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Synthesis of Fluorene-Based Oligomeric Organoboron Reagents via Kumada, Heck, and Stille Cross-Coupling Reactions

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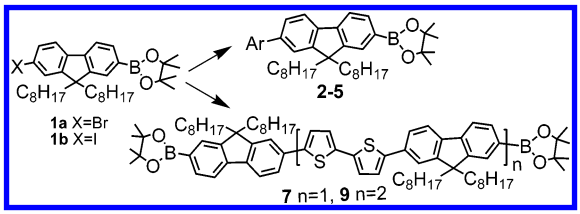

Boronic pinacol ester group is not reactive in Kumada, Heck and Stille coupling reaction conditions. Fluorene-based sophisticated organoboron compounds were synthesized by means of Palladium catalyzed Kumada, Heck and Stille cross-coupling reactions from halofluorenyl boronic esters.

Conjugated materials represent one of the most investigated classes of advanced materials in recent years because of their potential applications in electronics, photonics, and optoelectronics.[1] In contrast to conjugated polymers, monodisperse conjugated oligomers (MCOs) are characterized by well-defined structures and superior chemical purity.[1a−c] These intrinsic features are imperative for establishment of structure−property relationship and high performance optoelectronics. Meanwhile, MCOs are also well-defined building blocks of supramolecular systems and block copolymers.[2−4] Various rod-coil or rod-rod block cooligomers have been reported.[2,5] However, MCOs with terminal groups for further metal mediated cross-coupling reactions are still few.[6]

Organoboron compounds are key intermediates of Suzuki coupling reaction, which have been widely used in the synthesis of conjugated molecules. In general, arylboron reagents are prepared from lithium or Grignard reagents and trialkyl borates. However, the yield of lithium or Grignard reagents dramatically decreases with increasing molecular weight.[6b] Moreover, it is difficult to make the lithium reagents through lithium−halogen exchange while other reactive groups presence. Kumada, Stille and Heck cross-coupling reactions normally work well in the anhydrous condition, in which boronic acid or ester groups should not take part in the reaction. In fact, Stille coupling reaction has been used to synthesize conjugated building blocks carrying boronic ester group for subsequent Suzuki coupling reaction.[7−9] Of the conjugated systems, fluorene-based materials have attracted particular interest in recent years due to their superior light-emitting properties.[1e,3] Therefore in current work, we focus on the synthesis of various 2′-aryl-9′,9′-dioctyl-fluoren-7′-yl-4,4,5,5-tetramethyl-[1,3,2] dioxaborolanes and fluorene-based MCOs end-capped with boronic pinacol esters via Kumada, Stille or Heck coupling reactions started from halofluorenyl boronic pinacol esters.

We first selected compounds **1a** and **1b** as substrates to test the validity of three types of cross-coupling reactions in preparation of boronic reagent. Mono-dehalogenation of 2,7-dibromo/iodo-9,9-dioctylfluorene with *n*-butyllithium (*n*-BuLi) followed by treatment with tri(*i*-propyl) borate and 2 M aqueous HCl in succession yielded corresponding boronic acids,[10] which were refluxed with pinacol in tetrahydrofuran (THF) to afford boronic esters **1a** and **1b** in a two-step yield of 75% and 54%, respectively (Scheme 1). Gas chromatography−mass spectrometric (GC-MS) measurements revealed that the purity of **1a** and **1b** was 98.89% and 96.91%, respectively, and main impurity was 9′,9′-dioctyl-fluoren-2′-yl −4,4,5,5-tetramethyl-[1,3,2] dioxaborolane.

The results of Kumada, Heck and Stille reactions of compounds **1a** and **1b** with thienylmagnesium bromide, *p*-vinylbiphenyl and three tributylstannyl reagents are listed in Table 1. Kumada [11] reaction of **1a** with thienylmagnesium bromide gave compound **2** in a yield of 86%. Considering the Grignard reagent is also an organic base, this indicates that boronic ester group is stable and not reactive in the absence of water, even in the presence of strong bases. However, the reaction of **1b** (X=I) in the same condition only afforded a mixture of **2** and starting material **1b** with ∼52% **2** estimated by ^{1}H NMR and HPLC, even the reaction time was increased to 48 h. Reason to induce low yield is unclear yet. With triethylamine as the organic base and $Pd(OAc)_2$ as the catalyst, Heck coupling reactions[12] of **1a**

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(12) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009.

