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Synthesis of functionalized thiophenes and oligothiophenes by selective and iterative cross-coupling reactions using indium organometallics†

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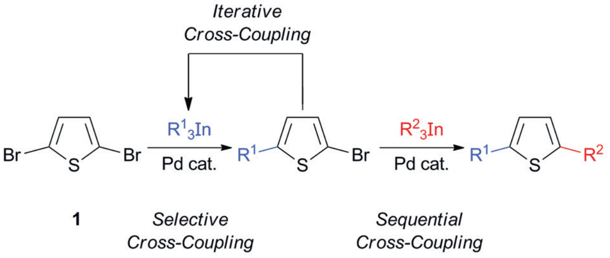
The synthesis of unsymmetrical 2,5-disubstituted thiophenes by selective and sequential palladium-catalyzed cross-coupling reactions of indium organometallics with 2,5-dibromothiophene is reported. Following an iterative coupling sequence, α-oligothiophenes were synthesized in good yields and with high atom economy.

Introduction

The thiophene ring is present in a wide variety of natural products and pharmaceuticals,[1] and functionalized thiophenes such as α-linked linear oligothiophenes are among the most promising polymers for the development of electronic devices such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs) and solar cells.[2] The synthesis of linear α-coupled thiophenes is usually performed from 2,5-dihalothiophenes by two-fold cross-coupling reactions to afford symmetrically α,α′-disubstituted oligothiophenes.[3] Unfortunately, there is a low differentiation between the two reactive positions and a second cross-coupling can occur readily, limiting the structural diversity provided by selective cross-coupling reactions.[4] To avoid this limitation, the synthesis of thiophenes furnished with two different halogens has been pursued to perform chemoselective cross-coupling reactions.[5]

In recent years we have shown that indium organometallics are useful reagents in metal-catalyzed cross-coupling reactions.[6] Besides the high efficiency, versatility, and selectivity in cross-coupling reactions, triorganoindium reagents (R_3In) are particularly effective in the synthesis of functionalized heterocyclic compounds[7] and highly selective in coupling reactions with 3,4-dihalomaleimides.[8] Herein, we report the novel use of indium organometallics in selective and iterative cross-coupling reactions applied to the synthesis of functionalized thiophenes and oligothiophenes. Using the commercially available 2,5-dibromothiophene as an electrophile, selective reactions should allow the successive incorporation of organic residues to afford non-symmetrically α,α′-disubstituted thiophenes and also enable iterative coupling reactions, after the first monocoupling reaction, by metallation of the remaining bromine atom and further coupling processes (Scheme 1).



Scheme 1 Iterative and selective cross-coupling reactions using 2,5-dibromothiophene (**1**).

Results and discussion

Our research started studying the reactivity of triorganoindium reagents in palladium-catalyzed cross-coupling with 2,5-dibromothiophene (**1**). Based on our experience in aryl–aryl coupling with indium reagents, $PdCl_2(dppf)$ complex was selected as palladium source.[7] In this way, the reaction of **1** with tri-(2-thienyl)indium (40 mol%), prepared in solution from 2-bromothiophene, in the presence of $PdCl_2(dppf)$ (4 mol%) provided the bromobithiophene **2a** selectively in 78% yield as the only isolated product, the dicoupling product being undetected (Table 1, entry 1). Analogously, the reaction using tri(benzo[*b*]thien-2-yl)-indium also gave the monocoupling product **2b** in 77% yield in a similar reaction time (entry 2). The growing interest of mixed heterocyclic polymers,[9] led us to try the reaction with a different heteroarylindium reagent. Under the same conditions, we found that the reaction of tri(2-furanyl)indium with **1** gave the cross-coupling product **2c** selectively in good yield (70%, entry 3). Since α-styrylthiophenes have been proposed as materials for new organic electronic devices,[10] we also assayed the monocoupling reaction with the conjugated alkenylindium derivative from

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† Electronic supplementary information (ESI) available: Copies of NMR spectra for compounds prepared. See DOI: 10.1039/c2ob25123j

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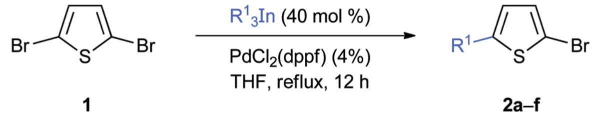
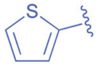
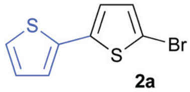
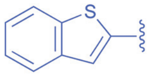
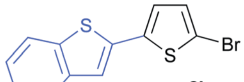
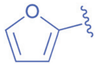
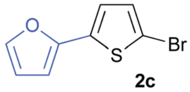
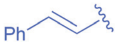
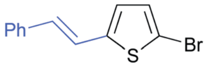
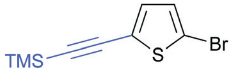
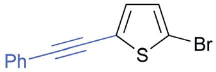
Table 1 Selective cross-coupling reactions of triorganoindium reagents with 2,5-dibromothiophene (**1**)



Entry	R^1	Product	Yield[a] (%)
1		 **2a**	78
2		 **2b**	77
3		 **2c**	70
4		 **2d**	55
5		 **2e**	53[b,c]
6		 **2f**	52[b,c]

[a] Isolated yield. [b] Using $Pd(PPh_3)_4$ (4 mol%). [c] The dicoupling product was isolated as byproduct (<15%).

