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To cite this version:

Yujia Liu, Nobuhiro Takeda, Armelle Ouali, Masafumi Unno. Synthesis, Characterization, and Functionalization of Tetrafunctional Double-Decker Siloxanes. Inorganic Chemistry, 2019, 58 (7), pp.4093-4098. 10.1021/acs.inorgchem.9b00416 . hal-02108359

HAL Id: hal-02108359

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Submitted on 11 Dec 2020

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Synthesis, Characterization and Functionalization of Tetrafunctional Double-Decker Siloxanes

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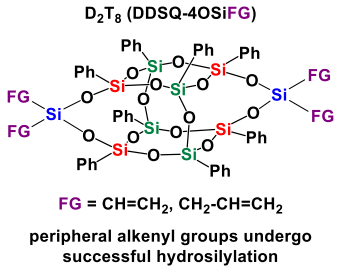
Supporting Information Placeholder

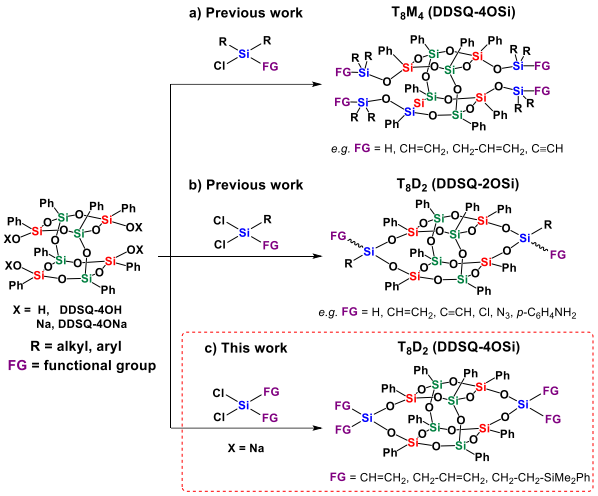
ABSTRACT: Novel tetravinyl- and tetraallyl-substituted closed double-decker siloxanes (DDSQ) were synthesized, characterized and their structures were elucidated by X-ray crystallographic analysis. Moreover, it was shown that peripheral olefins could successfully undergo hydrosilylation quantitatively. Such tetra-functionalizable DDSQ (DDSQ-Vinyl$_4$ and DDSQ-Allyl$_4$) thus constitute promising building blocks for more complex inorganic-organic hybrid materials.



Hybrid nanostructured molecules, combining the thermostability of inorganics with the chemical flexibility of organics, have recently attracted growing interest in many areas of chemistry. Among them, polyhedral oligomeric silsesquioxanes[1] (POSS), and especially cubic octasilsesquioxanes (T_8), involving inorganic nano-sized Si-O core and organic reactive peripheral parts, have been intensively studied and constitute a tunable platform for many applications.[2] Just over a decade ago, another class of POSS, the double-decker siloxanes (DDSQ), was reported by Yoshida *et al.* for the first time.[3] The current chemistry and applications of DDSQ have been recently reviewed by Marciniec *et al.*[4] Two possible structures may be distinguished: the first one is an open T_8M_4 (DDSQ-4OSi) architecture[5] (Scheme 1a) while the other one is a closed D_2T_8 (DDSQ-2OSi) framework (1b).[3b,6] Both of them are prepared from the same DDSQ-4OX (X = H or Na) precursor by nucleophilic substitution with the suitable functional chlorosilane or dichlorosilane respectively (Scheme 1a,b).[4,7] T_8M_4 and T_8D_2-DDSQ structures were applied in various areas of chemistry such as optics,[8] coordination chemistry[9] or polymer nanocomposites.[10-14]

