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Synthesis and Structural Analysis of Substituted Tripod-Shaped Tri- and Tetra(*p*-phenylene)s

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We report here the synthesis of several tripod-shaped oligo(*p*-phenylene)s with legs composed of three or four phenylene units. Each leg is end-capped with an iodine atom or a TMS or carboxyl group, and an ethoxy group is present on the functional arm. The tripod containing methyl tri(ethylene glycol) side chains was designed for biological applications. The key step in the synthesis is the Pd-catalyzed Suzuki cross-coupling reaction of the silicon-derived core molecule with the appropriately substituted *p*-biphenyl moiety. This synthesis should be considered a new strategy for these compounds, as iterative coupling of the substituted *p*-biphenyl building blocks with the first-generation tripods will allow the homologation of the tripod legs to obtain giant tripod-shaped oligo(*p*-phenylene)s. Also, the iodine end-capped leg with the ethoxy group on the functional arm permits modular design of the tripod for further functionalization, which will define the applications of the tripod-nanostructured surfaces. The structure of some of the synthesized tripods was studied through both experimental (Raman spectra) and theoretical (DFT calculation) methods.

Introduction

Controlling the orientation and spacing of functional moieties in organic thin films is of great importance for both the study of fundamental biomolecular interactions at interfaces and for biosensor applications. An optimal spacing exists between the functional moieties that are perpendicularly oriented on the film surface for maximizing the binding strength and density of target molecules. In addition, the thin films should resist the nonspecific adsorption of proteins and should ideally be readily functionalized by using bio-orthogonal reactions, such as click or Suzuki reactions.[1–3]

The most common method to control the average density of the functional groups on monolayer surfaces prepared by self-assembly of monodentate adsorbates is by co-deposition with inert analogous adsorbates. However, it is not possible to avoid nonrandomized mixing on the nanoscale that prevents controlling the spacing between the functional surface groups.[4,5]

To avoid this problem and to control the orientation of the functional moieties, several large, shape-persistent, and self-standing molecules have been developed, including: (i) "molecular caltrops" with four phenylacetylene legs extending from either a tetrahedral silicon core[6,7] or from an adamantane core,[8,9] (ii) conically shaped dendron adsorbates with a functional group at the core,[10–13] and (iii) tripod-shaped oligo(*p*-phenylene)s joined together by a single silicon atom[14,15] to be used for the functionalization of different surfaces (Figure 1). However, these reported tripod-shaped molecules cannot be used for biological applications, because the hydrophobic tripod framework, or in some cases its alkyl side chains,[14] are known to interact nonspecifically with protein molecules, thus interfering with the specific interaction of target molecules with the ligand on the focal point of the tripod. To overcome the problem, we must develop modified tripod molecules with appropriate side chains to avoid the interaction with protein molecules.

We have chosen tripodal oligo(*p*-phenylene)s as the ideal anisotropic adsorbates for two reasons. Firstly, we have shown that the *p*-phenylene legs are sufficiently rigid to maintain the perpendicular orientation of the functional arm at the focal point of the tripod with respect to the surface.[16,17] Secondly, the functional arm of these tripods can be readily functionalized on the surface; for example, the bromophenyl-terminated arm reacts on the surface with arylboronic acid derivatives through Suzuki coupling in high yield (>90%).[18]

A tripod with three hepta(*p*-phenylene) legs was synthesized by coupling of three hexa(*p*-phenylene) building blocks to a tetraphenylsilicon core, in accordance with retrosynthetic pathway A (Scheme 1).[14] The limitations of this approach include the low solubility of the oligo(*p*-phen-