β-bromostyrene, giving rise to the α-styrylthiophene **2d** in 55% yield (entry 4). Additionally, we also turned our interest towards oligoethynylthiophenes despite their synthesis having found important limitations.[11] Initially, the reaction of tri(trimethylsilylethynyl)indium and tri(phenylethynyl)indium with **1** using $PdCl_2(dppf)$ (4 mol%) afforded the monocoupling products **2e** and **2f** in modest yields (35–40% yield). However, these results were improved using $Pd(PPh_3)_4$ as palladium source (Table 1, entries 5 and 6), although in this case some dicoupling product was obtained as a byproduct (<15%). All the indium organometallics were prepared as a THF solution from the corresponding lithium derivatives using $InCl_3$ and used without isolation. In general, the reactivity and selectivity shown by the triorganoindium reagents in these palladium-catalyzed coupling reactions is comparable to or higher than other organometallics, highlighting the atom economy, since only 40 mol% of the organoindium reagent is necessary.

With the 2-bromothiophenes **2a–f** in hand, we devised that these monocoupling products can play a dual role in further transformations: they can be used as new electrophiles in sequential coupling reactions or as indium nucleophiles (after metallation and transmetallation) in iterative coupling processes. In order to demonstrate the efficiency of indium organometallics in the sequential synthesis of non-symmetrical thiophenes we tried aryl, heteroaryl and ethynylindium organometallics as second nucleophilic counterparts. Thus, the reaction of triphenylindium (50 mol%) with 5-bromo-2,2′-bithiophene (**2a**) using the same catalytic system as for the first coupling [$PdCl_2(dppf)$, (4 mol%)] afforded the corresponding non-symmetrically substituted thiophene **3a** in excellent 96% yield after 12 h at reflux (Table 2, entry 1). On the other hand, the reaction of **2a** with trialkynylindium reagents afforded the corresponding alkynylbithiophenes **3b** and **3c** in good yields (73% and 82%, respectively, entries 2 and 3). Interestingly, the bithiophene **3b** has shown antiviral activity[12] and the alcohol derived from the desilylation of **3c** has been reported as an antifungal metabolite.[13] Under the same conditions, the reaction of tri(2-thienyl)indium with **2b** afforded the trithienyl derivative **4** in 80% yield (entry 4). In a similar manner, 2-bromo-5-ethynylthiophenes **2e** and **2f** reacted with thienylindium derivatives providing a new series of bithienyl analogs **5** and **6a** (95% and 63% yield, respectively, entries 5 and 6). Compound **5** is a key precursor in the synthesis of arctic acid, a natural product that is of pharmacological interest.[14] As previously, we were also interested in the introduction of other heteroaryl groups in the second coupling. In this context, the reaction of the 2-furanylindium reagent with **2f** under the standard conditions gave **6b** in a good 75% yield (entry 7). Overall, these results demonstrate the efficiency and versatility of indium organometallics in the selective and sequential cross-coupling reactions for the synthesis of non-symmetrical 2,5-disubstituted thiophenes.

The next step in our study about the selectivity of triorganoindium reagents in the coupling reactions with 2,5-dibromothiophene involved the assessment of monocoupling products **2** in iterative cross-coupling reactions. The application of iterative processes is a powerful strategy that is commonly used in biosynthesis and has been recently extended to cross-coupling reactions,[15,16] and to the synthesis of oligothiophenes.[17] These sequences start with a molecule that contains a reactive functional group (“on”) and other groups that are unreactive or protected (“off”) to suppress uncontrolled polymerizations. After a selective coupling through the reactive group, the unreactive one is activated or deprotected (“on”) to repeat the coupling sequence. The high selectivity obtained in the first coupling reactions reveals compounds **2** as indium pronucleophiles, thus avoiding the protection–deprotection steps usually required in iterative sequences.

The first step in these iterative reactions involved the monocoupling reactions to afford **2a** and **2b** (Scheme 2). With these compounds in hand, the activation step was carried out by lithium–bromine exchange with *n*-BuLi and subsequent transmetallation with $InCl_3$ to give the corresponding thienylindium reagents that were used without isolation. A new selective monocoupling of these compounds with **1**, in the presence of $PdCl_2(dppf)$ (4%) as palladium source, afforded **7a** and **7b** in good yields (73% and 85%, respectively). Gratifyingly, a new iteration was also possible and proceeded in good yields to provide, after activation and cross-coupling, compounds **8a** and **8b** in satisfactory yields (59% and 50%, respectively).

Palladium-catalyzed cross-coupling reactions of an excess (70 mol%) of triorganoindium reagents with 2,5-dibromothiophene afforded the dicoupling products in good yields. As an example of these twofold cross-coupling reactions, we used the thienylindium reagents in iterative coupling reactions for the synthesis of symmetrically substituted α-oligothiophenes.