In general, the introduction of reactive groups onto the T_8M_4 and T_8D_2-DDSQ architectures is highly relevant to next include the DDSQ units in more complex systems (*e.g.* electronic or optic devices, coordination complexes, hybrid polymers,…). Along these lines, T_8M_4-DDSQ involving four H, alkenyl or ethynyl functional groups were recently designed.[15] Besides, the number of examples of difunctional closed T_8D_2-DDSQ architectures with one reactive group on each side has also increased (*e. g.* FG = *p*-C_6H_4-NH_2,[11] H,[12] alkenyl,[13] -$(CH_2)_3$-N_3,[14] -$(CH_2)_3$-Cl,[16] Scheme 1b). Difunctional T_8D_2-DDSQ are generally obtained as isomers mixtures, geometric *cis* and *trans*- isomer formation corresponding to the different spatial arrangements of the FG and R groups on the DDSQ core (Scheme 1b).[11,13,14] DDSQ involving two Si-H or two alkenyl groups (Scheme 1b, T_8D_2, FG = H or CH=CH_2 resp.) can be further functionalized by hydrosilylation for the former ones[12] or through catalytic metathesis, silylation or Heck couplings for the latter ones.[13]

Scheme 1. Structures and synthetic pathways of double-decker siloxanes (DDSQ) derivatives.



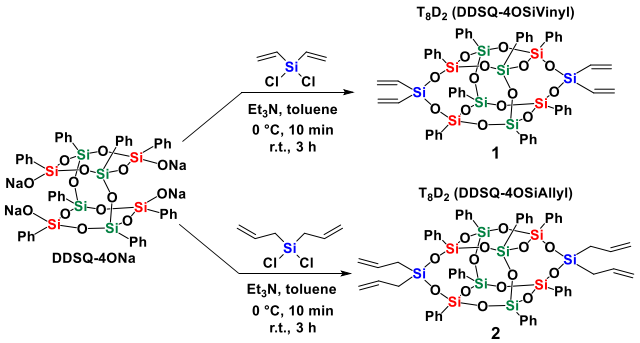
Although examples of tetrafunctional T_8M_4-DDSQ have already been reported,[15] the development of synthetic methodologies leading to other multivalent functionalizable DDSQ architectures is highly desirable. Along these lines, closed T_8D_2 architectures displaying four reactive groups have been hardly explored so far (Scheme 1c). Different properties are yet expected from these closed and more rigid DDSQ structures compared to related open tetrafunctional T_8M_4-DDSQ previously described.[15] Herein, the synthesis of novel tetravinyl- and tetraallyl-substituted closed T_8D_2-DDSQ (Scheme 2, DDSQ-Vinyl$_4$ (**1**) and DDSQ-Allyl$_4$ (**2**)) is reported. DDSQ **1** and **2** were characterized by several techniques including multinuclear NMR and mass spectroscopies, and their structures were elucidated by X-ray crystallography. Moreover, peripheral

alkenyl groups could be further successfully functionalized through hydrosilylation with Me_2PhSiH as model substrate, showing that reported tetra-functionalizable T_8D_2-DDSQ are promising precursors for inorganic-organic hybrid materials.

RESULTS AND DISCUSSION

DDSQ **1** and **2** were synthesized by the hydrolytic condensation of incompletely condensed silsesquioxane DDSQ-4ONa $(Ph_8Si_8O_8)(ONa)_4$[17] with commercially available divinyldichlorosilane and diallyldichlorosilane respectively in toluene (Scheme 2). The target tetra-substituted DDSQ **1** and **2** were obtained in 67% and 50% isolated yield respectively after washing of the crude products with 2-propanol. These isolated yields are higher than those generally obtained for difunctional T_8D_2-DDSQ (Scheme 1b), only one isomer being formed due to the symmetry of the dichlorosilane used (Scheme 1c). Noteworthy, DDSQ-4OH, obtained from DDSQ-4ONa under acidic conditions,[17] is often used as the precursor for the preparation of T_8D_2-DDSQ. The synthetic pathway proposed here allows not only to skip the hydrolysis step, but also to avoid the formation of HCl gas during the condensation. The presence of triethylamine was however required for obtaining better yields and selectivities, although its role can not be rationalized yet.

Scheme 2: Synthesis of DDSQ **1** and **2** from DDSQ-4ONa.