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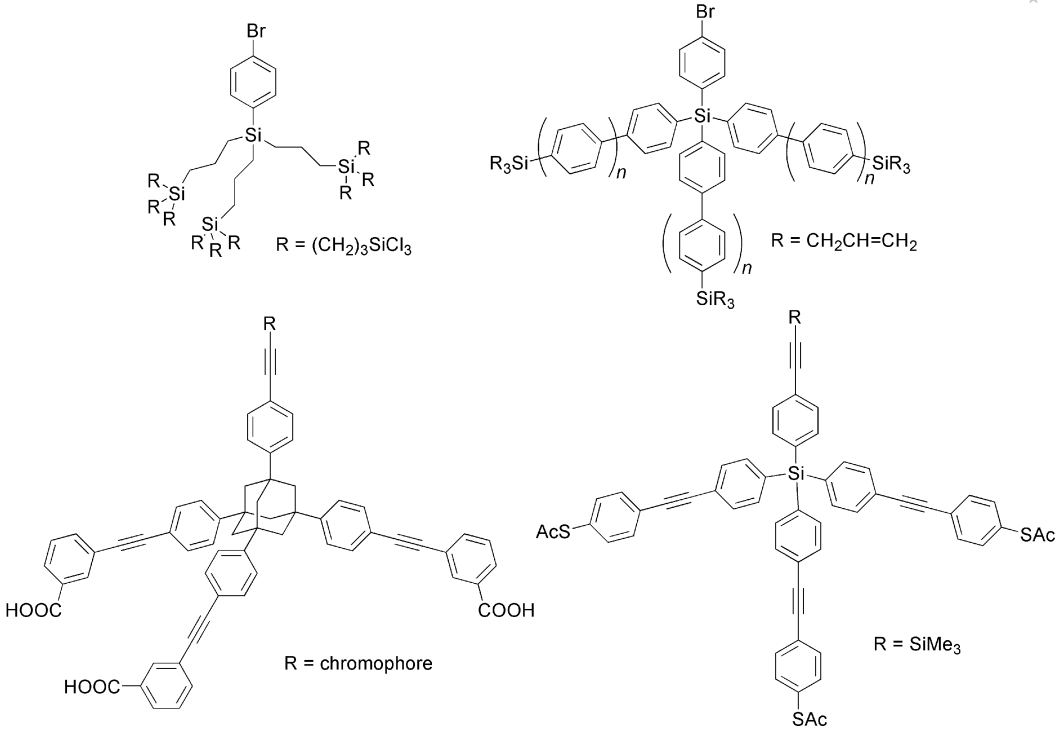
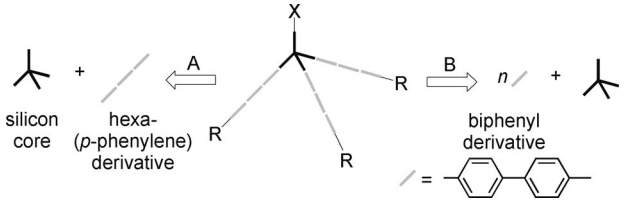


Figure 1. Self-standing and shape-persistent molecules for surface nanostructuration.

ylene) moieties, even with side chains, and the difficulty of chemical differentiation between both ends of the oligo(*p*-phenylene) moiety.



Scheme 1. Retrosynthetic analysis.

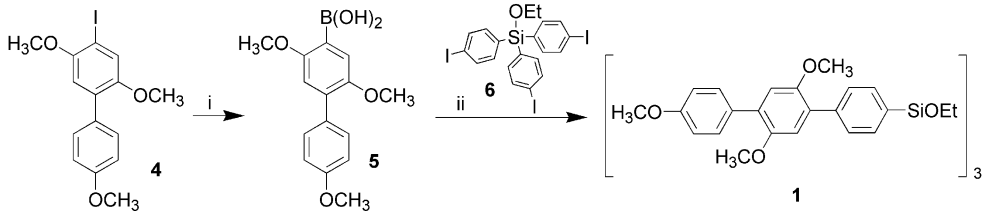
In this paper, we report the synthesis of several substituted tripod shaped *p*-phenylenes, with each tripod leg composed of three or four phenylene units, by coupling biphenyl derivatives to a silicon core, following an approach (Scheme 1, pathway B) that is conceptually different to that previously mentioned (Scheme 1, pathway A). The key step for the synthesis of the tripods is the Pd-catalyzed Suzuki cross-coupling of a triphenylene-silicon core with *p*-biphenyl building blocks. One of the tripods has oligo(ethylene glycol) (OEG) side chains for resisting any nonspecific adsorption of proteins.[19–24] Finally, a discussion on the structure of selected tripods was presented on the basis of Raman spectra and density functional theory calculations.

Results and Discussion

We first tested the above approach for the preparation of simple tripod **1** (Scheme 2). Biphenyl **4** was prepared by following the procedure reported by Lee[25] starting from 1,4-dibromo-2,5-dimethoxybenzene and *p*-trimethylsilylphenylboronic acid. The reaction of trimethoxy derivative **4** with *n*-butyllithium in THF followed by trimethoxy borate generated compound **5** in 28% yield (Scheme 2).