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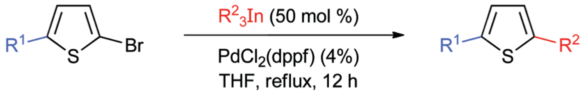
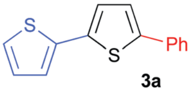
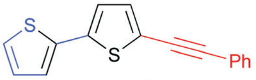
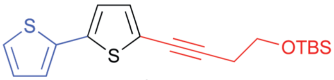
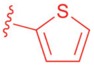
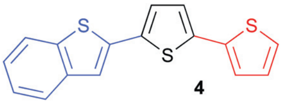
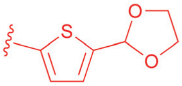
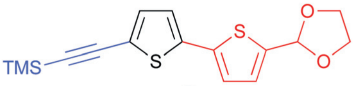
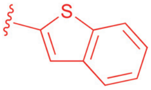
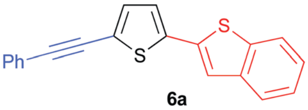
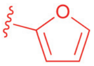
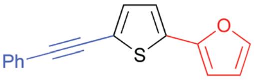
Table 2 Synthesis of non-symmetrical 2,5-disubstituted thiophenes by sequential cross-coupling reactions with triorganoindium reagents



2a–f **3–6**

Entry	2	R^2	Product	Yield[a] (%)
1	**2a**	Ph	 **3a**	96
2	**2a**		 **3b**	73
3	**2a**		 **3c**	82
4	**2b**		 **4**	80
5	**2e**		 **5**	95
6	**2f**		 **6a**	63
7	**2f**		 **6b**	75

[a] Isolated yield.

Interestingly, the reaction of the indium reagent derived from 2-bromobithiophene (**2a**) with (**1**), in the presence of $PdCl_2$(dppf), afforded α-quinquethiophene (**9a**, Scheme 3) in 66% yield after refluxing for 12 h. Analogously, the reaction of the indium reagent obtained from **2b** with **1** afforded the benzothienyl end-capped oligothiophene **9b** in 65% yield. These examples demonstrate the utility of indium organometallics towards the synthesis of α-oligothiophenes following an iterative-twofold coupling sequence.

Conclusions

In conclusion, we have studied the usefulness of indium organometallics in selective palladium-catalyzed cross-coupling reactions with 2,5-dibromothiophene. The reactions proceed in good yields and with high selectivity, and the monocoupling products were used further both as electrophiles in sequential cross-coupling syntheses and as pronucleophiles in iterative coupling sequences. These examples highlight the synthetic utility of triorganoindium reagents in cross-coupling reactions and include the syntheses of α-coupled oligothiophene structures by iterative coupling reactions. Further applications of this methodology in materials science are currently under investigation and the results will be published in due course.

Experimental

General methods

All reactions were carried out in flame dried glassware, under an argon atmosphere, using standard gastight syringes, cannulae, and septa. Tetrahydrofuran (THF) was dried by distillation from the sodium ketyl of benzophenone. Reaction temperatures refer to external bath temperatures. 1-[(*tert*-Butyldimethylsilyl)oxy]-3-butyne[18] and 2-(5-bromothiophen-2-yl)-1,3-dioxolane[19] were prepared according to the literature procedures. Butyllithium and phenyllithium were titrated prior to use. All other commercially available reagents were used as received. Organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated using a rotary evaporator at aspirator pressure. Reactions were monitored by TLC using precoated silica gel plates (Alugram® Xtra SIL G/UV_{254}, 0.20 mm thick) using UV light as visualizing agent and ethanolic phosphomolybdic acid as developing agent. Flash column chromatography was performed using 230–400 mesh

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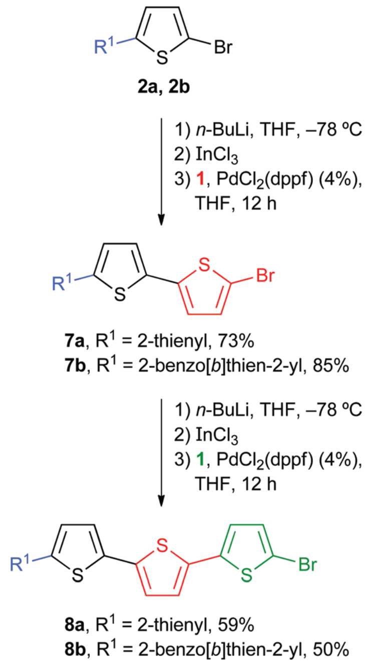
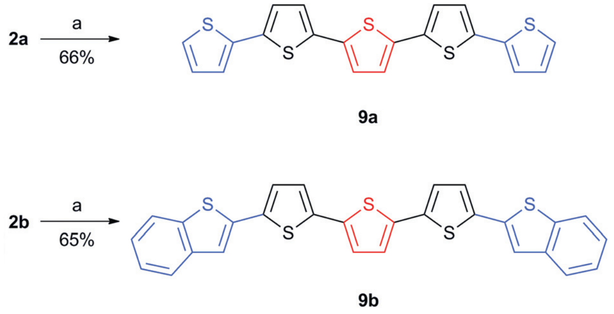


Scheme 2 Iterative cross-coupling reactions with triorganoindium reagents.



