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Synthesis of tripod-shaped oligo(phenylene)s with multiple ethenyl groups at the bases for chemisorption on hydrogen-terminated silicon surfaces

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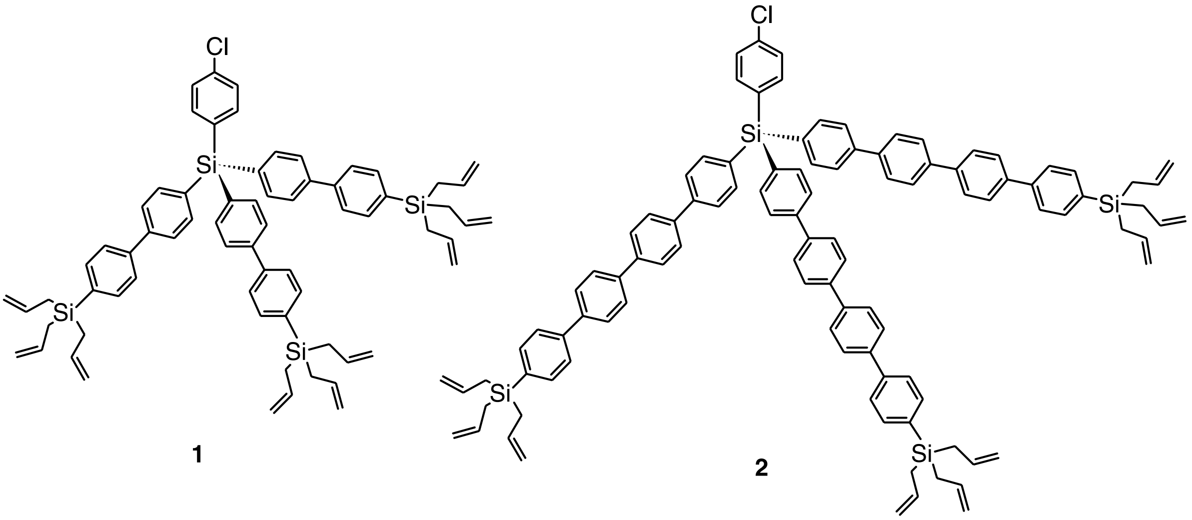
Abstract—This communication describes an efficient and convergent synthesis of monodisperse, nanometer-sized, and tripod-shaped oligo(phenylene)s with a triallylsilyl group at the base of each leg and a chlorophenyl group at the focal point of the tripod. These molecules were designed as model compounds for the study of chemisorption of rigid molecules containing multiple ethenyl groups on hydrogen-terminated silicon surfaces. The compounds were synthesized from *p*-chlorophenyl-tris(*p*-bromophenyl)silane via selective Pd-catalyzed Ishiyama–Miyaura reaction with bis(pinacolato)diboron, followed by Suzuki coupling with aryl dihalides to elongate the legs. The legs were then end-capped with triallylsilyl groups through Suzuki coupling with 4-triallyphenylboronic acid. © 2003 Elsevier Science Ltd. All rights reserved.

Hydrosilylation of 1-alkenes on hydrogen-terminated silicon surfaces leads to well-ordered and robust monolayers that bind to the silicon surfaces via strong Si–C bonds.[1–5] This new class of thin films that directly couples organic materials and semiconductors may find applications in sensors, nonlinear optics, and opto-electronics.[6–9] For many of these potential applications, it is desirable or necessary to control the orientation and density of the functional groups in the films. So far, surface hydrosilylation has been studied only with mono-ethenyl derivatives as the adsorbates. The molecular orientation in the resultant films is determined mainly by the packing and ordering of the molecules. The density of functional molecules in the film may be adjusted by co-deposition with inert molecules, but phase separation often perturbs the system.[10,11] We are interested in exploring the use of multidentate bonding with rigid molecules such as the tripod-shaped **1** and **2** to orient individual molecules, to control the density of the functional groups, and to enhance the stability of the films. Compared to the reported tripod-shaped and rigid adsorbates designed for chemisorption on gold or