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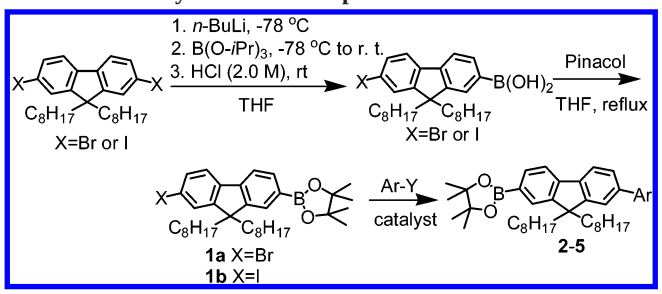
SCHEME 1. Synthesis of Compounds 2-5



and **1b** with *p*-vinylbiphenyl gave similar yield (55% and 50%, respectively). In Stille reactions,[13] 2-tributylstannyl thiophene and 5-tributylstannyl-2, 2′-bithiophene gave the better yield than *p*-tributylstannylbiphenyl. The relative low yield from *p*-tributylstannylbiphenyl can be attributed to its lower reactivity.[13b] Although aryl iodine is more reactive than aryl bromine in palladium-catalyzed Stille reactions as reported in the reference,[13b] the compound **1b** gave inferior yield than **1a** in Stille reactions. We found out that the Stille reactions of **1b** gave more deiodonation byproduct. The dehalogenation reaction was also observed by Nemoto in the preparation of boronic ester via Stille reaction.[7]

Based on aforementioned results of coupling reactions, two monodisperse fluorenyl/bithienyl cooligomers carrying two boronic ester end-capping groups were synthesized by means of Stille reaction. As shown in Scheme 2, the reactions of **1a** with organic tin derivatives **6** and **8** afforded compounds **7** and **9** in a yield of 37% and 45%, respectively, after purified by column chromatography and recrystallization.

Thienyl-terminated conjugated segments can be further functionalized or polymerized for building block copolymers or supramolecular system.[14] Compounds **2** and **3** with one boronic ester group can be used to synthesize monodisperse conjugated oligomers with thiophene end groups. As an example, compound **3** reacted with 2,7″-dibromo-[9,9,9′,9′,9″,9″-hexahexyl]-7, 2′;7′,2″-terfluorene (**10**) in a Suzuki coupling[15] condition yielded bithienyl-capped pentafluorene **11** in a yield of 60% after chromatography, as shown in Scheme 3.

In summary, we have demonstrated that boronic pinacol ester group is not reactive in Kumada, Heck and Stille coupling reaction conditions. Various fluorene-based organoboron compounds have been synthesized from 2-bromo or iodo-fluorenyl boronic pinacol ester via Kumada, Heck and Stille coupling reactions. Our results provide a new protocol to synthesize sophisticated arylboron compounds and MCOs with reactive end-capping groups as building blocks/intermediates for construction of complicated conjugated system.

Experimental Section

7′-(Thien-2-yl)-9′,9′-dioctyl-fluoren-2′-yl-4,4,5,5,-tetramethyl-[1,3,2]dioxaborolane (2).

A. From 1a by Stille reaction. In absence of light, a solution of 2-tributylstannyl thiophene (1.45 g, 3.90 mmol), **1a** (2.32 g, 3.90 mmol), and $Pd(PPh_3)_4$ (135 mg, 0.120 mmol) in 80 mL of anhydrous DMF and Toluene (1:1) was stirred for 24 h at 85 °C. The mixture was cooled to room temperature then poured into a large amount of water for extraction with methylene chloride. The organic extracts were washed with brine before dried over Na_2SO_4. Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel with petroleum ether:ethyl acetate (16:1) as the eluent to afford **2** (1.80 g, 77%) as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.84 (d, J = 7.56 Hz, 1H), 7.11−7.78 (m, 3H), 7.59−7.65 (m, 2H), 7.42 (dd, J = 7.20 Hz, J = 1.05 Hz, 1H), 7.33 (dd, J = 10.2 Hz, J = 1.02 Hz, 1H), 7.15 (m, 1H), 2.02−2.05 (m, 4H), 1.43 (s, 12H), 1.06−1.20 (m, 20H), 0.81−0.98 (m, 6H), 0.55−0.71 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 151.1, 149.0, 144.1, 142.6, 139.5, 132.8, 132.6, 127.8, 127.0, 123.8, 123.5, 121.9, 119.5, 119.2, 118.0, 82.7, 76.4, 76.0, 75.6, 54.2, 39.2, 30.8, 28.9, 28.2, 23.9, 22.6, 21.6, 13.0, 12.6. Molecular Mass: Calcd for $C_{39}H_{55}BO_2S$: 598.4016. Found: 598.4020 (MALDI-TOF MS). (HPLC: 95.67%).

