07): calcd. C 34.67, H 2.65; found C 34.89, H 2.72.

3,3′,4,4′-Tetramethoxy-5-pentamethylphenyl-2,2′-bithiophene (8): A pale-yellow solid; m.p. 115–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.16 (s, 6 H), 2.23 (s, 6 H), 2.26 (s, 3 H), 3.57 (s, 3 H), 3.83 (s, 3 H), 3.85 (s, 3 H), 3.94 (s, 3 H), 6.09 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.7, 16.9, 18.5, 57.2, 59.1, 59.9, 60.1, 94.2, 116.3, 117.9, 120.6, 129.3, 132.4, 134.2, 135.5, 142.3, 144.6, 145.0, 150.4 ppm. IR (KBr): $\tilde{\nu}$ = 3111, 2933, 1556, 1520, 1477, 1388, 1308, 1276, 1255, 1204, 1156, 1127, 1088, 1066, 1037, 997, 961, 750, 695 cm^{-1}. HRMS (FAB): calcd. for $C_{23}H_{28}O_4S_2$ $[M]^+$ 432.1249; found 432.1434.

3,3′,4,4′-Tetramethoxy-5,5′-bis(pentamethylphenyl)-2,2′-bithiophene (9): A pale-yellow solid; m.p. 268–271 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.18 (s, 12 H), 2.23 (s, 12 H), 2.26 (s, 6 H), 3.56 (s, 6 H), 3.91 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.7, 16.9, 18.5, 59.1, 60.0, 116.5, 120.4, 129.4, 132.4, 134.3, 135.5, 144.1, 145.2 ppm. IR (KBr): $\tilde{\nu}$ = 2935, 1557, 1474, 1381, 1263, 1208, 1160, 1040, 997, 971, 765, 747, 706 cm^{-1}. HRMS (FAB): calcd. for $C_{34}H_{42}O_4S_2$ $[M]^+$ 578.2525; found 578.2522.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of the coupling products.

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