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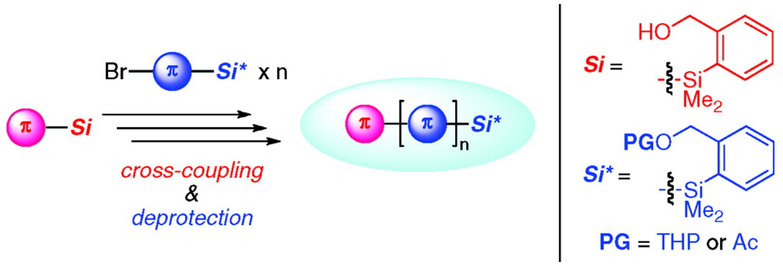

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A Silicon-Based Approach to Oligoarenes by Iterative Cross-Coupling Reactions of Halogenated Organo[(2-hydroxymethyl)phenyl]dimethylsilanes

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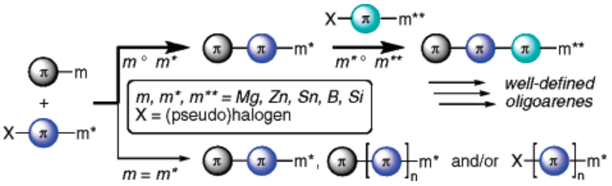
The structures of conjugated oligoarenes are playing key roles in photonic and optoelectronic materials such as organic light-emitting diodes, field-effect transistors, semiconductors, and fluorescent sensors.[1] Syntheses of oligoarenes have relied exclusively on the cross-coupling reaction, which allows direct connection of $C(sp^2)-C(sp^2)$ bonds with high chemo-, stereo-, and regiospecificities.[2] However, installation of a leaving group and a metallic center at terminal arenes is necessary to carry out the second cross-coupling reactions,[3] making the whole sequence leading to the desired oligoarenes a tedious multistep synthesis. Whereas iterative cross-coupling reactions of metalated organic halides would offer an efficient access to oligoarenes with well-defined structures (Scheme 1), it is hard to control their reaction modes (cross-coupling vs homocoupling, etc.) without precise discrimination between several nucleophilic moieties.[4,5]

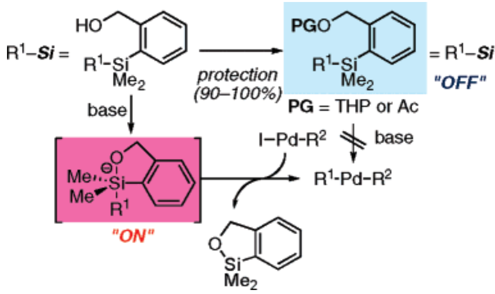
We report herein a silicon-based approach leading to defined oligoarene structures based on iterative cross-coupling reactions of organo[(2-hydroxymethyl)phenyl]dimethylsilanes. We have recently disclosed that the silicon reagents cross-couple with a range of electrophiles in the presence of a palladium catalyst and a weak base such as K_2CO_3 under mild conditions by virtue of the proximal hydroxy group.[6] Since the enhanced reactivity of the silicon reagents is "turned off" simply upon protection of the hydroxy group (Scheme 2), the compounds with a halogen and OH-protecting group are found to serve as promising coupling partners for the iterative cross-coupling sequence. Whereas a silicon-based cross-coupling reaction has gained significant importance in light of availability, stability, and nontoxicity of organosilicon compounds,[7] repetitive use of such silicon-based cross-coupling agents for the syntheses of oligoarenes has never been addressed before.[8]