B. From 1a by Kumada reaction. A solution of thienylmagnesium bromide (1.1 mL, 0.8 M, 0.88 mmol), **1a** (0.50 g, 0.84 mmol), and $Pd(dppf)Cl_2$ (7.0 mg, 0.0086 mmol) in 10 mL of anhydrous THF was stirred for 48 h at room temperature. The mixture was poured into a large amount of water for extraction with methylene chloride. The organic extracts were washed with brine and dried over Na_2SO_4. Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel with petroleum ether:ethyl acetate (16:1) as the eluent to afford **2** (0.42 g, 86%) as a light yellow oil. (HPLC: 96.30%).

7′-(2,2′-bithien-5-yl)-9′,9′-dioctyl-fluoren-2′-yl-4,4,5,5,-tetramethyl-[1,3,2]dioxaborolane (3). The procedure for the synthesis of **2** from **1a** by Stille reaction was followed to prepare **3** from **1a** and 5-tributylstannyl-2,2′-bithiophene in a yield of 79%. ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.85 (d, J = 7.59 Hz, 1H), 7.71−7.78 (m, 3H), 7.58−7.64 (m, 2H), 7.33 (d, J = 3.72 Hz, 1H), 7.26−7.27 (m, 2H), 7.21 (d, J = 3.81 Hz, 1H), 7.06−7.09 (m, 1H), 2.01−2.08 (m, 4H), 1.43 (s, 12H), 1.07−1.23 (m, 20H), 0.80−0.90 (m, 6H), 0.61−0.71 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 152.6, 150.5, 144.3, 143.9, 141.1, 137.9, 136.9, 134.2, 133.7, 129.3, 128.3, 127.9, 125.0, 124.9, 124.7, 124.0, 120.9, 120.3, 119.4, 84.1, 77.8, 77.6, 77.4, 74.0, 55.6, 40.6, 32.2, 30.3, 29.6, 28.3, 27.3, 25.3, 24.1, 23.0, 17.9, 14.4, 14.0. Anal. Calcd. for $C_{43}H_{57}BO_2S_2$: C, 75.85; H, 8.44. Found: C, 75.63; H, 8.11. Molecular Mass: Calcd for $C_{43}H_{57}BO_2S_2$: 680.3893. Found: 680.3808 (MALDI-TOF MS).

5,5′-Bis[9′,9′-dioctyl-fluoren-2′-yl-4,4,5,5,-tetramethyl-[1,3,2]-dioxaborolane]-2,2′-bithiophene (7). In absence of light, a solution of 5,5′-bis(tributylstannyl)-2,2′ -bithiophene (**6**) (0.74 g, 1.0 mmol), **1a** (1.20 g, 2.10 mmol) and $Pd(PPh_3)_4$ (70 mg, 0.060 mmol) in 30 mL of anhydrous DMF and Toluene (1:1) was stirred for 24 h at 85 °C. The mixture was cooled to room temperature then poured into a large amount of water for extraction with methylene chloride. The organic extracts were washed with brine and dried over Na_2SO_4. Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel with petroleum ether:ethyl acetate (8:1) as the eluent followed by recrystallization with petroleum ether gave pure **7** (0.44 g, 37%). ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.85 (d, J = 7.69 Hz, 2H), 7.72−7.78 (m, 6H), 7.60−7.66 (m, 4H), 7.36 (d, J = 1.88 Hz, 2H), 7.26 (d, J = 1.90 Hz,