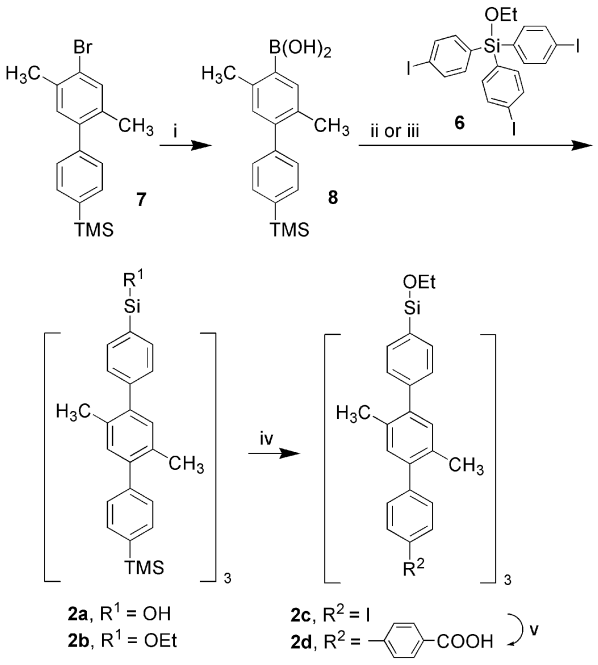
The use of a silicon atom as the core for constructing tripod structures was described by Tour.[6] The coupling of **5** with **6** under standard Suzuki conditions by using $Pd(PPh_3)_4$ as a catalyst produced tripod **1** in good yield (71%). We recently improved this reaction by using heterogeneous Pd/C nanoparticles as the catalyst[26] to obtain **1** in 75% yield. This catalyst avoids the removal of triphenylphosphane oxide from the conventional $Pd(PPh_3)_4$ catalyst and allows large-scale synthesis of the compound. Compound **1** is soluble in most organic solvents.

Following the same pathway, we prepared methylated tripods **2** (Scheme 3). We chose dimethylated *p*-biphenyl as the tripod leg as it can be easily brominated on the methyl groups (see below), allowing further functionalization. *p*-Biphenyl **7** was prepared by following the procedure reported by Müllen[27] in a repetitive approach starting from 5-bromo-2-iodo-*p*-xylene and *p*-trimethylsilylphenylboronic acid (62% yield). However, we obtained a better yield (98%) when compound **7** was synthesized from *p*-dibromoxylene and *p*-trimethylsilylphenylboronic acid under Suzuki monocoupling conditions: $Pd(PPh_3)_4$ and $CsCO_3$ in toluene/methanol. Then, boronic acid **8** was prepared in quantitative yield under the same conditions as those used to prepare **5**. Acid **8** is also soluble in DME and some other common organic solvents. The Suzuki reaction of **8** and the triiodide in a refluxing mixture of DME/water gave only trisubstituted product **2a**, in which hydrolysis of the ethylsiloxyl group was observed (Scheme 3). When the reaction



Scheme 2. Reagents and conditions: (i) 1. *n*BuLi/THF; 2. $B(OMe)_3$/THF; 3. H^+. (ii) **6**, $Pd(PPh_3)_4/CsCO_3$/toluene/abs. EtOH.

was carried out in toluene/absolute ethanol, no hydrolysis was observed, and tripod **2b** was obtained in 60% yield. The three TMS groups in **2b** could be readily replaced with an iodine atom, allowing the end-capping of the tripod legs with a variety of surface-active groups for chemisorption at different substrate surfaces. Thus, treatment of **2b** with ICl (3 equiv.) in CCl_4 gave triiodide **2c** in 45% yield. Suzuki coupling of **2c** with commercial *p*-carboxyphenylboronic acid gave carboxylic acid terminated tripod **2d** in 53% yield.



Scheme 3. Reagents and conditions: (i) 1. *n*BuLi/THF; 2. $B(OMe)_3$/THF; 3. H^+. (ii) **6**, $Pd(PPh_3)_4/CsCO_3$/DME/H_2O. (iii) **6**, $Pd(PPh_3)_4/CsCO_3$/toluene/abs. EtOH. (iv) **2b**, ICl/CCl_4. (v) **2c**, *p*-carboxyphenylboronic acid, $Pd(PPh_3)_4/CsCO_3$/toluene/abs. EtOH.

