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A new synthetic approach for functional triisopropoxyorganosilanes using molecular building blocks

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ABSTRACT

We report an efficient synthetic approach for well-designed organic-bridged alkoxysilanes, which allow the formation of highly functional organosilica hybrids under mild sol–gel conditions. A series of molecular building blocks containing a triisopropoxysilyl group were synthesized and used in cross-coupling reactions. The triisopropoxysilyl group showed a good tolerance for various organic transformations. 1,4-Diketo-3,6-dithienylpyrrolo[3,4-*c*]pyrrole-bridged triisopropoxysilane was successfully prepared, allowing rapid formation of organosilica hybrid without loss of functionality under mildly acidic conditions.

1. Introduction

Organosilica hybrid materials, such as periodic mesoporous organosilicas (PMOs)[1,2] and polysilsesquioxanes (PSQs)[3,4] have received considerable attention in the fields of catalysis, adsorbents, and optical devices.[5–7] These materials are typically prepared by acid- or base-catalyzed hydrolysis and polycondensation (sol–gel polymerization) of organic-bridged alkoxysilanes ($R[Si(OR')_3]_n$, $n \geq 2$, R: organic group, R′: Me, Et). The $-Si(OMe)_3$ and $-Si(OEt)_3$ groups are most frequently used for alkoxysilane precursors because they are readily hydrolyzed and condensed under mildly acidic or basic conditions to form stable siloxane networks. However, the high reactivity of $Si(OMe)_3$ and $Si(OEt)_3$ has limited the design and synthesis of alkoxysilane precursors with highly functional organic groups (R) and caused formidable problems during work-up and purification using silica gel chromatography.[8–10]

Recently, Shimada et al. found that allylsilyl ($R[Si(CH_2CH{=}CH_2)_m(OEt)_{=3-m}]_n$; $m=1–3$) groups behaved as the synthetic equivalent of alkoxysilyl groups, and were stable enough to allow purification using silica gel chromatography.[11,12] They also reported the synthesis of a series of molecular building blocks containing allylsilyl groups for synthesis of sol–gel precursors with highly functional organic groups via palladium-catalyzed coupling reactions.[13–15] However, the allylsilyl groups were hydrolyzed and condensed under harsher conditions, such as high temperatures or high concentrations of acid or base, or in the presence of expensive Lewis acids, which sometimes damaged the functional organic groups and/or caused undesired Si–C bond cleavage in the organosilane.[16–18]

Organosilanes with bulky alkoxysilyl groups, such as isopropoxysilyl [$-Si(O\textit{i}\text{-}Pr)_3$] have been used only to a limited extent to date, but have potential as ideal sol–gel precursors because of their medium stability and reactivity due to the steric bulk of the alkoxy group on the silicon atom.[19–21] However, synthetic methodologies have been limited to alkoxy exchange reactions of unstable chlorosilanes and/or less bulky alkoxysilanes.[22] Here, we report the preparation of a series of molecular building blocks containing triisopropoxysilyl groups and the synthesis of highly functional organosilica precursors via cross-coupling reaction of the building blocks (Scheme 1). The isopropoxysilyl group was found to show a good tolerance for various organic transformations. The resulting organosilica precursor was successfully hydrolyzed and condensed to form an organosilica hybrid without loss of functionality under mildly acidic conditions.

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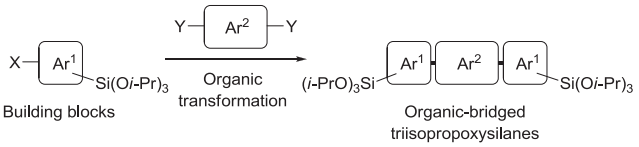
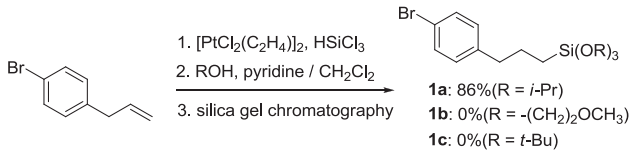


Scheme 1. Synthetic method for functional organic-bridged triisopropoxysilanes using molecular building blocks.

2. Results and discussion

First, we sought a suitable bulky alkoxysilyl group for the building blocks. 2-Methoxyethoxysilyl and *tert*-butoxysilyl groups, in addition to the isopropoxysilyl group, were introduced by hydrosilylation of allylbromobenzene with trichlorosilane in the presence of $[PtCl_2(C_2H_4)]_2$, followed by alkoxylation using appropriate alcohols in the presence of pyridine in CH_2Cl_2 (Scheme 2).[23] The triisopropoxysilyl group was efficiently introduced and showed sufficient stability during general work-up and silica gel chromatography. The bulkier linear tris(2-methoxyethoxy)silyl group was not retained during the reaction and purification, giving a complex mixture that contained none of the target compound. The introduction of the bulkier branched tri(*tert*-butoxy)silyl group failed due to steric hindrance during the alkoxylation reaction.



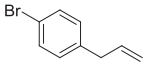
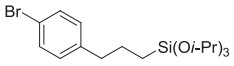
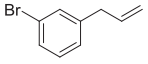
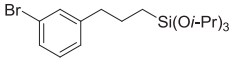
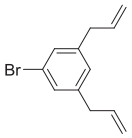
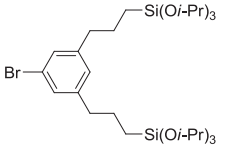
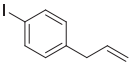
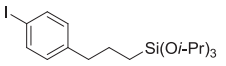
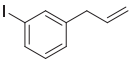
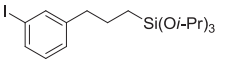
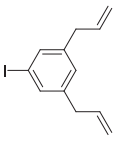
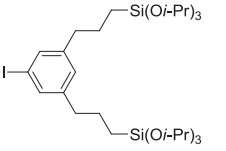
Scheme 2. Synthesis of bromobenzene-based molecular building blocks containing various bulky alkoxysilyl groups.