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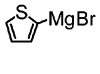
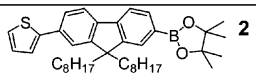
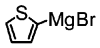
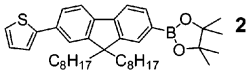
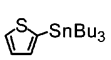
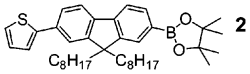
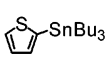
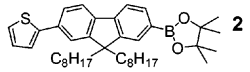
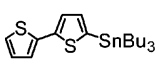
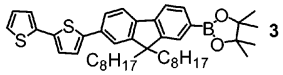
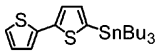
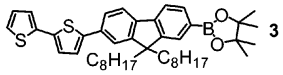
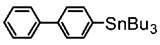
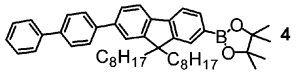
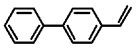
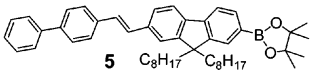
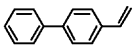
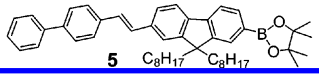
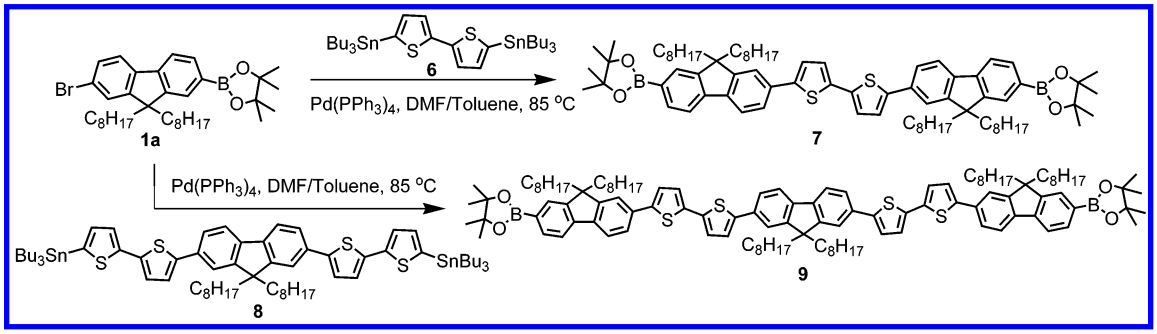
TABLE 1. Palladium Catalyzed Cross-coupling Reactions of the Compounds 1A and 1b

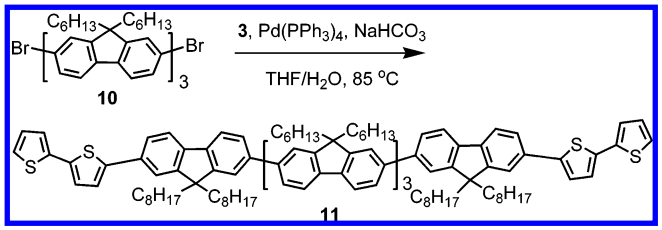
entry	X	Ar-Y	type	catalyst	product	yield (%)[a]
1	Br		Kumada [b]	$Pd(dppf)Cl_2$	 **2**	86
2	I		Kumada [b]	$Pd(dppf)Cl_2$	 **2**	22[e]
3	Br		Stille [c]	$Pd(PPh_3)_4$	 **2**	77
4	I		Stille [c]	$Pd(PPh_3)_4$	 **2**	58
5	Br		Stille [c]	$Pd(PPh_3)_4$	 **3**	79
6	I		Stille [c]	$Pd(PPh_3)_4$	 **3**	60
7	Br		Stille [c]	$Pd(PPh_3)_4$	 **4**	45
8	Br		Heck [d]	$Pd(OAc)_2$	 **5**	55
9	I		Heck [d]	$Pd(OAc)_2$	 **5**	50

[a] Yields after purification. [b] THF, refluxing 28 h. [c] DMF/toluene (1/1 v/v), 85 °C, 24 h. [d] DMF, NEt_3, tris (o-tolyl)phosphine, 110 °C, 24 h. [e] A mixture of **1b** and **2** with ~52% **2**.