Scheme 3 Twofold cross-coupling reactions with triorganoindium reagents. *Reagents and conditions*: (a) *n*-BuLi, THF, −78 °C, then $InCl_3$, −78 °C to rt, then **1**, $PdCl_2(dppf)$ (4 mol%), THF, 80 °C, 12 h.

silica gel packed in glass columns. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 MHz or 500 MHz for ^1H and 75 MHz or 125 MHz for ^{13}C, at ambient temperature, and calibrated to the solvent peak. DEPT data was used to assign carbon types. Mass spectra were obtained with EI ionization at 70 eV. Melting points are uncorrected.

Triorganoindium reagents

Triorganoindium compounds were prepared according to previously published methods[7b] by treatment of the corresponding organolithium reagents (3 equiv, ∼0.5 M in dry THF) with a solution of $InCl_3$ (1.1 equiv, ∼0.05 M in dry THF) at −78 °C and warming to room temperature and were used without isolation.

Phenylacetylene, trimethylsilylacetylene and furan were lithiated by treatment with *n*-BuLi (1 equiv) at −78 °C and warming to room temperature. Other organolithium reagents were prepared by metal–halogen exchange reactions with *n*-BuLi (1 equiv) at −78 °C in dry THF.

General procedure for the palladium-catalyzed cross-coupling reactions

In a Schlenk tube filled with argon, to a solution of the electrophile (0.5 mmol) and $PdCl_2(dppf)$ (0.02 mmol) in dry THF (2 mL), a solution of R_3In [∼0.05 M in THF, 0.2 mmol for the selective monocoupling (Table 1 and Scheme 2), 0.25 mmol for the sequential coupling reactions (Table 2) or 0.35 mmol for the twofold coupling reactions (Scheme 3)] was added, and the resulting mixture stirred at 80 °C for 12 h. The reaction was quenched by the addition of a few drops of MeOH and the mixture filtered through a short pad of Celite®, washing the solids with CH_2Cl_2 (15 mL). The filtrate was concentrated *in vacuo* and the residue was purified by flash chromatography to afford, after concentration and high vacuum drying, the corresponding cross-coupling product, except for compounds **9a** and **9b**, which were purified by crystallization after the filtration.

5-Bromo-2,2′-bithiophene (2a).[14a] Pale yellow solid (96 mg, 78%); mp 33–34 °C (MeOH) (lit.[14a] 32–33 °C); ν_{max}/cm^{-1} (ATR) 3070, 2923, 1581, 1504 and 1199; δ_H (300 MHz, $CDCl_3$) 6.93 (1 H, d, *J* 3.8), 6.99 (1 H, d, *J* 3.8), 7.03 (1 H, dd, *J* 5.1, 3.6), 7.13 (1 H, dd, *J* 3.6, 1.1) and 7.24 (1 H, dd, *J* 5.1, 1.1); δ_C (75 MHz, $CDCl_3$) 110.9 (C), 123.8 (CH), 124.1 (CH), 124.8 (CH), 127.9 (CH), 130.6 (CH), 136.4 (C) and 138.9 (C); MS (EI) *m*/*z* 246 (M^+, ^{81}Br, 100%), 244 (M^+, ^{79}Br, 98), 165 (45); HRMS (EI) *m*/*z* 243.9008 (M^+). Calc. for $C_8H_5S_2Br$: 243.9011.

2-(5-Bromothiophen-2-yl)benzo[*b*]thiophene (2b). Yellow solid (114 mg, 77%); mp 128–129 °C (CH_2Cl_2); Anal. Found: C, 49.16; H, 2.03. Calc. for $C_{12}H_7S_2Br$: C, 48.82; H, 2.39; ν_{max}/cm^{-1} (ATR) 3054, 2923, 1499, 1438, 1417, 819 and 792; δ_H (300 MHz, $CDCl_3$) 7.01 (1 H, d, *J* 3.9), 7.04 (1 H, d, *J* 3.9), 7.29–7.38 (3 H, m) and 7.71–7.79 (2 H, m); δ_C (75 MHz, $CDCl_3$) 112.2 (C), 120.0 (CH), 122.1 (CH), 123.6 (CH), 124.7 (CH), 124.8 (CH), 125.1 (CH), 130.8 (CH), 136.2 (C), 138.9 (C), 139.0 (C) and 140.1 (C); MS (EI) *m*/*z* 296 (M^+, ^{81}Br, 100%), 294 (M^+, ^{79}Br, 97), 171 (25); HRMS (EI) *m*/*z* 293.9167 (M^+). Calc. for $C_{12}H_7S_2Br$: 293.9167.