We then synthesized a variety of halogenated benzene-based building blocks with triisopropoxysilyl groups attached, as shown in Table 1. During this study, we found that allylhalobenzene was readily prepared by halogen–magnesium exchange reaction of bromobenzene derivatives with a mixture of *i*-PrMgCl and *n*-BuLi in cyclopentyl methyl ether followed by allylation with allyl bromide in the presence of CuCN.[24] Both hydrosilylation and isopropoxylation of *p*- and *m*-allylbromobenzene proceeded successfully to give the corresponding building blocks **1a** and **1d** in high yields of 86% and 85%, respectively (Table 1, entries 1 and 2). The bis-silylated building block **1e** could be synthesized from diallylated bromobenzene (Table 1, entry 3). In this case, hydrosilylation proceeded effectively in the presence of $(Bu_4N)_2PtCl_6$ as a catalyst.[25] A series of iodobenzene building blocks, **1f**–**h**, were also obtained under same reaction conditions (Table 1, entries 4–6).

Magnesium-containing building blocks were obtained from the iodobenzene-based building blocks (Table 2, entries 1–3). A Grignard exchange reaction of **1f** with *i*-PrMgCl·LiCl in a mixture of 1,4-dioxane/tetrahydrofuran (THF) (1:10 v/v) proceeded effectively at −40 °C for 4 h and gave the magnesium-containing building block **2a** quantitatively. It is notable that the triisopropoxysilyl group was stable towards *i*-PrMgCl·LiCl and the resulting magnesium reagent, owing to its bulky structure. Interestingly, no reaction occurred in the absence of 1,4-dioxane, and unreacted **1f** was recovered. This may be attributed to the formation of a magnesium complex between *i*-PrMgCl and the triisopropoxysilyl group. Indeed, the use of excess *i*-PrMgCl in THF gave the corresponding **2a**. The addition of 1,4-dioxane affects the dissociation of the magnesium complex, as reported by Knochel's group.[26] *m*-Silylated (**2b**) and bis-silylated (**2c**) Grignard reagents were also successfully obtained from corresponding iodo-building blocks under the same reaction conditions.

The magnesium-containing building blocks successfully underwent transmetallation upon treatment with other metal reagents. The transmetallation of **2a** with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in a mixture of 1,4-dioxane/THF (1:10 v/v) gave the borylated building block **2d** in 93% yield (Table 2, entry 4). The reaction of **2a** with trimethyltin chloride afforded the trimethylstannylated building block **2e** in a high yield of 87% (Table 2, entry 5).

Table 1
Synthesis of halogen-substituted molecular building blocks containing one or two triisopropoxysilyl groups[a]

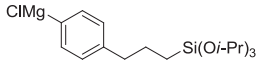
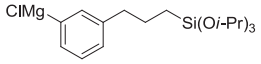
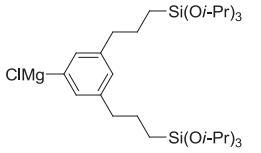
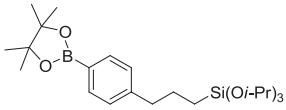
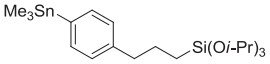
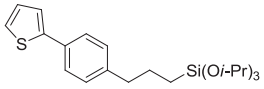
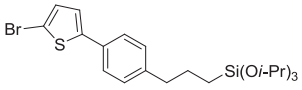
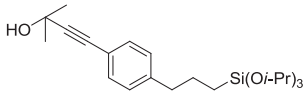
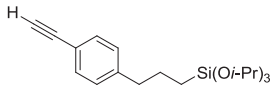
Entry	Substrate	Product		Yield %
1			**1a**	86
2			**1d**	85
3[b]			**1e**	83
4			**1f**	86
5			**1g**	85
6[b]			**1h**	84

[a] Reagents and conditions: (i) allylhalobenzene (1 equiv), $HSiCl_3$ (3.3 equiv), $[PtCl_2(C_2H_4)]_2$ (0.25 mol % Pt), rt, overnight, (ii) *i*-PrOH (4.5 equiv), pyridine (4.5 equiv), CH_2Cl_2, 0 °C–rt, 6 h.
[b] $[(Bu_4N)_2PtCl_6]$ (0.1 mol % Pt) was used as a catalyst.

With key building blocks in hand, we then examined the utility of the molecular building blocks as cross-coupling partners. The halogen-substituted building blocks can be used as coupling reagents for Suzuki–Miyaura[27] and Sonogashira–Hagihara cross-coupling reactions.[28] Suzuki–Miyaura coupling between **1f** and 2-thiophenboronic acid in the presence of $Pd(PPh_3)_4$ as a catalyst gave the thiophene-substituted building block **2f** in 71% yield (Table 2, entry 6). Notably, in the reaction, the use of a basic aqueous solution did not affect the hydrolysis of the triisopropoxysilyl group. The α-proton on thiophene ring in **2f** was readily brominated using *N*-bromosuccinimide (NBS) to afford the bromothiophene building block **2g** in 81% yield (Table 2, entry 7). The resulting **2g** is a useful coupling partner for the construction of π-conjugated thiophene bridging groups. Sonogashira–Hagihara coupling between **1a** and 2-methyl-3-butyn-2-ol in the presence of $PdCl_2(PPh_3)_2$/CuI as a catalyst gave the ethynylated compound **2h** in 86% yield (Table 2, entry 8). The resulting **2h** can easily be deprotected using NaH to afford the terminal ethyne-substituted building block **2i** in 71% yield without decomposition of the triisopropoxysilyl group (Table 2, entry 9). The obtained **2i** can then be used as a coupling partner for Sonogashira–Hagihara coupling and/or click reactions with azide compounds.[29]

Materials based on 1,4-diketo-3,6-dithienylpyrrolo[3,4-*c*]pyrrole (DTDPP) have attracted tremendous attention in the fields of solar cells and field effect transistors because of their promising optical and electrical properties.[30,31] DTDPP-bridged silane

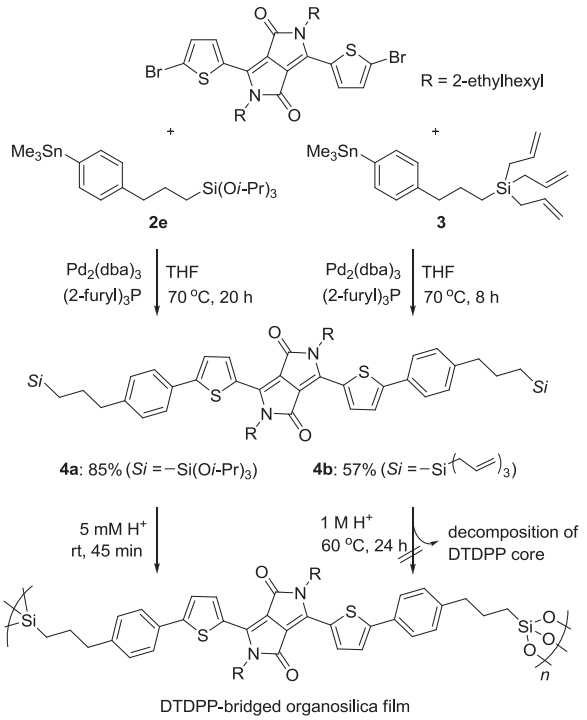
Table 2
Synthesis of functional molecular building blocks