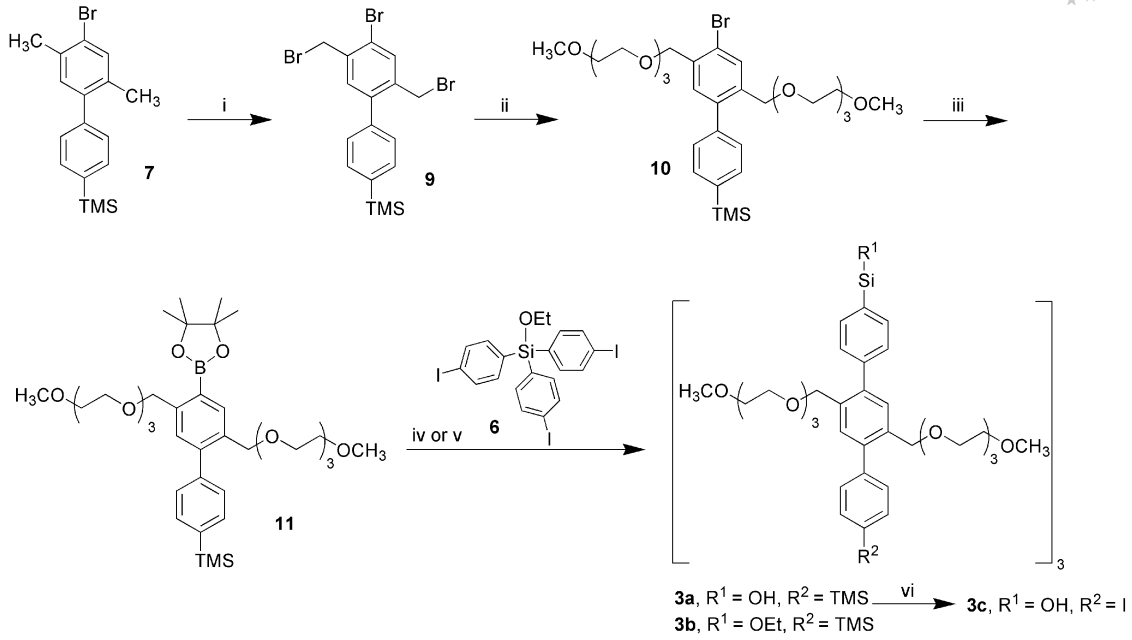
The synthesis of tri(ethylene glycol) monomethyl ether substituted tripod **3** was carried out from **7** (Scheme 4). Benzylic bromination of **7** catalyzed with AIBN in the presence of NBS in refluxing CCl_4 gave tribromo derivative **9** in good yield (52%). The coupling of **9** with commercial tri(ethylene glycol) monomethyl ether was carried out with Na in dry benzene to obtain **10** in 59% yield. Because we had observed that the monolithiation of aryl bromides in the presence of ethylene glycol substituents fails,[17] we decided to prepare the boronic ester by using a palladium-catalyzed reaction.[28] Thus, bromide **10** was treated with bis(pinacolato)diboron in the presence of KOAc and $Pd(dppf)_2Cl_2$ as a catalyst in DME to provide **11** in 55% yield (Scheme 4). Coupling of **11** with triiodide **6** gave OEG-modified tripod **3a** in 43% yield. As above, the TMS terminated *p*-phenylenes could be exchanged with an iodine atom (compound **3c**) that can be used for applying various functionalities. Again, when the reaction was performed in aprotic solvent, no hydrolysis of the Si–OEt bond in **3b** was observed during the Suzuki coupling.

Finally, more simple compound **12** was prepared by coupling *p*-methoxycarboxyphenylboronic acid pinacol ester with **6** in the presence of Ag_2CO_3 and $Pd(PPh_3)_4$ as a catalyst (Scheme 5). This compound was prepared to check the accuracy of the theoretical results.

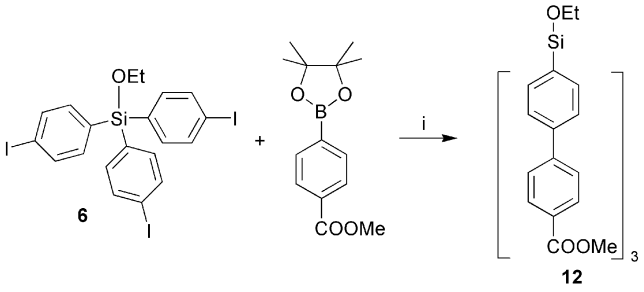
Structural Analysis

As described before, we chose tripodal oligo(*p*-phenylene)s as the ideal anisotropic adsorbates for silicon surfaces due to the rigidity of the *p*-phenylene chain. These compounds have proved to be rigid enough to maintain the perpendicular orientation of the functional head with respect to the surface during the deposition process. To support this statement we have optimized four different tripodal structures for obtaining precise information about their footprint areas and heights once the tripod is anchored to the surface by the three legs.