2-(5-Bromo-2-thienyl)furan (2c).[20] Colorless oil (80 mg, 70%); ν_{max}/cm^{-1} (ATR) 3112, 2924, 2852, 1464, 1152, 988 and 789; δ_H (300 MHz, $CDCl_3$) 6.44 (1 H, dd, *J* 3.4, 1.8), 6.47 (1 H, dd, *J* 3.5, 0.8), 6.98 (2 H, s) and 7.40 (1 H, dd, *J* 1.8, 0.8); δ_C (75 MHz, $CDCl_3$) 105.3 (CH), 111.1 (C), 111.7 (CH), 122.5 (CH), 130.5 (CH), 135.2 (C), 141.9 (CH) and 148.4 (C); MS (EI) *m*/*z* 230 (M^+, ^{81}Br, 33%), 228 (M^+, ^{79}Br, 31), 77 (100); HRMS (EI) *m*/*z* 227.9238 (M^+). Calc. for C_8H_5OSBr: 227.9239.

(*E*)-2-Bromo-5-styrylthiophene (2d).[10] Orange solid (67 mg, 55%); mp 97–99 °C (hexanes) (lit.[10] 96–98 °C); ν_{max}/cm^{-1} (ATR) 3023, 2921, 2852, 2362, 1430, 949 and 797; δ_H (300 MHz, $CDCl_3$) 6.80 (1 H, d, *J* 4.0), 6.82 (1 H, d, *J* 16), 6.95 (1 H, d, *J* 3.8), 7.10 (1 H, d, *J* 16.0) and 7.23–7.46 (5 H, m); δ_C (75 MHz, $CDCl_3$) 111.1 (C), 121.2 (CH), 126.2 (CH), 126.3 (2 × CH), 127.9 (CH), 128.7 (2 × CH), 128.8 (CH), 130.5 (CH), 136.6 (C) and 144.5 (C); MS (EI) *m*/*z* 266 (M^+, ^{81}Br, 100%),

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264 (M^+, ^{79}Br, 98); HRMS (EI) *m/z* 263.9605 (M^+). Calc. for $C_{12}H_9SBr$: 263.9603.

2-Bromo-5-[2-(trimethylsilyl)ethynyl]thiophene (2e).[5a] Yellow oil (69 mg, 53%); ν_{max}/cm^{-1} (ATR) 3070, 2920, 2349, 1504 and 1443; δ_H (300 MHz, $CDCl_3$) 0.24 (9 H, s), 6.90 (1 H, d, *J* 3.9) and 6.96 (1 H, d, *J* 3.9); δ_C (75 MHz, $CDCl_3$) −0.30 (3 × CH_3), 96.4 (C), 100.1 (C), 113.1 (C), 129.8 (CH), 132.3 (C) and 132.9 (CH); MS (EI) *m/z* 260 (M^+, ^{81}Br, 38%), 258 (M^+, ^{79}Br, 35), 245 (M − CH_3, ^{81}Br, 100), 243 (M − CH_3, ^{79}Br, 96); HRMS (EI) *m/z* 257.9521 (M^+). Calc. for $C_9H_{11}SiSBr$: 257.9529.

2-Bromo-5-(phenylethynyl)thiophene (2f).[21] White solid (68 mg, 52%); mp 73–74 °C (hexanes) (lit.[21] 72–74 °C); Anal. Found: C, 54.84; H, 2.30. Calc. for $C_{12}H_7SBr$: C, 54.77; H, 2.68; ν_{max}/cm^{-1} (ATR) 3078, 3055, 2359, 2339, 1754, 1597, 1526 and 1442; δ_H (300 MHz, $CDCl_3$) 6.97 (1 H, d, *J* 3.9), 7.03 (1 H, d, *J* 3.9), 7.35–7.38 (3 H, m) and 7.50–7.53 (2 H, m); δ_C (75 MHz, $CDCl_3$) 81.6 (C), 94.0 (C), 113.1 (C), 122.5 (C), 125.1 (C), 128.4 (2 × CH), 128.7 (CH), 130.1 (CH), 131.4 (2 × CH) and 132.2 (CH); MS (EI) *m/z* 264 (M^+, ^{81}Br, 100%), 262 (M^+, ^{79}Br, 98), 183 (33); HRMS (EI) *m/z* 261.9445 (M^+). Calc. for $C_{12}H_7SBr$: 261.9446.

5-Phenyl-2,2′-bithiophene (3a).[22] Yellow solid (117 mg, 96%); mp 119–121 °C (hexanes) (lit.[22] 120–121 °C); ν_{max}/cm^{-1} (ATR) 3057, 2921, 1597, 1487, 1457 and 886; δ_H (300 MHz, $CDCl_3$) 7.03 (1 H, dd, *J* 5.1, 3.7), 7.15 (1 H, d, *J* 3.7), 7.20–7.23 (3 H, m), 7.30 (1 H, br d, *J* 7.4), 7.38 (2 H, dd, *J* 7.6, 1.4) and 7.61 (2 H, dd, *J* 7.4, 1.1); δ_C (75 MHz, $CDCl_3$) 123.6 (CH), 123.7 (CH), 124.4 (CH), 124.6 (CH), 125.6 (2 × CH), 127.6 (CH), 127.8 (CH), 128.9 (2 × CH), 134.1 (C), 136.7 (C), 137.4 (C) and 143.1 (C); MS (EI) *m/z* 242 (M^+, 55%); HRMS (EI) *m/z* 242.0215 (M^+). Calc. for $C_{14}H_{10}S_2$: 242.0218.