Entry	Substrate	Product		Yield %
1[a]	**1f**		**2a**	Quant.[h]
2[a]	**1g**		**2b**	Quant.[h]
3[a]	**1h**		**2c**	Quant.[h]
4[b]	**2a**		**2d**	93
5[c]	**2a**		**2e**	87
6[d]	**1f**		**2f**	71
7[e]	**2f**		**2g**	81
8[f]	**1a**		**2h**	86
9[g]	**2h**		**2i**	71

[a] Reagents and conditions: *i*-PrMgCl·LiCl, 1,4-dioxane/THF (1:10), −40 °C, 4 h.
[b] 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, −40 °C–rt, overnight.
[c] Trimethyltin chloride, −40 °C–rt, overnight.
[d] $Pd(PPh_3)_4$, 2-thiopheneboronic acid, $NaHCO_3$ aqueous, 1,4-dioxane, 85 °C, 24 h.
[e] NBS, DMF, rt, 2 h.
[f] $PdCl_2(PPh_3)_2$, CuI, 2-methyl-3-butyn-2-ol, Et_3N, 80 °C, 24 h.
[g] NaH, toluene, 115 °C, 1 h.
[h] Conversion of substrates **1f**–**h**.

precursors were synthesized by cross-coupling reaction using building blocks, as shown in Scheme 3. Migita–Kosugi–Stille cross-coupling between **2e** and dibrominated DTDPP gave the desired DTDPP-bridged triisopropoxysilane **4a** in high yield (85%).[32,33] The corresponding DTDPP-bridged triallylsilane **4b** also synthesized using triallylsilane building block **3** (see Experimental section). Both functional precursors were purified by silica gel chromatography and isolated in pure form.

An organosilica hybrid film was readily obtained from the DTDPP-bridged triisopropoxysilane **4a** by sol–gel polymerization under mildly acidic conditions. A purple solution of the precursor **4a** containing aqueous hydrochloric acid (HCl, 5 mM in THF) was smoothly converted to a dark blue sol by stirring for only 45 min. The color change indicated the formation of a soluble siloxane oligomer in the sol. The obtained sol formed a solid organosilica film by spin-coating and drying under reduced pressure. The resulting organosilica film showed absorption maxima at 564 nm and 609 nm, attributed to an intramolecular charge transfer



Scheme 3. Synthesis of DTDPP-bridged triisopropoxysilane **4a** and triallylsilane **4b**, and preparation of organosilica films.

transition in the DTDPP unit, which indicated that the optical properties of the DTDPP unit remained after formation of the organosilica film (Fig. 1). However, the corresponding DTDPP-bridged triallylsilane **4b** did not form an organosilica film under same sol–gel conditions. Unfortunately, the color of the sol faded under highly acidic conditions (1 M in THF), and an organosilica film did not form. This indicates decomposition of the donor–acceptor–donor structure in the DTDPP skeleton during preparation of the sol. The triisopropoxysilyl group proved to be useful in the synthesis of functional organosilica hybrids without loss of organic group functionality.

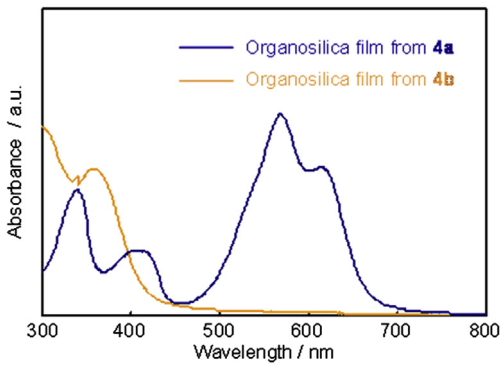


Fig. 1. UV–vis absorption spectra of organosilica films prepared from DTDPP-bridged silane precursors **4a** and **4b**.

3. Conclusions

In conclusion, we developed a novel synthetic route for π-conjugated organosilica precursors by using molecular building blocks containing one or two triisopropoxysilyl groups. The synthesized molecular building blocks could be used as coupling partners for various palladium-catalyzed cross-coupling reactions. Indeed, opto- and electroactive organosilanes were successfully synthesized and

isolated in pure form. Furthermore, one organosilane was readily hydrolyzed and condensed to give an organosilica hybrid without loss of functionality. This innovative approach is expected to extend and complement the conventional approach using allylsilane-based molecular building blocks and will lead to significant development of organosilica hybrids.

4. Experimental

4.1. Methods and materials

All reactions were carried out under argon using standard high vacuum and Schlenk-line techniques. Unless otherwise noted, all materials, including dry solvents, were purchased from commercial suppliers (Sigma–Aldrich, Tokyo Chemical Industry Co., Ltd., and Wako Pure Chemical Industries Ltd.) and used without further purification.

Nuclear magnetic resonance (NMR) spectra were recorded on a Jeol JNM-EXC400P spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C). Chemical shifts are reported in δ parts per million referenced to an internal tetramethylsilane standard (δ 0.00) for ^{1}H NMR and chloroform-*d* (δ 77.0) for ^{13}C NMR, respectively. Mass spectra were recorded on a Micromass GCT Premier mass spectrometer (FI: field ionization) and Micromass Q-TOF mass spectrometer (ESI: electrospray ionization). Ultraviolet-visible (UV–vis) absorption spectra were measured using a Jasco V-670 spectrometer.