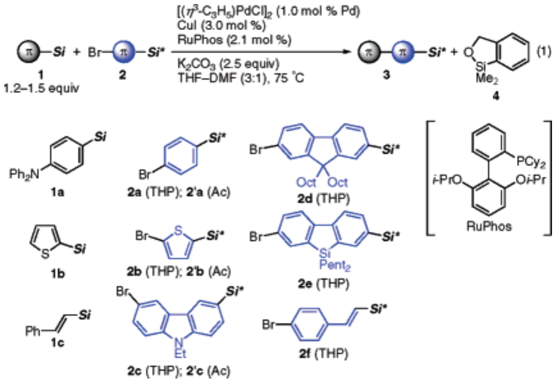
To verify our strategy, we synthesized various organo[(2-hydroxymethyl)phenyl]dimethylsilanes bearing a bromo group and either THP or acetyl protection,[9] and examined their cross-coupling reactions (eq 1 and Table 1). The reaction of 4-(diphenylamino)phenylsilane **1a** (12 mmol) with THP-protected 4-bromophenylsilane **2a** (10 mmol) proceeded smoothly in the presence of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (1.0 mol % Pd), RuPhos (2.1 mol %),[10] CuI (3.0 mol %), and K_2CO_3 (25 mmol) in THF−DMF (3:1) at 75 °C for 7 h to give 4-silylated biphenyl **3aa** in 88% yield (entry 1).[11] Recyclable silicon residue **4** was also isolated in 86% yield.[6] The acetyl protection of **2′a** also tolerated the present conditions to give the corresponding biaryl **3′aa** in 93% yield (entry 2), demonstrating flexibility of the present protocol depending on the functional groups of target molecules. The coupling of **1a** with various brominated arylsilanes even on a gram scale also met with success, giving a range of silylated biaryls in a highly chemoselective manner with good to excellent yields (entries 3−8). It is worth noting that the mild reaction conditions utilizing K_2CO_3 as a base for the present silicon-based cross-coupling technology allow the participation of silafluorene substrate **2e** with its C−Si bonds being completely intact (entry 8). The alkenylsilane functionality of **2f** was inert upon protection of the hydroxy group, and the arylsilane moiety of **1a** exclusively underwent the cross-coupling reaction (entry 9). Thienylsilane **1b** also cross-coupled successfully to give 2-thienyl-substituted silicon compounds including silylated bithiophene **3bb** even on a gram-scale (entries 10 and 11). Similar cross-coupling reactions using (*E*)-styrylsilane **1c** took place in the absence of a copper cocatalyst to give phenylenevinylenes with a silyl terminus in good yields (entries 12 and 13).

Scheme 1. Cross-Coupling Reaction with Halogenated Organometallics



Scheme 2. Modulation of Reactivity of Organo[2-(hydroxymethyl)phenyl]dimethylsilanes





The next cross-coupling reaction of the silylated biaryls thus obtained was examined subsequently. For example, deprotection of the hydroxy group of **3bb** under acidic conditions proceeded smoothly to give silylbithiophene with a free hydroxy group **5** in 89% yield, whereas treatment of **3bb** with *n*-BuLi followed by bromination with 1,2-dibromo-1,1,2,2-tetrafluoroethane afforded 5-bromo-5′-silyl-2,2′-bithiophene **6** in 90% yield (Scheme 3). The high stability of the silylated biaryl under both acidic and basic transformations is remarkable and ascribed to its tetraorganosilane structure. The coupling reaction of **5** and **6** succesfully gave silylated quarterthiophene **7** in 82% yield. Bromination leading to **8** followed by cross-coupling with 2,5-disilyl-substituted thiophene **1d** gave

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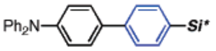
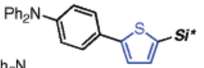
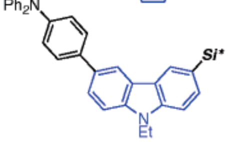
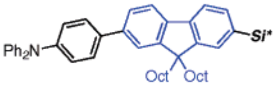
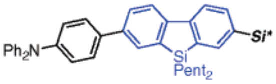
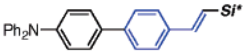
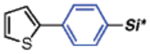
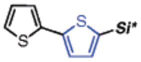
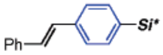
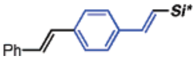
Table 1. Cross-Coupling Reaction of Organo[2-(hydroxymethyl)phenyl]dimethylsilanes (**1**) with Halogenated Organo[2-(alkoxymethyl)phenyl]dimethylsilanes (**2**)

entry	**1** (equiv)	**2**	time (h)	product	yield (%)[a]
1[b] 2	**1a** (1.2) **1a** (1.2)	**2a** **2'a**	7 22		88 (**3aa**) 93 (**3'aa**)
3[c] 4[c]	**1a** (1.2) **1a** (1.2)	**2b** **2'b**	8 7		81 (**3ab**) 81 (**3'ab**)
5 6	**1a** (1.2) **1a** (1.5)	**2c** **2'c**	22 18		85 (**3ac**) 94 (**3'ac**)
7[d]	**1a** (1.5)	**2d**	30		93 (**3ad**)
8[e,f]	**1a** (1.5)	**2e**	24		82 (**3ae**)
9	**1a** (1.2)	**2f**	17		93 (**3af**)
10[c,g,h]	**1b** (1.2)	**2a**	6		96 (**3ba**)
11[g,i]	**1b** (1.2)	**2b**	6		96 (**3bb**)
12[j]	**1c** (1.2)	**2a**	7		90 (**3ca**)
13[j]	**1c** (1.2)	**2f**	22		90 (**3cf**)