Crystals were next grown and the structures of **1** and **2** could be studied by X-ray crystallography (Figures 1 and 2). As expected, both symmetrical structures were very similar. The Si-O bond lengths were in the ranges of 1.605(6)–1.636(7) Å (average 1.617(6) Å) for **1** and 1.607(9)–1.634(8) Å (average 1.619(9) Å) for **2** which was in accordance with previously reported T_8D_2-DDSQ including symmetrical tetraphenyl-[7] or unsymmetrical divinyl-[13d] DDSQ. Si–C lengths were also consistent with those found in the same previous reports (in the ranges of 1.839(2)–1.847(7) Å (average 1.842(5) Å) for **1** and 1.845(6)–1.869(2) Å (average 1.852(6) Å) for **2**). Besides, in compound **1**, the Si–O–Si bond angles vary from 137.2(2) to 161.0(8)° and in compound **2**, the Si–O–Si bond angles are in the range of 138.8(8)-166.3(7)°. The Si–O–Si bond angles in two compounds display a considerable variation due to the presence of both 8- and 10-membered rings. Such phenomenon was also observed previously for tetraphenyl-[7] or divinyl-[13d] DDSQ.

DDSQ **1** and **2** were analyzed by matrix-assisted laser desorption/ionization coupled time-of-flight (MALDI-TOF) mass spectroscopy and the experimental mass spectra were in very good agreement with the calculated molecular weight (see SI, Figure S8). ^{1}H, ^{13}C and ^{29}Si NMR spectroscopies were also performed to characterize DDSQ **1** and **2**. Both ^{29}Si NMR spectra clearly displayed signals corresponding to the D-group silicon atoms (**Si** in blue, Scheme 2), Si atoms bonded to two oxygen atoms, at δ –46.7 in **1** and –28.5 in **2**.[11b] The shielding observed in the case of **2** might be rationalized by the enhanced electro-donating properties of the allyl substituents compared to the vinyl ones. Besides, the ^{29}Si resonances at δ –78.2 and –78.8 ppm, respectively for **1** and **2**, have been assigned to T-group silicon atoms from the core, nearest to the D-group silicon atoms (**Si** in red connected to three oxygen atoms).[11b] The other internal T-group silicon atoms (**Si** in green) gave rise to singlets at δ –79.5 and δ –79.6 ppm (for **1** and **2** respectively). In conclusion, these spectroscopic data, confirmed by ^{1}H and ^{13}C NMR spectra (ESI, S2–S4), are consistent with the successful synthesis of **1** and **2**.

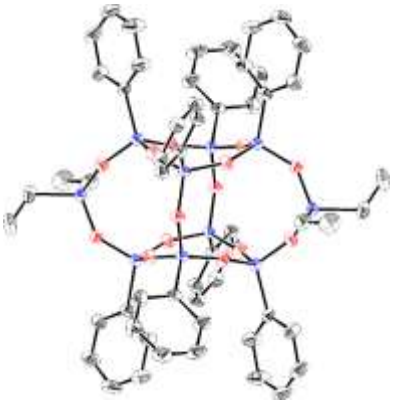


Figure 1. Crystal structure of **1**. Black: carbon; blue: silicon; red: oxygen. Thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity.

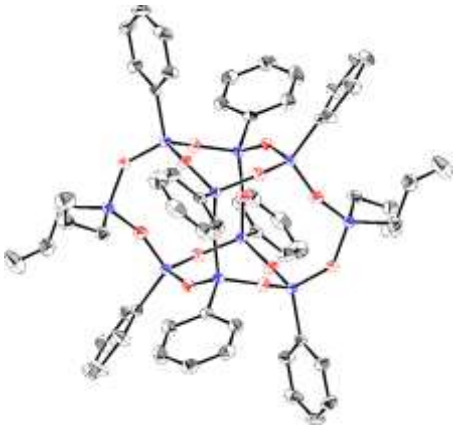


Figure 2. Crystal structure of **2**. Black: carbon; blue: silicon; red: oxygen. Thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity.