5-(2-Phenylethynyl)-2,2′-bithiophene (3b).[23] Yellow solid (97 mg, 73%); mp 91–92 °C (hexanes) (lit.[23] 89–90 °C); ν_{max}/cm^{-1} (ATR) 3054, 2920, 2201, 1441 and 802; δ_H (300 MHz, $CDCl_3$) 7.04 (1 H, dd, *J* 5.1, 3.6), 7.09 (1 H, d, *J* 3.8), 7.18–7.22 (2 H, m), 7.25 (1 H, dd, *J* 5.2, 1.1), 7.34–7.39 (3 H, m) and 7.51–7.54 (2 H, m); δ_C (75 MHz, $CDCl_3$) 82.6 (C), 94.1 (C), 122.0 (C), 122.9 (C), 123.6 (CH), 124.2 (CH), 125.0 (CH), 128.0 (CH), 128.4 (2 × CH), 128.5 (CH), 131.4 (2 × CH), 132.8 (CH), 136.8 (C) and 138.9 (C); MS (EI) *m/z* 266 (M^+, 100%); HRMS (EI) *m/z* 266.0218 (M^+). Calc. for $C_{16}H_{10}S_2$: 266.0218.

5-[4-[(*tert*-Butyldimethylsilyl)oxy]but-1-yn-1-yl]-2,2′-bithiophene (3c). Pale yellow oil (143 mg, 82%); Anal. Found: C, 62.38; H, 6.79. Calc. for $C_{18}H_{24}OSiS_2$: C, 62.02; H, 6.94; ν_{max}/cm^{-1} (ATR) 2953, 2927, 2855, 1470, 1251, 1101 and 834; δ_H (300 MHz, $CDCl_3$) 0.13 (6 H, s), 0.95 (9 H, s), 2.68 (2 H, t, *J* 7.0), 3.84 (2 H, t, *J* 7.0), 7.00–7.05 (3 H, m), 7.17 (1 H, dd, *J* 3.6, 1.1) and 7.23 (1 H, dd, *J* 5.1, 1.1); δ_C (75 MHz, $CDCl_3$) −5.2 (2 × CH_3), 18.4 (C), 24.2 (CH_2), 25.9 (3 × CH_3), 61.7 (CH_2), 74.7 (C), 92.5 (C), 122.7 (C), 123.3 (CH), 124.0 (CH), 124.5 (CH), 127.9 (CH), 132.0 (CH), 136.9 (C) and 137.7 (C); MS (EI) *m/z* 348 (M^+, 10%), 291 (M − C_4H_9, 100), 217 (M − C_4H_9OSi, 23); HRMS (EI) *m/z* 348.1019 (M^+). Calc. for $C_{18}H_{24}OSiS_2$: 348.1032.

2-[(2,2′-Bithiophen)-5-yl]benzo[*b*]thiophene (4). Pale yellow solid (119 mg, 80%); mp 186–187 °C (hexanes); Anal. Found: C, 64.78; H, 3.75. Calc. for $C_{16}H_{10}S_3$: C, 64.39; H, 3.38; ν_{max}/cm^{-1} (ATR) 3063, 2921, 2851, 1449, 820 and 794; δ_H (300 MHz, $CDCl_3$) 7.04 (1 H, dd, *J* 5.1, 3.6), 7.1 (1 H, d, *J* 3.6), 7.20 (1 H, d, *J* 3.7), 7.23 (1 H, dd, *J* 5.8, 1.1), 7.31–7.40 (3 H, m), 7.50 (1 H, br s) and 7.80–7.81 (2 H, m); δ_C (75 MHz, $CDCl_3$) 119.6 (CH), 121.4 (CH), 122.1 (CH), 123.4 (CH), 124.4 (CH), 124.6 (CH), 124.7 (CH), 124.8 (CH), 125.7 (CH), 127.9 (CH), 136.1 (C), 136.9 (C), 137.4 (C), 139.1 (C), 139.4 (C) and 140.3 (C); MS (EI) *m/z* 298 (M^+, 100%); HRMS (EI) *m/z* 297.9935 (M^+). Calc. for $C_{16}H_{10}S_3$: 297.9939.