Quantum chemical calculations are currently an essential complementary tool for structural research as is the analysis of vibrational spectra. The geometries of the four selected tripods, compounds **2c**, **2d**, **3c**, and **12** (Figure 2) were fully optimized without imposing any constraints by using the functional hybrid B3LYP with either 6-31G (compounds **12** and **2d**) or LanL2DZ (compounds **2c** and **3c**) basis sets (see the Experimental section). In the case of compound **3c**, the OEG side chains were initially directed to be almost in parallel with the functional arm to enable the legs to bind to the surface. This initial configuration remained unchanged during the optimization process, as can be seen in Figure 2. These compounds are representative of tripods having two (i.e., **12**), three (i.e., **2c** and **3c**), and four (i.e., **2d**) phenylene units in each leg, covering triangular areas with sides of 18, 26, 26, and 33 Å, respectively. This means there is 2 Å for the silicon central head and an increase of 8 Å per phenylene unit in each leg. The areas covered are ca. 135, 299, 286, and 462 $Å^2$, respectively. Concerning the height of the tripods, the silicon atom is 3, 4, 4, and 6 Å above its respective base.



Scheme 4. Reagents and conditions: (i) NBS/AIBN/CCl_4; (ii) tri(ethylene glycol)monomethyl ether/Na/benzene. (iii) Bis(pinacolato)diboron/Pd(dppf)$_2Cl_2$/KOAc/DME. (iv) **6**, $Pd(PPh_3)_4/CsCO_3$/DME/H_2O. (v) **6**, $Pd(PPh_3)_4/CsCO_3$/toluene/abs. EtOH. (vi) **3a**, ICl/CCl_4.



Scheme 5. Reagents and conditions: (i) $Pd(PPh_3)_4/Ag_2CO_3$/THF.

Raman spectroscopy has repeatedly demonstrated its value in studying the structure of complex molecules of biological interest.[29–32] Moreover, Raman intensities of oligo(*p*-phenylene)s have been related to the number of phenyl rings in the molecule, as well as to its planarity and rigidity, given that these depend on the conjugation of the system.[16] Figure 3 shows the experimental Raman spectra of solid **12**, **2c**, and **3c** with two, three, and three phenylene rings in each leg, respectively. Compound **2d** was obtained as a syrup in very small quantities, and therefore, it was not possible to purify it and obtain its Raman spectrum. However, for the smallest compounds **12** and **2c**, it was possible to calculate the theoretical Raman spectrum. The respective B3LYP/6-31G and LanL2DZ calculated spectra are also shown in Figure 3. The force fields do not show imaginary wavenumbers, which confirms that the optimized structure of these compounds corresponds to a minimum. A very good agreement between the experimental and the theoretical wavenumbers and intensities is observed, which once again demonstrates the value of DFT methods for analyzing the vibrational spectrum of complex molecules for which no previous vibrational analysis could be made. The strongest Raman bands correspond to characteristic normal modes of the oligo(*p*-phenylene) legs and are assigned as shown in the calculated spectra of Figure 3 according to the main internal coordinate contributing to each fundamental.

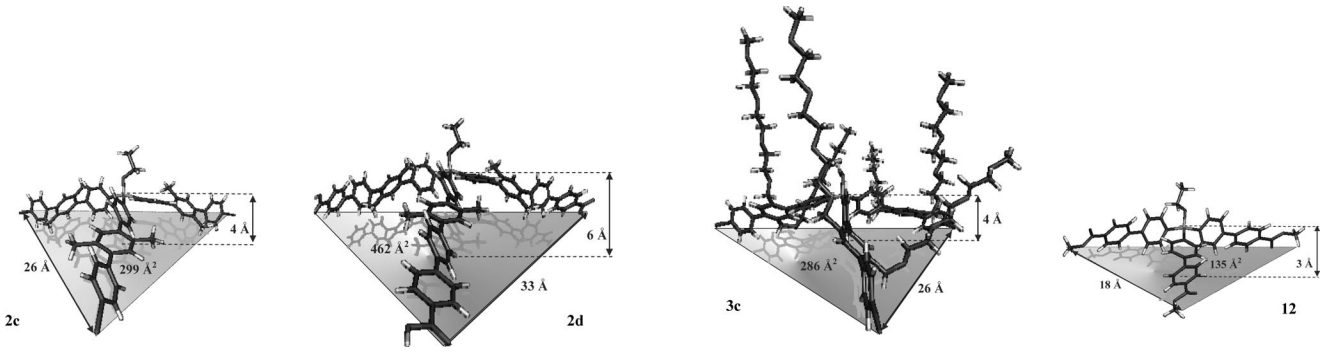


Figure 2. B3LYP-optimized structures of compounds **2c**, **2d**, **3c**, and **12**.