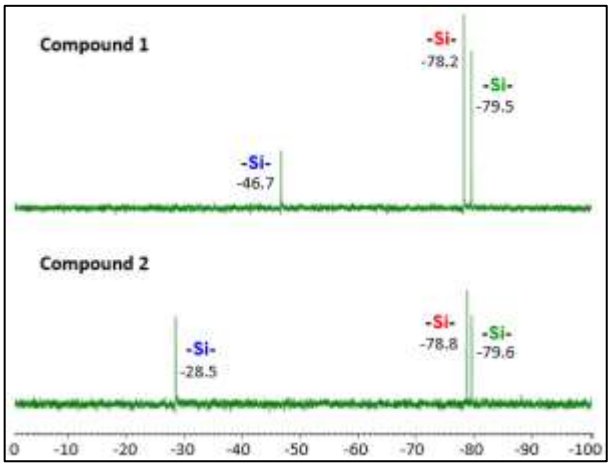
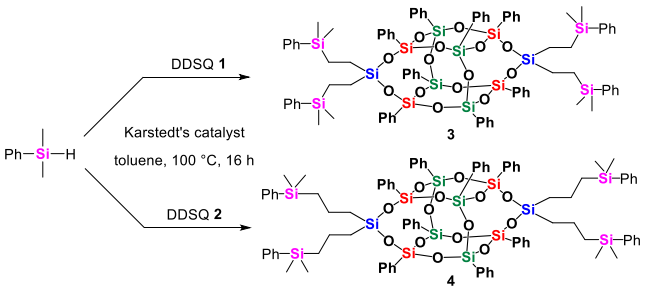


Figure 3. ^{29}Si NMR spectra ($CDCl_3$) for the DDSQ **1** and **2**. Chemical shifts are in ppm unit.

With the new functionalizable T_8D_2-DDSQ **1** and **2** in hand, the reactivity of external alkenyl (vinyl and allyl) groups was next explored. Catalytic hydrosilylation was thus performed by using dimethylphenylsilane as a model substrate (Scheme 3) in the presence of the Karstedt's catalyst. Expected T_8D_2-DDSQ **3** and **4**, respectively obtained from **1** and **2**, were obtained in 70 and 77% isolated yields respectively, after recrystallization of the crude product from a chloroform/2-propanol mixture. Crystals were next grown and the structures of **3** and **4** could be studied by X-ray crystallography (Figures 4, 5). The Si–O bond lengths were found to be quite similar to those observed for **1** and **2** (in the range of 1.597(5)–1.634(7) Å (average 1.617(6) Å) for **3** and in the range of 1.608(2)–1.624(2) (average 1.616(8) Å) for **4**). The Si–O–Si bond angles vary from 135.2(0) to 173.8(2)° in **3** and from 147.2(5) to 156.2(8)° in **4**. This large deviation of bond angels clearly indicates the flexible structure of the framework. ^{29}Si NMR spectra of **3** and **4** displayed expected and previously described signals for T silicon atoms (red and green ones) corresponding to the DDSQ core (see SI). For **3**, the signals of D silicon atoms (blue color) were shifted to δ –21.4 as compared to δ –46.7 in **1** which is in the favor of a successful reduction of the vinyl function. Noteworthy, the appearance of a new singlet at δ –0.9 and δ –3.5 ppm for **3** and **4** respectively, is consistent with the formation of the carbosilane moiety[18] and therefore the successful and quantitative hydrosilylation of vinyl and allyl units. Data obtained from ^{1}H and ^{13}C NMR and MALDI-TOF spectroscopies confirmed the structures of **3** and **4** (see SI, Figures S5–S6, S9). To our knowledge, the only previous example of tetrafunctionalizable DDSQ involves four reactive Si-Cl bonds[3b] likely to react with hydroxylated compounds. The non-hydrolizable unsaturated C-C bonds reported here open the way to many possibilities in terms of functionalizations beyond hydrosilylation such as other hydroelementations (hydroaminations, hydroborations…), metathesis or Heck couplings.