4.2. Synthetic procedures and characterization

4.2.1. Synthesis of allylhalobenzene derivatives

4.2.1.1. 1-Allyl-4-bromobenzene. A 200 mL three-neck round-bottom flask connected to a dropping funnel and dry argon flow was charged with a stir bar, 1,4-dibromobenzene (15.0 g, 63.6 mmol), and dry cyclopentyl methyl ether (35 mL). The mixture was cooled to −5 °C, and isopropylmagnesium chloride solution (2.0 M in THF) (12.7 mL, 25.4 mmol) and *n*-BuLi solution (1.6 M in hexane) (31.8 mL, 50.9 mmol) were added dropwise over a period of 30 min, respectively. The reaction mixture was stirred for 4 h at −5 °C. Copper (I) cyanide (285 mg, 3.18 mmol, 5 mol % Cu) was added at once, and the reaction mixture was stirred for 5 min at −5 °C. Allyl bromide (10.8 mL, 127.7 mmol) was then added dropwise over a period of 30 min at −5 °C. It was then allowed to reach room temperature and stirred for 15 h. The precipitated magnesium salt was filtered off and the resulting organic phase was extracted with diethyl ether and washed with saturated NH_4Cl aqueous solution and brine and dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude residue was purified by bulb-to-bulb distillation (150 Pa, 50 °C) affording title compound as a transparent colorless liquid (12.2 g, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.33 (d, J=6.8 Hz, 2H), 5.03–5.09 (m, 2H), 5.87–5.97 (m, 1H), 7.05 (d, J=8.4 Hz, 2H), 7.40 (t, J=8.4 Hz, 2H). The same procedure was followed for the synthesis of 1-allyl-3-bromobenzene as described below.

4.2.1.2. 1-Allyl-3-bromobenzene. Transparent colorless liquid. Yield: 93%. Bp: 150 Pa, 50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.35 (d, J=6.8 Hz, 2H), 5.06–5.11 (m, 2H), 5.87–5.97 (m, 1H), 7.10–7.17 (m, 2H), 7.31–7.34 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.7, 116.5, 122.4, 127.2, 129.1, 129.9, 131.6, 136.4, 142.3.

4.2.1.3. 1-Allyl-3,5-dibromobenzene. A 500 mL three-neck round-bottom flask connected to a dropping funnel and dry argon flow was charged with a stir bar, 1,3,5-tribromobenzene (25.4 g, 80.7 mmol), and dry cyclopentyl methyl ether (120 mL). The mixture was cooled to −5 °C, and isopropylmagnesium chloride solution (2.0 M in THF) (16.2 mL, 32.4 mmol) and *n*-BuLi solution (2.5 M in hexane) (25.8 mL, 64.5 mmol) were added dropwise over a period of 30 min, respectively. The reaction mixture was stirred for 8 h at −5 °C. Copper (I) cyanide (723 mg, 8.0 mmol, 10 mol % Cu) was added at once, and the reaction mixture was stirred for 5 min at −5 °C. Allyl bromide (10.2 mL, 120.6 mmol) was then added dropwise over a period of 30 min at −5 °C. It was then allowed to reach room temperature and stirred for 15 h. The precipitated magnesium salt was filtered off and the resulting organic phase was extracted with diethyl ether and washed with saturated NH_4Cl aqueous solution and brine and dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure affording title compound as a transparent light brown liquid (21.4 g, 96% yield), which was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.33 (d, J=6.8 Hz, 2H), 5.08–5.15 (m, 2H), 5.83–5.94 (m, 1H), 7.27 (d, J=1.6 Hz, 2H), 7.50 (t, J=1.6 Hz, 1H).

4.2.1.4. 1-Bromo-3,5-diallylbenzene. A 500 mL three-neck round-bottom flask connected to a dropping funnel and dry argon flow was charged with a stir bar and 1-allyl-3,5-dibromobenzene (21.4 g, 77.5 mmol), dry cyclopentyl methyl ether (100 mL). The mixture was cooled to −5 °C, and isopropylmagnesium chloride solution (2.0 M in THF) (16.2 mL, 32.5 mmol) and *n*-BuLi solution (2.5 M in hexane) (25.8 mL, 64.5 mmol) were added dropwise over a period of 30 min, respectively. The reaction mixture was stirred for 8 h at −5 °C. Copper (I) cyanide (705 mg, 7.8 mmol, 10 mol % Cu) was added at once, and the reaction mixture was stirred for 5 min at −5 °C. Allyl bromide (10.2 mL, 120.6 mmol) was then added dropwise over a period of 30 min at −5 °C. It was then allowed to reach room temperature and stirred for 15 h. The precipitated magnesium salt was filtered off and the resulting organic phase was extracted with diethyl ether and washed with saturated NH_4Cl aqueous solution and brine and dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude residue was purified by bulb-to-bulb distillation (150 Pa, 100 °C) affording title compound as a transparent colorless liquid (17.5 g, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.33 (d, J=6.8 Hz, 4H), 5.05–5.11 (m, 4H), 5.86–5.96 (m, 2H), 6.92 (s, 1H), 7.25 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.8, 116.5, 122.4, 127.7, 129.3, 136.5, 142.3. FI-HRMS m/z calcd for $C_{12}H_{13}Br$ (M^+): 236.0201; found: 236.0204.

4.2.1.5. 1-Allyl-4-iodobenzene. A 200 mL three-neck round-bottom flask connected to a dropping funnel and dry argon flow was charged with a stir bar, 1-allyl-4-bromobenzene (12.0 g, 60.9 mmol), and dry cyclopentyl methyl ether (30 mL). The mixture was cooled to −5 °C, and isopropylmagnesium chloride solution (2.0 M in THF) (15.2 mL, 30.4 mmol) and *n*-BuLi solution (2.5 M in hexane) (24.4 mL, 61.0 mmol) were added dropwise over a period of 30 min, respectively. The reaction mixture was stirred for 6 h at −5 °C. The resulting reaction mixture was then added dropwise to a solution of iodine (23.2 g, 91.4 mmol) in THF (100 mL) at −78 °C. It was then allowed to reach room temperature and stirred for 18 h. The resulting mixture was quenched with saturated NH_4Cl aqueous solution at 0 °C, and organic phase was extracted with diethyl ether and washed with brine and dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude residue was purified by bulb-to-bulb distillation (150 Pa, 70 °C) affording title compound as a transparent colorless liquid (13.4 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.33 (d, J=6.6 Hz, 2H), 5.04–5.10 (m, 2H), 5.86–5.97 (m, 1H), 6.94 (d, J=8.3 Hz, 2H), 7.61 (d, J=8.3 Hz, 2H). The same procedure was followed for the synthesis of 1-allyl-3-iodobenzene and 1,3-diallyl-5-iodobenzene as described below.