SCHEME 2. Synthesis of Monodisperse Conjugated Oligomers7 and 9



SCHEME 3. Synthesis of Monodisperse Conjugated Oligomer11



2H), 2.04−2.06 (m, 8H), 1.43 (s, 24H), 1.08−1.24 (m, 40H), 0.81−0.86 (m, 12H), 0.66 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 152.6, 150.5, 144.3, 144.0, 141.1, 137.0, 134.3, 133.7, 129.3, 127.9, 124.8, 124.1, 121.0, 120.3, 119.4, 84.1, 77.8, 77.4, 77.0, 55.7, 40.6, 32.2, 30.4, 29.6, 25.3, 24.1, 23.0, 14.5. Anal. Calcd. for $C_{78}H_{108}B_2O_4S_2$: C, 78.37; H, 9.11. Found: C, 78.11; H, 9.25. Molecular Mass: Calcd for $C_{78}H_{108}B_2O_4S_2$: 1194.7875. Found: 1195.5976 (MALDI-TOF MS).

Compound 9. The procedure for the synthesis of **7** was followed to prepare **9** as a yellow solid in a yield of 45%. ^1H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.82 (d, J = 7.53 Hz, 2H), 7.69−7.75 (m, 6H), 7.61−7.63 (m, 4H), 7.57 (s, 4H), 7.34 (d, J = 3.66 Hz, 4H), 7.24 (d, J = 3.81 Hz, 4H), 2.04−2.06 (m, 12H), 1.43 (s, 24H), 1.08−1.24 (m, 60H), 0.81−0.86 (m, 18H), 0.66 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 152.7, 152.2, 150.5, 144.3, 144.2, 144.0, 141.0, 140.7, 137.0, 134.3, 133.7, 133.4, 129.3, 125.1, 124.9, 124.1, 121.0, 120.6, 120.3, 119.4, 84.1, 77.8, 77.4, 77.0, 55.7, 40.8, 40.7, 32.2, 30.4, 29.6, 25.4, 24.1, 23.0, 14.5, 14.1. Anal. Calcd. for $C_{115}H_{152}B_2O_4S_4$: C, 79.00; H, 8.76. Found: C,78.74; H, 8.86. Molecular Mass: Calcd for $C_{115}H_{152}B_2O_4S_4$: 1747.0759. Found: 1747.0728 (MALDI-TOF MS).

Compound 11. In absence of light, a solution of 2,7″-dibromo-[9,9,9′,9′,9″,9″- hexahexyl] −7,2′;7′,2″-terfluorene (**10**) (0.42 g, 0.36 mmol), **3** (0.54 g, 0.80 mmol), $NaHCO_3$ (1.00 g, 12.0 mmol)and $Pd(PPh_3)_4$ (18 mg, 0.16 mmol) in 30 mL of anhydrous THF and 10 mL water was refluxed for 28 h. The mixture was cooled to room temperature then poured into a large amount of water for extraction with methylene chloride. The

organic extracts were washed with brine and dried over Na_2SO_4. Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel with petroleum ether: methylene chloride (8:1) as the eluent to afford **11** (0.45 g, 60%) as a light yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.62−7.89 (m, 30H), 7.36 (d, J = 3.78 Hz, 2H), 7.27−7.29 (m, 4H), 7.24 (d, J = 3.70 Hz, 2H), 7.08−7.11 (m, 2H), 2.14−2.21 (m, 20H), 1.05−1.28 (m, 80H), 0.80−0.90 (m, 46H). ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 152.2, 152.1, 144.4, 141.1, 141.0, 140.8, 140.4, 140.2, 138.0, 136.8, 133.2, 128.3, 126.6, 125.1, 124.7, 123.9, 121.9, 120.6, 120.4, 77.8, 77.4, 77.0, 70.5, 55.7, 40.8, 32.2, 31.9, 30.4, 30.1, 29.6, 24.3, 23.0, 14.4. Anal. Calcd. for $C_{149}H_{186}S_4$: C, 85.00; H, 8.90. Found: C, 84.95; H, 8.62. Molecular Mass: Calcd for $C_{149}H_{186}S_4$: 2103.3437. Found: 2105.1782 (MALDI-TOF MS). (HPLC: 97.25%).

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Supporting Information Available: Experimental procedure and characterization for all intermediates and compounds not included in Experimental Section, ^{1}H NMR spectra of all compounds, GC−MS spectra of key intermediates and UV−vis absorption spectra of compounds **7**, **9**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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