Scheme 3: Hydrosilylation of DDSQ **1** and **2**.



Noteworthy, for all T_8D_2-DDSQ **1** to **4**, the results of thermogravimetric (TG) analysis in N_2 show high Td_5 (388 °C for **1**, 452 °C for **2**, 440 °C for **3** and 446 °C for **4**, see SI, Figures S14–S16) demonstrating their high thermal stability. As a point of comparison, the related non-functionalizable T_8D_2-DDSQ bearing 4 phenyl groups was previously reported to display a Td_5 of 425 °C which is in the same order of magnitude.[7] The melting point (Tm) of compounds **1-4** decreased following the order of the side siloxane chain length.

In summary, novel T_8D_2-DDSQ involving four reactive substituents, either vinyl- or allyl-, were prepared, characterized and their structures were elucidated by X-ray crystallographic analysis. The synthetic method is simple and the expected T_8D_2-DDSQ **1** and **2** could be isolated in good yields and very high purities. In addition, terminal alkenyl substituents were shown to successfully undergo hydrosilylation with dimethylphenylsilane used as a model substrate. DDSQ **1** and **2** thus constitute promising building blocks for inorganic-organic hybrid materials and applications are currently studied in our laboratories.

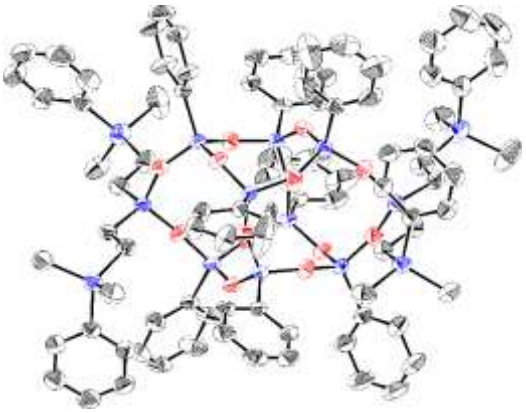


Figure 4. Crystal structure of **3**. Black: carbon; blue: silicon; red: oxygen. Thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity.

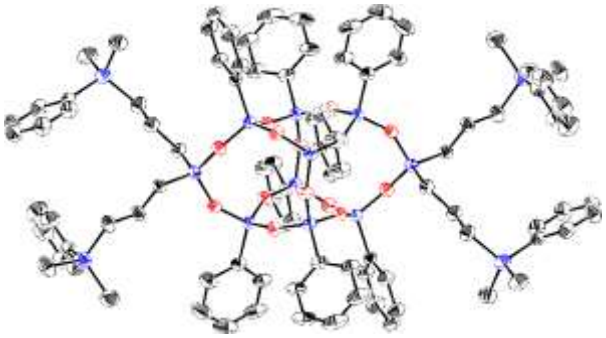


Figure 5. Crystal structure of **4**. Black: carbon; blue: silicon; red: oxygen. Thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity.

EXPERIMENTAL SECTION

THF was dried using mBRAUN purification system. Toluene was distilled from calcium hydride, stored on 4 Å activated molecular sieves under an argon atmosphere. Triethylamine was distilled from potassium hydroxide, stored on potassium hydroxide under an argon atmosphere with protection from light. Divinyldichlorosilane and diallyldichlorosilane were purchased from Shin-Etsu Chemical Co., Ltd and used without further purification. All reactions were performed under argon atmosphere. The Fourier transformation nuclear magnetic resonance (NMR) spectra were obtained using a JEOL JNM-ECS 300 (^{1}H at 300.53 MHz, ^{13}C at 75.57 MHz, ^{29}Si at 59.71 MHz), JEOL JNM-ECA 400 (^{1}H at 399.78 MHz) and JEOL JNM-ECA 600 (^{1}H at 600.17 MHz, ^{13}C at 150.91 MHz, ^{29}Si at 119.24 MHz) NMR instruments. For ^{1}H NMR, chemical shifts are reported as units (ppm) relative to $SiMe_4$ (TMS) and the residual solvents peaks were used as standards. For ^{13}C NMR and ^{29}Si NMR, chemical shifts are reported as units (ppm) relative to $SiMe_4$ (TMS), the residual solvents peaks were used as standards and spectra were obtained with complete proton decoupling. MALDI-TOF mass analysis were carried out with a Shimadzu AXIMA Performance instrument using 2,5-dihydroxybenzoic acid (dithranol) as the matrix and $AgNO_3$ as the ion source. All reagents used were of analytical grade. Elemental analyses were performed by the Center for Material Research by Instrumental Analysis (CIA), Gunma University, Japan. Infrared spectra were