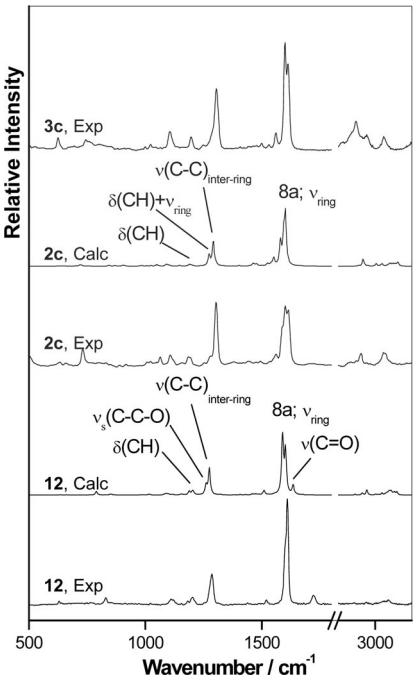


Figure 3. Experimental and B3LYP calculated Raman spectra of compounds **2c**, **3c**, and **12**.

The characteristic and very strong Raman bands at ca. 1270 and 1600 cm^{-1} are assigned to $\nu(C–C)_{interring}$ and aromatic $\nu(C–C)_{ring}$ (mode 8a; ν_{ring}) stretching fundamentals, respectively. Other Raman bands recorded at around 1200 cm^{-1} are also characteristic of these oligomers and are assigned to the δ(CH) in-plane bending of the CH aromatic bonds. These bands are always present in the Raman spectra of oligo(*p*-phenylene)s and can be used as a test for the quality of the synthetic routes in these samples.[33,34] As discussed in previous studies,[16] the splitting and broadening of the band at ca. 1600 cm^{-1}, as observed in the spectrum of **12** as a shoulder and well pronounced in the cases of compounds **2c** and **3c**, are due to the presence of nonequivalent benzene rings in each leg. This behavior is reproduced by the DFT force fields, which predict two strong bands at 1601 and 1580 cm^{-1} for compound **12** and three bands at 1601, 1595, and 1580 cm^{-1} for compound **2c**. In the latter, these aromatic $\nu(C–C)_{ring}$ bands are assigned to each one of the three different aromatic rings of the leg. The terminal ring substituted by iodine shows the lowest wavenumber at 1580 cm^{-1} and the central ring shows the highest one at 1601 cm^{-1}. As a result of the splitting, the intensity of the band at 1600 cm^{-1} is reduced, causing an apparent enhancement in the weaker band at 1270 cm^{-1}.

The Raman spectra of a series of penta(*p*-phenylene) derivatives have previously been studied by our group,[16] where the changes in the intensity ratio between the bands recorded at ca. 1280 and 1220 cm^{-1} were considered. They were found to be related to the planarity of these molecules. It has been demonstrated[35,36] that the Raman intensity ratio I_{1280}/I_{1220} in oligo(*p*-phenylene)s is related to the number of phenyl rings in the molecule and its planarity. This intensity ratio decreases as the number of conjugated phenyl rings increases, therefore indicating greater conjugation in the system and an increase in the molecular rigidity. The calculated structures show a dependence on the oligomer length and the torsional angle between the phenyl rings: a higher number of aromatic rings would result in a lower torsional angle[37] and, therefore, more planarity. The optimized structures of compounds **12** and **2c** show similar torsional angles of 36 and 47°, respectively. Although a higher planarity is expected in **2c** due to the extra aromatic ring, the presence of two substituents in the central ring of the leg explains a higher torsional angle.

Generally speaking, the lack of equivalence between the phenylene rings complicates the analysis of the Raman intensities and prevents us from drawing conclusions about the planarity/rigidity of the tripods studied. In spite of this, the ratio I_{1280}/I_{1220} is very similar for unsubstituted tri(*p*-phenylene) (I_{1280}/I_{1220} = 5)[35] and for compounds **3c** and **2d** (I_{1280}/I_{1220} = 6), indicating that the structure of the tripods and the rigidity of the legs is not significantly affected by very large substituents.