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2

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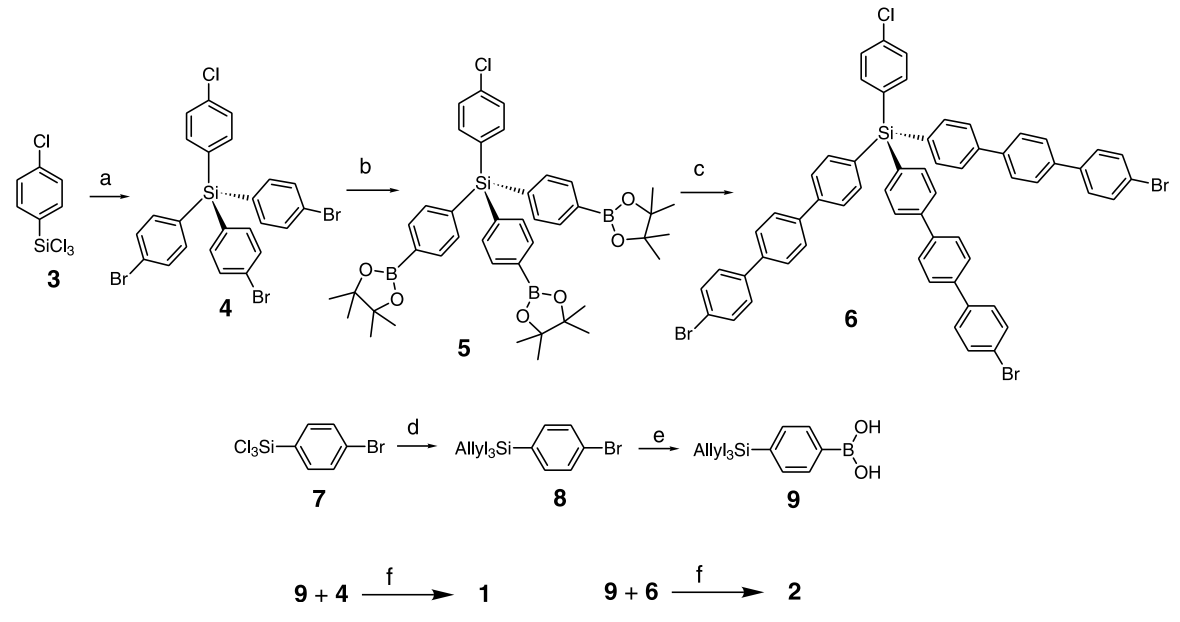

Scheme 1. *Reagents and conditions*: (a) 1,4-dibromobenzene, *n*-BuLi, ether, rt, 12 h, 43%; (b) bis(pinacolato)diboron (3.3 equiv.), $PdCl_2$(dppf) (3 mol%), KOAc, DMSO, 80°C, 3 h, 83%; (c) 4-bromo-4′-iodobiphenyl (3.3 equiv.), $Pd(PPh_3)_4$ (3 mol%), aq. Na_2CO_3, toluene, 85°C, 12 h, 75%; (d) allylMgBr, ether, reflux, 12 h, 79%. (e) *n*-BuLi, −78°C; then B(O-*i*Pr)$_3$, −78°C to rt, 12 h; 2 M HCl; 67%. (f) **9** (3.3 equiv.), $Pd(PPh_3)_4$ (3.0 mol%), aq. Na_2CO_3, toluene, 85°C, 12 h, 82% for **1** and 70% for **2**.

oxide surfaces,[12–15] **1** and **2** have a larger footprint, and can form multiple Si–C bonds with a hydrogen-terminated silicon surface via hydrosilylation, exposing the focal point of the tripod (–PhCl group) for further derivatization, e.g. through Pd-catalyzed coupling reactions.[16,17] Furthermore, the size and rigidity of these molecules make it possible to image the single molecules chemisorbed at flat silicon surfaces by scanning tunneling microscopy (STM). Herein, we describe the syntheses of **1** and **2**.

The reaction of **3** with *p*-bromophenylmagnesium bromide at room temperature generated compound **4** in 43% yield (Scheme 1), where one of the four arms bears a less reactive group (Cl). Using silicon atom as the core for constructing tripod structures has been described by Yao and Tour.[14] Following the procedures developed by Miyaura et al.,[18] the bromine atoms in **4** were replaced with pinacolboronate groups by reaction with 3.3 equiv. of bis(pinacolato)diboron to provide **5** in high yield (83%). The triboronate derivative **5** served as a building block to elongate the three legs by Suzuki coupling with oligo(phenylene)s end-capped with different halide atoms. Thus, Suzuki coupling of **5** with 3.3 equiv. of 4-bromo-4′-iodobiphenyl selectively provided the tribromide derivative **6** in 75% yield. The tribromide **6** can be end-capped with a variety of surface-active groups for chemisorption at different substrate surfaces. For example, to introduce ethenyl groups to **6** for chemisorption on hydrogen-terminated surfaces, allyl groups were introduced to 4-bromophenyltrichlorosilane (**7**) to provide **8** in 79% yield, which was converted to the boronic acid **9** in 67% yield by Li–Br exchange and quenching with B(O-*i*Pr)$_3$. The Suzuki coupling of **4** with 3 equiv. of **9** in toluene under catalytic amount of $(Ph_3P)_4Pd$ afforded **1** in 82% yield. The same conditions were then applied to couple **6** with **9** to furnish the larger tripod molecules **2** in 70% yield. Satisfactory characterization data have been obtained for all new compounds.[19]

In conclusion, we report an efficient and convergent synthesis of nanometer-sized and tripod-shaped oligophenylenes **1** and **2** that are end-capped with multiple allyl groups. The synthetic scheme can be applied to the synthesis of other derivatives of oligophenylene tripods. The triallyl groups at the base of each leg permit the enlargement of the tripod base by repeating hydrosilylation with $HSiCl_3$ and alkenylation with a Grignard reagent to generate carbosilane dendrons[20] for chemisorption on a variety of surfaces.[21,22]