measured with a Shimadzu FTIR-8400S. The thermogravimetric analyses were carried out with a Rigaku thermal gravimetric analyzer (Thermoplus TG-8120). The investigations were carried out under nitrogen flow (250 mL min^{-1}) with a heating rate 10 °C min^{-1}. All samples were measured with temperatures ranging from 50 °C to 1000 °C, where they remained for 5 minutes. Weight loss and heating rate were continuously recorded along the experiment.

Synthesis of 1. Divinyldichlorosilane (0.85 mL, 6.0 mmol) was added dropwise to a mixture of DDSQ-4ONa (2.314 g, 2.0 mmol) and triethylamine (0.81 mL, 6.0 mmol) in toluene (23.5 mL) at 0 °C. The mixture was then allowed to stir at room temperature for 3 h. Chloroform was added to the reaction mixture, and the organic layer was washed with saturated ammonium chloride aqueous solution and brine. The organic phase was dried over anhydrous sodium sulfate and evaporated to afford a crude solid further purified by washing with 2-propanol to give **1** (1.64 g, 67 %) as colorless crystals. Spectral data for **1**: ^{1}H NMR (600.17 MHz, $CDCl_3$): δ 5.99-6.16 (m, 12H), 7.19-7.22 (m, 8H), 7.27-7.28 (m, 8H), 7.41-7.46 (m, 16H), 7.57-7.58 (m, 8H) ppm. $^{13}C\{^{1}H\}$ NMR (150.91 MHz, $CDCl_3$): δ 127.76, 127.97, 130.49, 130.57, 131.09, 131.93, 133.62, 134.17, 134.28, 136.00 ppm. $^{29}Si\{^{1}H\}$ NMR (119.24 MHz, $CDCl_3$): δ -46.68, -78.21, -79.54 ppm. MALDI-TOF MS (*m/z*): 1252.31 ($[M+Na]^+$, calcd 1252.86).

Synthesis of 2. Same procedure as for the synthesis of **1** from diallyldichlorosilane (1.0 mL, 6.0 mmol). The crude product was further purified by washing with 2-propanol to give **2** (1.298 g, 50 %) as a colorless crystal. Spectral data for **2**: ^{1}H NMR (600.17 MHz, $CDCl_3$): δ 1.79-1.83 (m, 8H), 4.77-4.92 (m, 8H), 5.77-5.84 (m, 4H), 7.21-7.57 (m, 40 H) ppm. $^{13}C\{^{1}H\}$ NMR (150.91 MHz, $CDCl_3$): δ 22.79, 127.83, 127.94, 130.59, 131.05, 131.85, 132.40, 134.19 ppm. $^{29}Si\{^{1}H\}$ NMR (119.24 MHz, $CDCl_3$): δ -28.49, -78.75, -79.58 ppm. MALDI-TOF MS (*m/z*): 1308.31 ($[M+Na]^+$, calcd 1308.97).