Conclusions

We have carried out the synthesis of several tripod-shaped molecules including one with tri(ethylene glycol) mono methyl ether side chains on the tripod legs (i.e., **3a**–**c**) designed for biological applications. The key step in the synthesis is the Pd-catalyzed Suzuki cross-coupling reaction of the triiodophenylsilane as the core of the tripod with substituted biphenyl moieties. Due to the presence of the iodine atom, the three tripod legs can be end-capped with a variety of functional groups for surface immobilization, such as carboxylic acid groups (i.e., **2d**) for attachment onto amino-terminated surfaces. Iterative coupling of the substituted biphenyl building blocks with first-generation tripods **1**–**3** will allow the homologation of the tripod legs to give giant tripod-shaped oligo(*p*-phenylene)s, which is currently being undertaken in our laboratories.

Experimental Section

General: Compounds **4** and **6** were prepared according to literature procedures.[6,25] Compound **7** was prepared following the procedure described in the Experimental Section or according to a known procedure.[27] Melting points were determined with a Gallenkamp instrument. UV spectra were recorded with a Hewlett–Packard 8452A spectrophotometer, and IR spectra were recorded with Beckman Aculab IV and Perkin–Elmer 883 spectrophotometers. Mass spectrometry was done with a Thermo Finnigan instrument by using the direct injection and electron ionization (EI) modes. HRMS were recorded with a Micromass (Autospec-Q) spectrometer. ^1H and ^{13}C NMR spectra were recorded with a 400 MHz ARX 400 Bruker spectrometer by using the residual solvent peak in $CDCl_3$ (δ_H 7.24 ppm for ^1H and δ_C = 77.0 ppm for ^{13}C) or CD_3SOCD_3 (δ_H = 2.50 ppm for ^1H and δ_C = 39.5 ppm for ^{13}C). TLC analyses were performed on Merck silica gel 60 F 254 plates, and column chromatography was performed on silica gel 60 (0.040–

0.063 mm). Raman spectra were recorded with a Renishaw Invia micro-Raman spectrometer by using the 514.5 nm exciting line from an argon ion laser. The microscope was equipped with a 50× objective (numerical aperture of 0.75). To avoid excessive heating during measurement of the Raman spectra, the output power of the laser was 3 mW on the sample surface by using 10% of the maximum laser power and co-adding 5 scans of 10 s of exposure. The resolution was set at 4 cm^{-1} and the geometry of micro-Raman measurements was 180°. The micro-Raman measurements were performed by putting the sample in a glass slide. Before each measurement, the instrument was calibrated with a standard Si sample (520 cm^{-1}).

Computational Details: All calculations were carried out with the GAUSSIAN 03 program package.[38] Density functional theory calculations by using Becke's three parameter hybrid function combined with the Lee–Yang–Parr correlation function (B3LYP)[39] was chosen owing to its good performance in predicting molecular structure as well as force fields.[40]

Tripod 1

2,5-Dimethoxy-*p*-(4′-methoxyphenyl)phenylboronic Acid (5): Under an argon atmosphere, *n*-butyllithium (1.6 M in hexanes, 2.9 mL, 4.6 mmol) was added over a solution of **4**[25] (1.32 g, 8.40 mmol) in anhydrous THF (30 mL) at –78 °C. The reaction mixture was stirred at –78 °C for 1 h. After this period, a solution of trimethylborate (1.24 mL, 11.07 mmol) in THF (50 mL) was added at –78 °C. Then, the cold bath was removed, and the mixture was left to reach room temperature over 12 h. HCl (1 M, 15 mL) was added, and the resulting solution was stirred for 1.5 h. The organic phase was extracted with CH_2Cl_2 (3 × 10 mL) and water (1 × 10 mL), dried with $MgSO_4$, filtered, and concentrated under vacuum. The residue was separated by column chromatography (CH_2Cl_2) to give **5** as a yellowish solid (283 mg, 28%). M.p. 99–100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, J = 8.4 Hz, 2 H, Ar-H), 7.40 (s, 1 H, Ar-H), 6.95 (d, J = 8.4 Hz, 2 H, Ar-H), 6.86 (s, 1 H, Ar-H), 3.89 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 3.79 (s, 3H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7 (C), 153.7 (C), 150.7 (C), 131.3 (C), 130.51 (C), 130.50 (2 CH), 116.5 (CH), 113.5 (2 CH), 112.5 (CH), 56.2 (OCH_3), 55.7 (OCH_3), 55.2 (OCH_3) ppm. MS: *m*/*z* (%) = 289 (10), 288 (100) $[M]^+$. HRMS (ESI): calcd. for $C_{15}H_{17}BO_5$ 288.1169; found 288.1164.