4.2.1.6. 1-Allyl-3-iodobenzene. Transparent colorless liquid. Yield: 87%. Bp: 150 Pa, 100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.33 (d, J=6.4 Hz,

2H), 5.06–5.11 (m, 2H), 5.86–5.97 (m, 1H), 7.02 (t, *J*=8.0 Hz, 1H), 7.15 (d, *J*=8.0 Hz, 1H), 7.53 (d, *J*=8.0 Hz, 1H), 7.54 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.7, 94.5, 116.5, 127.9, 130.1, 135.1, 136.5, 137.5, 142.4.

4.2.1.7. 1,3-Diallyl-5-iodobenzene. Transparent colorless liquid. Yield: 77%. Bp: 200 Pa, 110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.30 (d, *J*=6.8 Hz, 4H), 5.05–5.11 (m, 4H), 5.85–5.95 (m, 2H), 6.96 (s, 1H), 7.38 (d, *J*=1.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.6, 94.6, 116.4, 128.3, 135.3, 136.5, 142.4. FI-HRMS *m*/*z* calcd for $C_{12}H_{13}I$ (M^+): 284.0062; found: 284.0051.

4.2.2. Synthesis of molecular building blocks containing bulky alkoxysilyl group

*4.2.2.1. 1-Bromo-4-(3-(triisopropoxysilyl)propyl)benzene (**1a**).* A 500 mL three-neck round-bottom flask connected to a condenser and dry argon flow was charged with a stir bar, 1-allyl-4-bromobenzene (12.0 g, 60.9 mmol), and $[PtCl_2(C_2H_4)]_2$ (4.0 mg, 6.8 μmol, 0.25 mol % Pt). The mixture was cooled to 0 °C, and trichlorosilane (20.0 mL, 198 mmol) was then added dropwise over a period of 15 min at 0 °C. After complete addition of the trichlorosilane, the temperature was progressively raised to room temperature. The mixture was stirred for 18 h at room temperature. The reaction mixture was concentrated under reduced pressure and the residue was dissolved in dry CH_2Cl_2 (50 mL). The resulting solution was then carefully added dropwise to a mixed solution of dry 2-propanol (21.0 mL, 274 mmol) and dry pyridine (22.2 mL, 274 mmol) in dry CH_2Cl_2 (200 mL) over a period of 30 min at 0 °C, and the resulting mixture was stirred for 6 h at room temperature. The reaction mixture was then concentrated under reduced pressure. The precipitated pyridinium salt was filtered off, and residue was extracted with hexane (300 mL). The combined organic phase was concentrated under reduced pressure, and the resulting crude residue was purified by silica gel chromatography (eluent: hexane/EtOAc=10:1) affording **1a** as a transparent colorless liquid (21.2 g, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.57–0.61 (m, 2H), 1.17 (d, *J*=6.4 Hz, 18H), 1.67–1.71 (m, 2H), 2.58 (t, *J*=7.2 Hz, 2H), 4.18 (sept, *J*=6.4 Hz, 3H), 7.04 (d, *J*=8.8 Hz, 2H), 7.37 (d, *J*=8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.6, 25.0, 25.6, 38.6, 64.9, 119.3, 130.3, 131.2, 141.5. FI-HRMS *m*/*z* calcd for $C_{18}H_{31}BrO_3Si$ (M^+): 402.1226; found: 402.1224. The same procedure was followed for the synthesis of compounds **1d**, **1f**, and **1g** as described below.

*4.2.2.2. 1-Bromo-3-(3-(triisopropoxysilyl)propyl)benzene (**1d**).* Transparent colorless liquid. Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.58–0.62 (m, 2H), 1.18 (d, *J*=6.4 Hz, 18H), 1.67–1.75 (m, 2H), 2.60 (t, *J*=7.6 Hz, 2H), 4.19 (sept, *J*=6.4 Hz, 3H), 7.08–7.15 (m, 2H), 7.28–7.32 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.9, 25.2, 25.9, 39.1, 65.2, 122.6, 127.5, 129.0, 130.0, 131.9, 145.2. FI-HRMS *m*/*z* calcd for $C_{18}H_{31}BrO_3Si$ (M^+): 402.1226; found: 402.1211.

*4.2.2.3. 1-Iodo-4-(3-(triisopropoxysilyl)propyl)benzene (**1f**).* Transparent colorless liquid. Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.57–0.61 (m, 2H), 1.17 (d, *J*=6.4 Hz, 18H), 1.57–1.73 (m, 2H), 2.57 (t, *J*=7.6 Hz, 2H), 4.18 (sept, *J*=6.4 Hz, 3H), 6.92 (d, *J*=8.4 Hz, 2H), 7.57 (d, *J*=8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.6, 24.9, 25.6, 38.7, 64.9, 90.5, 130.7, 137.2, 142.2. FI-HRMS *m*/*z* calcd for $C_{18}H_{31}IO_3Si$ (M^+): 450.1087; found: 450.1065.

*4.2.2.4. 1-Iodo-3-(3-(triisopropoxysilyl)propyl)benzene (**1g**).* Transparent colorless liquid. Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.57–0.61 (m, 2H), 1.18 (d, *J*=6.0 Hz, 18H), 1.66–1.74 (m, 2H), 2.57 (t, *J*=7.6 Hz, 2H), 4.19 (sept, *J*=6.0 Hz, 3H), 6.99 (d, *J*=8.0 Hz, 1H), 7.12 (d, *J*=8.0 Hz, 1H), 7.50 (d, *J*=8.0 Hz, 1H), 7.53 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.6, 24.9, 25.6, 38.7, 64.9, 94.4, 127.8, 129.9, 134.6, 137.5, 145.0. FI-HRMS *m*/*z* calcd for $C_{18}H_{31}IO_3Si$ (M^+): 450.1087; found: 450.1091.