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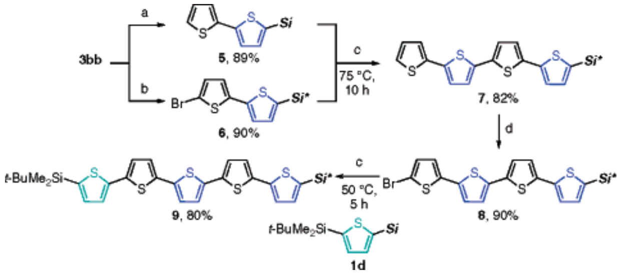
[a] Isolated yields based on **2**. [b] The reaction was carried out on a 10 mmol scale, and **4** was also isolated in 86% yield based on the conversion of **1a** (88%). [c] Reaction run using 3 mol % Pd. [d] Reaction run on a 20 mmol scale. [e] Reaction run on a 0.10 mmol scale. [f] Reaction run using 5 mol % Pd. [g] (dppf)PdCl$_2$•CH$_2$Cl$_2$ was used. [h] The reaction was carried out at 50 °C. [i] Reaction run on a 20 mmol scale. [j] Without CuI.

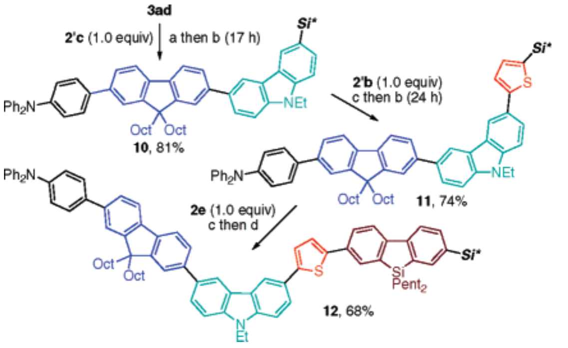
Scheme 3. Convergent Synthesis of Disilylated Quinquethiophene[a]



[a] Reagents and Conditions: (a) PPTS (20 mol %), MeOH, 40 °C, 2 h; (b) *n*-BuLi, TMEDA, THF, −40 °C to room temp, 1 h, then BrCF$_2$CF$_2$Br, −40 °C, 1 h; (c) (dppf)PdCl$_2$•CH$_2$Cl$_2$ (3 or 5 mol %), CuI (9 or 5 mol %), K$_2$CO$_3$ (2.5 equiv), THF−DMF (3:1); (d) *n*-BuLi, TMEDA, THF, −78 °C, 5 min, then BrCF$_2$CF$_2$Br, −40 °C, 1 h.

unsymmetrically disilylated quinquethiophene **9**, which would enjoy potential application to two-photon absorption materials.[12] On the other hand, linear extension of silylated biaryl **3ad** was performed with the deprotection−cross-coupling sequence employing **2′c**, **2′b**, and **2e**, affording highly conjugated protected oligoarenylsilane **12** in an efficient manner (Scheme 4).

Scheme 4. Linear Synthesis of Highly Conjugated Oligoarenylsilane by Iterative Cross-Coupling−Deprotection Sequence[a]



[a] Reagents and Conditions: (a) TsOH•H$_2$O (2 mol %), MeOH−CH$_2$Cl$_2$ (1:1), room temp, overnight; (b) [(η^3-C$_3$H$_5$)PdCl]$_2$ (1 or 5 mol % Pd), RuPhos (2 or 11 mol %), CuI (3 or 5 mol %), K$_2$CO$_3$ (2.5 equiv), THF−DMF (3:1), 75 °C; (c) DIBAL-H (1.1 equiv), CH$_2$Cl$_2$, −78 °C, 2 h; (d) (dppf)PdCl$_2$•CH$_2$Cl$_2$ (5 mol %), CuI (5 mol %), K$_2$CO$_3$ (2.5 equiv), THF-DMF (3:1), 75 °C, 24 h.

In summary, the iterative cross-coupling strategy utilizing organo[(2-hydroxymethyl)phenyl]dimethylsilanes has been demonstrated as a novel and efficient silicon-based entry to oligoarenes with well-defined structure. Mild and divergent conditions for the cross-coupling and deprotection steps provide the stable tetraorganosilicon-type reagents with high potency in applications to synthetic new functional materials.

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Supporting Information Available: Detailed experimental procedures including spectroscopic and analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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