5-(1,3-Dioxolan-2-yl)-5′-[2-(trimethylsilyl)ethynyl]-2,2′-bithiophene (5). Yellow solid (159 mg, 95%); mp 72–73 °C (hexanes); Anal. Found: C, 57.48; H, 5.35. Calc. for $C_{16}H_{18}O_2SiS_2$: C, 57.45; H, 5.42; ν_{max}/cm^{-1} (ATR) 2964, 2882, 2145, 1378, 1247, 1197 and 836; δ_H (300 MHz, $CDCl_3$) −0.30 (9 H, s), 4.03 (2 H, dd, *J* 4.6, 2.6), 4.13 (2 H, dd, *J* 4.6, 2.6), 6.08 (1 H, s), 7.00 (1 H, d, *J* 3.8), 7.06 (2 H, s) and 7.12 (1 H, d, *J* 3.8); δ_C (75 MHz, $CDCl_3$) −0.17 (3 × CH_3), 65.3 (2 × CH_2), 97.3 (C), 100.1 (CH), 122.2 (C), 123.5 (CH), 123.7 (CH), 126.2 (C), 126.9 (CH), 133.4 (CH), 137.6 (C), 138.6 (C) and 141.4 (C); MS (EI) *m/z* 334 (M^+, 100%), 262 (M − C_3H_9Si, 28); HRMS (EI) *m/z* 334.0514 (M^+). Calc. for $C_{16}H_{18}O_2SiS_2$: 334.0512.

2-[5-(Phenylethynyl)thiophen-2-yl]benzo[*b*]thiophene (6a). Yellow solid (100 mg, 63%); mp 163–164 °C (hexanes); Anal. Found: C, 75.58; H, 3.74. Calc. for $C_{20}H_{12}S_2$: C, 75.91; H, 3.82; ν_{max}/cm^{-1} (ATR) 3049, 2921, 2199, 1441, 791 and 740; δ_H (500 MHz, $CDCl_3$) 7.20 (1 H, d, *J* 3.8), 7.23 (1 H, d, *J* 3.8), 7.32–7.40 (5 H, m), 7.43 (1 H, br s), 7.54–7.56 (2 H, m) and 7.75–7.84 (2 H, m); δ_C (125 MHz, $CDCl_3$) 82.5 (C), 94.6 (C), 120.3 (CH), 122.2 (CH), 123.6 (CH), 124.8 (CH), 124.82 (CH), 124.83 (CH), 124.9 (CH), 124.92 (CH), 128.4 (CH), 128.6 (CH), 131.4 (CH), 132.8 (CH), 136.5 (C), 137.2 (C), 138.7 (C), 139.2 (C), 139.5 (C) and 140.2 (C); MS (EI) *m/z* 316 (M^+, 100%); HRMS (EI) *m/z* 316.0377 (M^+). Calc. for $C_{20}H_{12}S_2$: 316.0375.

2-[5-(Phenylethynyl)thiophen-2-yl]furan (6b). Yellow oil (94 mg, 75%); Anal. Found: C, 76.39; H, 4.25. Calc. for $C_{16}H_{10}OS$: C, 76.77; H, 4.03; ν_{max}/cm^{-1} (ATR) 3079, 2924, 2853, 2201, 1805, 1441, 1014 and 975; δ_H (500 MHz, $CDCl_3$) 6.48 (1 H, dd, *J* 3.4, 1.8), 6.56 (1 H, dd, *J* 3.4, 0.7), 7.15 (1 H, d, *J* 3.8), 7.22 (1 H, d, *J* 3.8), 7.36–7.39 (3 H, m), 7.44 (1 H, dd, *J* 1.8, 0.7) and 7.53–7.55 (2 H, m); δ_C (125 MHz, $CDCl_3$) 82.7 (C), 94.1 (C), 105.9 (CH), 111.9 (CH), 121.8 (C), 122.3 (CH), 122.9 (C), 128.4 (2 × CH), 128.5 (CH), 131.4 (2 × CH), 132.7 (CH), 135.0 (C), 142.1 (CH) and 148.9 (C); MS (EI) *m/z* 250 (M^+, 100%); HRMS (EI) *m/z* 250.0445 (M^+). Calc. for $C_{16}H_{10}OS$: 250.0447.

5-Bromo-2,2′:5′,2″-terthiophene (7a).[24] Yellow solid (120 mg, 73%); mp 140–141 °C (hexanes) (lit.[24] 141–142 °C); ν_{max}/cm^{-1} (ATR) 3067, 2923, 2852, 1499, 1426, 832 and 789; δ_H (300 MHz, $CDCl_3$) 6.92 (1 H, d, *J* 3.8), 6.98 (1 H, d, *J* 3.8), 7.01–7.09 (3 H, m), 7.18 (1 H, dd, *J* 3.6, 1.0) and 7.24 (1 H, dd, *J* 5.1, 1.1); δ_C (75 MHz, $CDCl_3$) 111.0 (C), 123.7 (CH), 123.9

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(CH), 124.3 (CH), 124.6 (CH), 124.7 (CH), 127.9 (CH), 130.7 (CH), 135.1 (C), 136.7 (C), 136.8 (C) and 138.6 (C); MS (EI) *m*/*z* 328 (M^+, ^{81}Br, 100%), 326 (M^+, ^{79}Br, 97), 248 (M − Br, 10); HRMS (EI) *m*/*z* 325.8889 (M^+). Calc. for $C_{12}H_7S_3Br$: 325.8888.