*4.2.2.5. 1,3-Bis(3-(triisopropoxysilyl)propyl)-5-bromobenzene (**1e**).* A 300 mL three-neck round-bottom flask connected to a condenser and dry argon flow was charged with a stir bar, 1-bromo-3,5-diallylbenzene (4.50 g, 19.0 mmol), dry diethyl ether (12 mL), and dry CH_2Cl_2 (15 mL). After the addition of a solution of $(Bu_4N)_2PtCl_6$ (17.0 mg, 19.0 μmol, 0.1 mol % Pt) in dry CH_2Cl_2 (3 mL), trichlorosilane (7.50 mL, 74.3 mmol) was then added dropwise over a period of 15 min at 0 °C. After complete addition of the trichlorosilane, the temperature was progressively raised to room temperature. The mixture was stirred overnight at room temperature. The reaction mixture was concentrated under reduced pressure and the residue was dissolved in dry CH_2Cl_2 (75 mL). The resulting solution was then carefully added dropwise to a mixed solution of dry 2-propanol (13.0 mL, 170 mmol) and dry pyridine (14.0 mL, 170 mmol) in dry CH_2Cl_2 (100 mL) over a period of 30 min at 0 °C, and the resulting mixture was stirred for 3 h at room temperature. The reaction mixture was then concentrated under reduced pressure. The precipitated pyridinium salt was filtered off and residue was extracted with hexane (300 mL). The combined organic phase was concentrated under reduced pressure, and the resulting crude residue was purified by silica gel chromatography (eluent: hexane/EtOAc=10:1) affording **1e** as a transparent colorless liquid (10.2 g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.58–0.62 (m, 4H), 1.18 (d, *J*=6.4 Hz, 36H), 1.65–1.73 (m, 4H), 2.56 (t, *J*=8.0 Hz, 4H), 4.19 (sept, *J*=6.4 Hz, 6H), 6.88 (s, 1H), 7.12 (d, *J*=1.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7, 24.9, 25.6, 38.9, 64.9, 122.0, 127.6, 128.8, 144.6. FD-HRMS *m*/*z* calcd for $C_{30}H_{57}BrO_6Si_2$ (M^+): 648.2877; found: 648.2869. The same procedure was followed for the synthesis of compound **1h** as described below.

*4.2.2.6. 1,3-Bis(3-(triisopropoxysilyl)propyl)-5-iodobenzene (**1h**).* Transparent colorless liquid. Yield: 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.57–0.62 (m, 4H), 1.18 (d, *J*=6.0 Hz, 36H), 1.64–1.72 (m, 4H), 2.53 (t, *J*=7.6 Hz, 4H), 4.19 (sept, *J*=6.0 Hz, 6H), 6.92 (s, 1H), 7.33 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7, 24.9, 25.6, 38.8, 64.9, 94.3, 128.3, 134.8, 144.7. ESI-HRMS *m*/*z* calcd for $C_{30}H_{57}INaO_6Si_2$ ($M+Na^+$): 719.2623; found: 719.2668.

*4.2.2.7. 4-(3-(Triisopropoxysilyl)propyl)phenylmagnesium chloride (**2a**).* A 20 mL Schlenk flask connected to dry argon flow was charged with a stir bar, **1f** (247 mg, 0.55 mmol), and dry THF (5 mL). The mixture was cooled to −40 °C, and isopropylmagnesium chloride lithium chloride complex solution (1.3 M in THF) (0.85 mL, 1.10 mmol) and dry 1,4-dioxane (0.50 mL) were added dropwise over a period of 5 min, respectively. The reaction mixture was stirred for 4 h at −40 °C. Conversion of starting material was check by ^{1}H NMR after the quenching water. The same procedure was followed for the preparation of compound **2b** and **2c**.

*4.2.2.8. 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(3-(triisopropoxysilyl)propyl)benzene (**2d**).* A 20 mL Schlenk flask connected to dry argon flow was charged with a stir bar and **2a** (0.55 mmol) in dry THF/dry 1,4-dioxane (6.35 mL). The mixture was cooled to −40 °C, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (225 μL, 1.10 mmol) was added one-portion. It was then allowed to reach room temperature and stirred for 18 h. The resulting mixture was quenched with saturated NH_4Cl aqueous solution at 0 °C, and organic phase was extracted with diethyl ether and washed with brine and dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure affording **2d** as a transparent colorless liquid (230 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.59–0.63 (m, 2H), 1.17 (d, *J*=6.0 Hz, 18H), 1.33 (s, 12H), 1.69–1.76 (m, 2H), 2.64 (t, *J*=7.6 Hz, 2H), 4.18 (sept, *J*=6.0 Hz, 3H),

7.18 (d, J=8.0 Hz, 2H), 7.71 (d, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7, 24.5, 24.8, 25.5, 39.5, 64.8, 83.6, 128.0, 133.8, 134.7, 146.0. FI-HRMS m/z calcd for $C_{24}H_{43}BO_5Si$ (M^+): 450.2973; found: 450.2978.

*4.2.2.9. 4-(3-(Triisopropoxysilyl)propyl)-1-(trimethylstannyl)benzene (**2e**).* A 100 mL two-neck round-bottom flask connected to dry argon flow was charged with a stir bar and **2a** (3.33 mmol) in dry THF/dry 1,4-dioxane (38 mL). The mixture was cooled to −40 °C, trimethyltin chloride (1.33 g, 6.67 mmol) was added one-portion. It was then allowed to reach room temperature and stirred for 18 h. The resulting mixture was quenched with saturated NH_4Cl aqueous solution at 0 °C, and organic phase was extracted with diethyl ether and washed with brine and dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure affording **2e** as a transparent colorless liquid (1.41 g, 87% yield). Compound **2e** was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.27 (t, J=27.6 Hz, 9H), 0.62–0.66 (m, 2H), 1.18 (d, J=6.4 Hz, 18H), 1.69–1.76 (m, 2H), 2.61 (t, J=8.0 Hz, 2H), 4.19 (sept, J=6.4 Hz, 3H), 7.17 (d, J=7.6 Hz, 2H), 7.40 (d, J=7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ −9.6, 11.9, 25.1, 25.6, 39.4, 64.8, 128.4, 135.7, 138.6, 142.7. ESI-HRMS m/z calcd for $C_{21}H_{40}NaO_3SiSn$ ($M+Na^+$): 511.1666; found: 511.1679.

*4.2.2.10. 4-(Thiophen-2-yl)-1-(3-(triisopropoxysilyl)propyl)benzene (**2f**).* A 500 mL three-neck round-bottom flask connected to a condenser and dry argon flow was charged with a stir bar, **1f** (6.60 g, 14.7 mmol), 2-thiopheneboronic acid (2.82 g, 22.0 mmol), sodium hydrogen carbonate (2.46 g, 29.3 mmol), dry 1,4-dioxane (220 mL), and degassed distilled water (22 mL). After the mixture was stirred for 10 min at room temperature, $Pd(PPh_3)_4$ (400 mg, 0.35 mmol, 2.4 mol % Pd) was added one-portion under argon flow. The temperature was progressively raised to 85 °C and then the reaction mixture was stirred for 24 h. The reaction mixture was then concentrated under reduced pressure and the resulting crude residue was purified by silica gel chromatography (eluent: hexane/$CHCl_3$=1:1) affording **2f** as a transparent light yellow liquid (4.24 g, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.61–0.66 (m, 2H), 1.18 (d, J=6.4 Hz, 18H), 1.70–1.78 (m, 2H), 2.64 (t, J=7.6 Hz, 2H), 4.19 (sept, J=6.4 Hz, 3H), 7.06 (dd, J=5.2 Hz, 3.6 Hz, 1H), 7.18 (d, J=8.0 Hz, 2H), 7.23 (dd, J=5.2 Hz, 1.2 Hz, 1H), 7.26 (dd, J=3.6 Hz, 0.8 Hz, 1H), 7.51 (d, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7, 25.0, 25.5, 38.9, 64.8, 122.5, 124.2, 125.8, 127.8, 129.0, 131.8, 142.0, 144.5. FI-HRMS m/z calcd for $C_{22}H_{34}O_3SSi$ (M^+): 406.1988; found: 406.1977.