Acknowledgements

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19. **Characterization data for 4**: ^{1}H NMR ($CDCl_3$, 300 MHz): 7.34 (d, 6H, $J=8.1$ Hz), 7.39 (s, 2H), 7.40 (s, 2H), 7.54 (d, 6H, $J=8.1$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): 137.6, 137.4, 136.8, 131.4, 130.9, 128.5, 125.4; MS (EI, *m*/*z*): calcd for $C_{24}H_{16}Br_3ISi$ (M^+) 603.8, found 603.8. Anal. calcd: C, 47.44; H, 2.65. Found: C, 47.48; H, 2.55. **5**: ^{1}H NMR ($CDCl_3$, 300 MHz): 1.90 (d, 18H, $J=8.4$ Hz), 4.89–4.98 (m, 18H), 5.75–5.89 (m, 9H), 7.41 (d, 2H, $J=8.7$ Hz), 7.58 (d, 2H, $J=8.7$ Hz), 7.62 (d, 12H, $J=8.1$ Hz), 7.68 (d, 12H, $J=8.1$ Hz); MS (EI, *m*/*z*): calcd for $C_{69}H_{73}ClSi_4$ (M^+) 1048, found 1048. Anal. calcd: C, 78.92; H, 7.01. Found: C, 78.69; H, 7.01. **6**: ^{1}H NMR ($CDCl_3$, 300 MHz): 1.94 (d, 18H, $J=8.4$ Hz), 4.93–5.02 (m, 18H), 5.79–5.94 (m, 9H), 7.45 (d, 2H, $J=8.7$ Hz), 7.61–7.78 (m, 50H); ^{13}C NMR ($CDCl_3$, 75 MHz): 142.0, 141.4, 139.9, 139.9, 139.7, 139.6, 137.8, 136.9, 136.3, 134.8, 134.2, 133.8, 132.7, 132.6, 128.3, 127.6, 127.5, 127.4, 127.4, 126.4, 126.3, 114.4, 19.7. **8**: ^{1}H NMR ($CDCl_3$, 300 MHz): 1.83–1.86 (m, 6H), 4.88–4.95 (m, 6H), 5.69–5.84 (m, 3H), 7.37 (d, 2H, $J=8.4$ Hz), 7.70 (d, 2H, $J=8.4$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): 135.8, 134.0, 133.4, 130.9, 124.3, 114.6, 19.4; MS (EI, *m*/*z*): calcd for $C_{15}H_{39}BrSi$ (M^+) 306.0, found 306.0. Anal. calcd: C, 58.63; H, 6.23. Found: C, 58.55; H, 6.17. **9**: ^{1}H NMR ($CDCl_3$, 300 MHz): 1.93 (d, 6H, $J=7.8$ Hz), 4.91–4.99 (m, 6H), 5.75–5.90 (m, 3H), 7.67 (d, 2H, $J=7.8$ Hz), 8.21 (d, 2H, $J=7.8$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): 140.9, 134.6, 133.8, 133.6, 111.5, 19.4. **1**: ^{1}H NMR ($CDCl_3$, 300 MHz): 1.90 (d, 18H, $J=8.4$ Hz), 4.89–4.98 (m, 18H), 5.75–5.89 (m, 9H), 7.41 (d, 2H, $J=8.7$ Hz), 7.58 (d, 2H, $J=8.7$ Hz), 7.62 (d, 12H, $J=8.1$ Hz), 7.67 (d, 12H, $J=8.1$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): 142.2, 141.4, 137.7, 136.8, 136.3, 135.1, 134.8, 134.4, 133.7, 132.6, 128.3, 126.7, 126.4, 114.4, 19.6; MS (EI, *m*/*z*): calcd for $C_{69}H_{73}ClSi_4$ (M^+) 1048, found 1048. Anal. calcd: C, 78.92; H, 7.01. Found: C, 78.69; H, 7.01. **2**: ^{1}H NMR ($CDCl_3$, 300 MHz): 1.94 (d, 18H, $J=8.4$ Hz), 4.93–5.02 (m, 18H), 5.79–5.94 (m, 9H), 7.45 (d, 2H, $J=8.7$ Hz), 7.61–7.78 (m, 50H); ^{13}C NMR ($CDCl_3$, 75 MHz): 142.0, 141.4, 139.9, 139.9, 139.7, 139.6, 137.8, 136.9, 136.3, 134.8, 134.2, 133.8, 132.7, 132.6, 128.3, 127.6, 127.5, 127.4, 127.4, 126.4, 126.3, 114.4, 19.7; MALDI-TOF-MS with CF_3COOAg as the matrix: calcd for $C_{105}H_{97}ClSi_4Ag$ ($[M+Ag]^+$) 1611.54, found 1611.44.
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