2-[5′-Bromo-(2,2′-bithiophen)-5-yl]benzo[*b*]thiophene (7b).[25] Yellow solid (160 mg, 85%); mp 130–132 °C (THF); ν_{max}/cm^{-1} (ATR) 3065, 2924, 2853 and 817; δ_H (300 MHz, $CDCl_3$) 6.95 (1 H, d, *J* 3.9), 7.00 (1 H, d, *J* 3.9), 7.05 (1 H, d, *J* 3.8), 7.18 (1 H, d, *J* 3.8), 7.28–7.38 (2 H, m), 7.39 (1 H, s) and 7.71–7.83 (2 H, m); δ_C (75 MHz, $CDCl_3$) 111.4 (C), 120.0 (CH), 122.2 (CH), 123.5 (CH), 124.0 (CH), 124.65 (CH), 124.70 (CH), 124.8 (CH), 125.7 (CH), 130.8 (CH), 136.2 (C), 136.6 (C), 138.4 (C), 139.1 (C), 140.2 (C) and 140.3 (C); MS (EI) *m*/*z* 378 (M^+, ^{81}Br, 100%), 376 (M^+, ^{79}Br, 98), 298 (M − Br, 22), 216 (M − C_4H_2SBr, 65); HRMS (EI) *m*/*z* 375.9041 (M^+). Calc. for $C_{16}H_9S_3Br$: 375.9044.

5-Bromo-2,2′:5′,2″:5″,2‴-quaterthiophene (8a).[26] Yellow solid (121 mg, 59%); mp 225–227 °C (CH_2Cl_2) (lit.[26] 226–227 °C); ν_{max}/cm^{-1} (ATR) 2955, 2922, 2852, 1728, 1455, 1284 and 789; δ_H (500 MHz, $CDCl_3$) 6.92 (1 H, d, *J* 3.9), 6.98 (1 H, d, *J* 3.9), 7.01–7.10 (5 H, m), 7.18 (1 H, dd, *J* 3.6, 1.1) and 7.23 (1 H, dd, *J* 5.1, 3.6); δ_C (125 MHz, $CDCl_3$) 111.1 (C), 123.8 (CH), 123.9 (CH), 124.2 (CH), 124.4 (CH), 124.5 (CH), 124.62 (CH), 124.66 (CH), 127.9 (CH), 130.7 (CH), 135.1 (C), 135.6 (C), 136.4 (C), 136.6 (C), 136.9 (C) and 138.5 (C); MS (EI) *m*/*z* 410 (M^+, ^{81}Br, 100%), 408 (M^+, ^{79}Br, 97); HRMS (EI) *m*/*z* 407.8767 (M^+). Calc. for $C_{16}H_9S_4Br$: 407.8765.

2-[5″-Bromo-(2,2′:5′,2″-terthiophen)-5-yl]benzo[*b*]thiophene (8b). Orange solid (115 mg, 50%); mp 190–192 °C (CH_2Cl_2); ν_{max}/cm^{-1} (ATR) 3065, 2920, 2851, 1731, 1517, 1453, 1426 and 822; δ_H (500 MHz, THF-d_8) 7.10 (1 H, dd, *J* 7.1, 3.8), 7.19–7.21 (1 H, m), 7.24–7.26 (2 H, m), 7.32–7.44 (4 H, m), 7.55 (1 H, br s), 7.77–7.80 (1 H, m) and 7.83–7.87 (1 H, m); MS (EI) *m*/*z* 460 (M^+, ^{81}Br, 20%), 458 (M^+, ^{79}Br, 18), 380 (M − Br, 100); HRMS (EI) *m*/*z* 457.8921 (M^+). Calc. for $C_{20}H_{11}S_4Br$: 457.8921.

2,2′:5′,2″:5″,2‴:5‴,2⁗-Quinquethiophene (9a).[27] Orange solid (136 mg, 66%); mp 258–259 °C (toluene) (lit.[27] 256–257 °C); ν_{max}/cm^{-1} (ATR) 3085, 3065, 1496, 1449, 1426, 1068, 1049, 831 and 790; δ_H (300 MHz, $CDCl_3$) 7.03 (2 H, dd, *J* 5.1, 3.6), 7.08 (6 H, s), 7.18 (2 H, dd, *J* 3.6, 1.1) and 7.23 (2 H, dd, *J* 5.1, 1.1); MS (EI) *m*/*z* 412 (M^+, 100%); HRMS (EI) *m*/*z* 411.9539 (M^+). Calc. for $C_{20}H_{12}S_5$: 411.9537.

5,5″-Bis(benzo[*b*]thiophen-2-yl)-2,2′:5′,2″-terthiophene (9b).[25] Orange solid (toluene) (166 mg, 65%); ν_{max}/cm^{-1} (ATR) 3056, 2854, 1561, 1438, 817 and 742; δ_H (300 MHz, $CDCl_3$) 7.19–7.24 (2 H, m), 7.30–7.39 (8 H, m), 7.52 (2 H, br s) and 7.71–7.83 (4 H, m); MS (EI) *m*/*z* 512 (M^+, 17%), 429 (M − C_4H_3S, 20), 298 (100); HRMS (EI) *m*/*z* 511.9834 (M^+). Calc. for $C_{28}H_{16}S_5$: 511.9850.

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