*4.2.2.11. 4-(5-Bromothiophen-2-yl)-1-(3-(triisopropoxysilyl)propyl)benzene (**2g**).* A 100 mL two-neck round-bottom flask connected to dry argon flow was charged with a stir bar, **2f** (1.05 g, 2.58 mmol), and dry DMF (30 mL). After the mixture was stirred for 10 min at 0 °C, *N*-bromosuccinimide (636 mg, 3.57 mmol) was added one-portion under argon flow. The reaction mixture was stirred for 2 h at room temperature. The organic phase was extracted with hexane and concentrated under reduced pressure. The resulting crude residue was purified by silica gel chromatography (eluent: hexane/EtOAc=10:1) affording **2g** as a transparent light yellow liquid (1.01 g, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.61–0.65 (m, 2H), 1.18 (d, J=6.4 Hz, 18H), 1.69–1.77 (m, 2H), 2.63 (t, J=7.6 Hz, 2H), 4.19 (sept, J=6.4 Hz, 3H), 6.99 (s, 2H), 7.17 (d, J=8.4 Hz, 2H), 7.40 (d, J=8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7, 25.0, 25.6, 38.9, 64.8, 110.7, 122.6, 125.5, 129.1, 130.7, 131.1, 142.6, 146.1. FI-HRMS m/z calcd for $C_{22}H_{33}BrO_3SSi$ (M^+): 484.1103; found: 484.1096.

*4.2.2.12. 1-(3-Hydroxy-3-methyl-1-butynyl)-4-(3-(triisopropoxysilyl)propyl)benzene (**2h**).* A 500 mL three-neck round-bottom flask connected to a condenser and dry argon flow was charged with a stir bar, **1a** (7.13 g, 17.6 mmol), $PdCl_2(PPh_3)_2$ (495 mg, 0.71 mmol), CuI (135 mg, 0.70 mmol), and dry Et_3N (70 mL). After the mixture was stirred for 1 min at room temperature, 2-methyl-3-butyn-2-ol (2.10 mL, 21.5 mmol) was added. The temperature was progressively raised to 80 °C and then the reaction mixture was stirred for 20 h. The reaction mixture was then concentrated under reduced pressure and the resulting crude residue was purified by silica gel chromatography (eluent: hexane/EtOAc=10:1) affording **2h** as a transparent light yellow liquid (6.21 g, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.57–0.61 (m, 2H), 1.17 (d, J=6.4 Hz, 18H), 1.61 (s, 6H), 1.66–1.74 (m, 2H), 2.62 (t, J=7.6 Hz, 2H), 4.18 (sept, J=6.4 Hz, 3H), 7.10 (d, J=8.4 Hz, 2H), 7.31 (d, J=8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.6, 24.8, 25.5, 31.5, 39.0, 64.8, 65.6, 82.3, 93.0, 119.8, 128.5, 131.5, 143.0. FI-HRMS m/z calcd for $C_{23}H_{38}O_4Si$ (M^+): 406.2539; found: 406.2545.

*4.2.2.13. 1-Ethynyl-4-(3-(triisopropoxysilyl)propyl)benzene (**2i**).* A 300 mL three-neck round-bottom flask connected to a condenser and dry argon flow was charged with a stir bar, **2h** (10.0 g, 24.6 mmol), and dry toluene (150 mL). After the mixture was stirred for 5 min at room temperature, sodium hydride (60%, dispersion in paraffin liquid, 195 mg, 4.88 mmol) was added. The temperature was progressively raised to 115 °C and then the reaction mixture was stirred for 1 h. The reaction mixture was then concentrated under reduced pressure and the resulting crude residue was purified by silica gel chromatography (eluent: hexane/$CHCl_3$=2:1) affording **2i** as a transparent light yellow liquid (6.08 g, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.57–0.62 (m, 2H), 1.17 (d, J=6.0 Hz, 18H), 1.69–1.73 (m, 2H), 2.63 (t, J=8.0 Hz, 2H), 3.03 (s, 1H), 4.18 (sept, J=6.0 Hz, 3H), 7.12 (d, J=8.4 Hz, 2H), 7.39 (d, J=8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.6, 24.8, 25.6, 39.1, 64.9, 76.4, 83.9, 119.2, 128.5, 132.0, 143.6. FI-HRMS m/z calcd for $C_{20}H_{32}O_3Si$ (M^+): 348.2121; found: 348.2129.

4.2.3. Synthesis of molecular building blocks containing triallylsilyl group

4.2.3.1. 1-Iodo-4-(3-(triallylsilyl)propyl)benzene. A 300 mL three-neck round-bottom flask connected to a condenser and dry argon flow was charged with a stir bar, 1-allyl-4-iodobenzene (6.0 g, 24.6 mmol), and $[PtCl_2(C_2H_4)]_2$ (7.25 mg, 12.3 μmol, 0.1 mol % Pt). The mixture was cooled to 0 °C, and trichlorosilane (15.0 mL, 149 mmol) was then added dropwise over a period of 15 min at 0 °C. After complete addition of the trichlorosilane, the temperature was progressively raised to room temperature. The mixture was stirred for 15 h at room temperature. The reaction mixture was concentrated under reduced pressure and the residue was dissolved in dry diethyl ether (10 mL). The mixture was cooled to 0 °C, and allylmagnesium bromide solution (1.0 M in diethyl ether, 98.0 mL, 98.0 mmol) were added dropwise over a period of 30 min. The reaction mixture was stirred for 20 h at room temperature. The resulting mixture was quenched with saturated NH_4Cl aqueous solution at 0 °C, and organic phase was extracted with diethyl ether and washed with brine and dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude residue was purified by bulb-to-bulb distillation (130 Pa, 90 °C) affording title compound as a transparent colorless liquid (5.73 g, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.60–0.63 (m, 2H), 1.58 (d, J=8.0 Hz, 6H), 1.56–1.66 (m, 2H), 2.55 (t, J=8.0 Hz, 2H), 4.84–4.89 (m, 6H), 5.70–5.81 (m, 3H), 6.91 (d, J=8.0 Hz, 2H), 7.59 (d, J=8.0 Hz, 2H). FI-HRMS m/z calcd for $C_{18}H_{25}ISi$ (M^+): 396.0770; found: 396.0766.