Synthesis of 3. To a mixture of **1** (123 mg, 0.1 mmol) and dimethylphenylsilane (92 uL, 0.6 mmol) in toluene (0.6 mL), Karstedt catalyst (2% Pt, commercial bottle, diluted 100 times in distilled toluene under argon, 112 µL, 0.0025 mmol) was added at room temperature. When the addition was finished, the mixture was allowed to stir for 10 minutes at room temperature and then heated to 100 °C for 16 hours. The reaction mixture was passed through a silica plug and the filtrate evaporated to dryness to afford a slightly yellowish solid further purified by recrystallization from chloroform and 2-propanol to give **3** (0.124 g, 70%) as a colorless crystal. Spectral data for **3**: ^{1}H NMR (600.17 MHz, $CDCl_3$): δ 0.10 (s, 24H), 0.54-0.57 (m, 8H), 0.79-0.82 (m, 8H), 7.12-7.14 (m, 8H), 7.19-7.35 (m, 32H), 7.38-7.43 (m, 12H), 7.50 (dd, J = 9.28, 1.37 Hz, 8 H) ppm. $^{13}C\{^{1}H\}$ NMR (150.91 MHz, $CDCl_3$): δ -3.53, 6.36, 7.35, 127.81 (overlapped), 127.95, 128.81, 130.44, 130.46, 131.25, 132.34, 133.74, 134.12, 134.19, 139.23 ppm. $^{29}Si\{^{1}H\}$ NMR (119.24 MHz, $CDCl_3$): δ -0.93, -21.37, -78.21, -79.17 ppm. MALDI-TOF MS (*m/z*): 1797.59 ($[M+Na]^+$, calcd 1797.93).

Synthesis of 4. Same procedure as for the synthesis of **3** from **2** (129 mg, 0.1 mmol). The crude product was further purified by recrystallization from chloroform and 2-propanol to give **4** (0.141 g, 77%) as a colorless crystal. Spectral data for **4**: ^{1}H NMR (600.17 MHz, $CDCl_3$): δ 0.05 (s, 2 H), 0.72-0.81 (m, 16H), 1.42-1.48 (m, 8H), 7.15-7.18 (m, 8H), 7.22-7.30 (m, 20H), 7.33-7.45 (m, 24H), 7.51-7.52 (m, 8H) ppm. $^{13}C\{^{1}H\}$ NMR (150.91 MHz, $CDCl_3$): δ -3.05, 17.54, 19.89, 20.21, 127.78, 127.81, 127.94, 128.78, 130.43, 130.47, 131.28, 132.32, 133.62, 134.10, 134.25, 139.82 ppm. $^{29}Si\{^{1}H\}$ NMR (119.24 MHz, $CDCl_3$): δ 3.45, -18.95, -78.34, -79.17 ppm. MALDI-TOF MS (*m/z*): 1853.70 ($[M+Na]^+$, calcd 1854.04).

Crystallography.

For crystal data, data collection and refinement, see supporting information (S10-S11). CCDC 1880537 (**1**), CCDC 1880536 (**2**), CCDC 1880538 (**3**) and CCDC 1887329 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic data Centre via www.ccdc.cam.ac.uk/data_request/cif.

ASSOCIATED CONTENT

Supporting Information

^{1}H, ^{13}C, ^{29}Si NMR spectra, MALDI-TOF-MS spectra, IR spectra, crystallographic data and TGA for **1**, **2**, **3** and **4**. The Supporting Information is available free of charge on the ACS Publications website.

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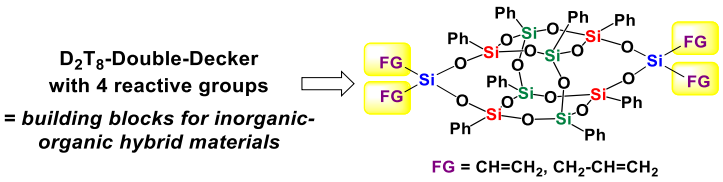

Novel tetravinyl- and tetraallyl-substituted closed double-decker siloxanes (DDSQ) were synthesized and peripheral olefins shown to successfully undergo hydrosilylation quantitatively. Such tetra-functionalizable DDSQ thus constitute promising building blocks for more complex inorganic-organic hybrid materials.