*4.2.3.2. 4-(3-(Triallylsilyl)propyl)-1-(trimethylstannyl)benzene (**3**).* A 100 mL two-neck round-bottom flask connected to dry argon flow was charged with a stir bar, 1-iodo-4-(3-(triallylsilyl)propyl) benzene (2.32 g, 5.85 mmol), and dry THF (16 mL). The mixture was

cooled to 0 °C, and isopropylmagnesium chloride solution (2.0 M in THF) (6.0 mL, 12.0 mmol) was added dropwise over a period of 5 min. The reaction mixture was stirred for 8 h at 0 °C. Then, trimethyltin chloride (2.40 g, 12.0 mmol) was added one-portion. It was then allowed to reach room temperature and stirred for 15 h. The resulting mixture was quenched with saturated NH_4Cl aqueous solution at 0 °C, and organic phase was extracted with diethyl ether and washed with brine and dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure affording **3** as a transparent colorless liquid (2.50 g, 99% yield). Compound **3** was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.28 (t, J=24.8 Hz, 9H), 0.64–0.68 (m, 2H), 1.58 (d, J=8.4 Hz, 6H), 1.62–1.68 (m, 2H), 2.59 (t, J=7.6 Hz, 2H), 4.83–4.89 (m, 6H), 5.71–5.81 (m, 3H), 7.15 (d, J=8.0 Hz, 2H), 7.41 (d, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ −9.6, 11.5, 19.5, 25.7, 39.9, 113.5, 128.2, 134.3, 135.8, 138.8, 142.4. FI-HRMS m/z calcd for $C_{21}H_{34}SiSn$ (M^+): 434.1452; found: 434.1446.

4.2.4. Synthesis of DTDPP-bridged organosilane

*4.2.4.1. 3,6-Bis(5-(4-(triisopropoxysilyl)propyl)phenylthiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione (**4a**).* A 100 mL two-neck round-bottom flask connected to a condenser and dry argon flow was charged with a stir bar, **2e** (420 mg, 0.86 mmol), 3,6-di(2-bromothien-5-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-*c*]pyrrole-1,4-dione (198 mg, 0.29 mmol), tris(dibenzylideneacetone) dipalladium(0) (13.3 mg, 0.015 mmol, 10 mol% Pd), tri(2-furyl) phosphine (14.6 mg, 0.058 mmol, 20 mol%), and dry THF (30 mL). The temperature was progressively raised to 70 °C and then the reaction mixture was stirred for 20 h. The reaction mixture was then concentrated under reduced pressure and the resulting crude residue was purified by flash chromatography (eluent: hexane/EtOAc=40:1) affording **4a** as a dark blue tacky solid (289 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.62–0.66 (m, 4H), 0.87 (t, J=6.8 Hz, 6H), 0.91 (t, J=7.2 Hz, 6H), 1.19 (d, J=6.4 Hz, 36H), 1.24–1.42 (m, 16H), 1.72–1.80 (m, 4H), 1.90–2.00 (m, 2H), 2.67 (t, J=7.6 Hz, 4H), 4.03–4.13 (m, 4H), 4.20 (sept, J=6.4 Hz, 6H), 7.23 (d, J=8.4 Hz, 4H), 7.42 (d, J=4.0 Hz, 2H), 7.58 (d, J=8.4 Hz, 4H), 8.96 (d, J=4.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.6, 11.8, 14.1, 23.1, 23.7, 25.0, 25.6, 28.6, 30.4, 39.0, 39.2, 46.0, 64.9, 108.0, 124.0, 126.0, 128.3, 129.3, 130.7, 136.8, 139.8, 143.8, 150.0, 161.7. ESI-HRMS m/z calcd for $C_{66}H_{100}N_2NaO_8S_2Si_2$ ($M+Na^+$): 1191.6357; found: 1191.6323. The same procedure was followed for the synthesis of DPP-bridged triallylsilane (**4b**) as described below.

*4.2.4.2. 3,6-Bis(5-(4-(triallylsilyl)propyl)phenylthiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione (**4b**).* Dark blue tacky solid. Yield: 57%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.64–0.68 (m, 4H), 0.87 (t, J=7.2 Hz, 6H), 0.92 (t, J=7.2 Hz, 6H), 1.23–1.44 (m, 16H), 1.59 (d, J=8.4 Hz, 12H), 1.64–1.72 (m, 4H), 1.91–1.98 (m, 2H), 2.65 (t, J=7.6 Hz, 4H), 4.03–4.11 (m, 4H), 4.84–4.91 (m, 12H), 5.71–5.82 (m, 6H), 7.22 (d, J=8.0 Hz, 4H), 7.44 (d, J=4.0 Hz, 2H), 7.59 (d, J=8.0 Hz, 4H), 8.96 (d, J=4.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.6, 11.3, 14.1, 19.5, 23.1, 23.6, 25.5, 28.5, 30.3, 39.2, 39.6, 45.9, 108.0, 113.6124.0, 126.0, 128.3, 129.2, 130.7, 134.2, 136.8, 139.7, 143.4, 149.8, 161.6. ESI-HRMS m/z calcd for $C_{66}H_{88}N_2NaO_2S_2Si_2$ ($M+Na^+$): 1083.5724; found: 1083.5712.

4.2.5. Preparation of DTDPP-bridged organosilica film. DTDPP-bridged organosilane **4a** (12.4 mg, 10.6 μmol) was dissolved in THF (3.4 mL) and then 2 mol/L HCl aqueous solution (8.5 μL) was added to the solution (5 mM in THF). The mixture was stirred at room temperature for 45 min. The sol solution was coated on a quartz glass plate by spin-coating (1000 rpm, 30 s) and dried under reduced pressure to give an organosilica film.

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