Ethoxy Tri(2′,5′,4′′-trimethoxy[4,1′;4′,1′′]terphenyl)silane (1): Under an argon atmosphere, compound **6**[6] (0.08 g, 0.11 mmol), **5** (0.10 g, 0.36 mmol), Cs_2CO_3 (0.02 g, 0.64 mmol), and $Pd(PPh_3)_4$ (0.04 g, 0.03 mmol) were dissolved in a degassed (Ar) mixture of toluene (5 mL) and absolute EtOH (4 mL). The reaction mixture was stirred for 12 h at room temperature. After this period, the reaction was filtered through Celite, and the solution was dried with $MgSO_4$. The solvent was removed in vacuo to give a crude reaction that was separated by column chromatography (CH_2Cl_2/cyclohexanes, 9:1) to obtain **1** as a yellowish foam (80 mg, 71%). M.p. 68–70 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 8 Hz, 6 H, Ar-H), 7.63 (d, J = 8 Hz, 6 H, Ar-H), 7.52 (d, J = 8 Hz, 6 H, Ar-H), 6.98 (s, 3 H, Ar-H), 6.97 (d, J = 8 Hz, 6 H, Ar-H), 6.96 (s, 3 H, Ar-H), 3.97 (q, J = 7 Hz, 2 H, OCH_2CH_3), 3.84 (s, 9 H, 3 OCH_3), 3.79 (s, 9 H, 3 OCH_3), 3.78 (s, 9 H, 3 OCH_3), 1.31 (t, J = 7 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8 (3 C), 150.6 (3 C), 150.5 (3 C), 139.9 (3 C), 135.3 (6 CH), 133.0 (3 C), 130.6 (3 C), 130.5 (6 CH), 130.2 (3 C), 129.6 (3 C), 128.8 (6 CH), 114.7 (3 CH), 114.5 (3 CH), 113.6 (6 CH), 60.5 (OCH_2CH_3), 56.4 (6 OCH_3), 55.3 (3 OCH_3), 18.5 (OCH_2CH_3) ppm. MS: *m*/*z* (%) = 1030 (100) $[M]^+$, 985 (19), 711 (30), 675 (30), 505 (29). HRMS (ESI): calcd. for $C_{65}H_{62}O_{10}Si$ 1030.4112; found 1030.4107.

Suzuki Coupling Procedure for the Reaction of 5 with 6 under Pd/C Catalysis: Under an argon atmosphere, a 25-mL round-bottomed flask was charged with Pd/C[26] (12 mg), boronic acid **5** (0.14 g, 0.49 mmol), K_2CO_3 (0.11 g, 0.75 mmol), and dimethylacetamide (DMA)/water (20:1, 8 mL). This mixture was degassed with argon purge for 5 min, and the reaction was initiated by the addition of **6** (0.10 g, 0.15 mmol) and placed in an oil bath at 70 °C for 12 h. The catalyst was filtered off and washed with acetonitrile (50 mL). The combined organic layer was concentrated to dryness under vacuum to give a crude residue, which was separated by column chromatography (CH_2Cl_2/cyclohexanes, 9:1) to obtain **1a** as a yellowish foam (117 mg, 75%).

Tripods 2

(4′-Bromo-2′,5′-dimethyl)biphenyl-4-yltrimethylsilane (7): An oven-dried round-bottomed flask was fitted with a condenser, placed under an argon atmosphere, and charged with *p*-trimethylsilyl phenylboronic acid (5.00 g, 25.76 mmol), *p*-dibromoxylene (34.00 g, 128.79 mmol), Cs_2CO_3 (16.80 g, 51.52 mmol), and $Pd(PPh_3)_4$ (2.98 g, 2.58 mmol). The flask was evacuated and refilled with argon (3×) and then toluene/methanol (1:1, 200 mL) was added. The reaction mixture was heated to reflux for 18 h. When the reaction was complete, the inorganic solids were removed by filtration through Celite and washing with several portions of dichloromethane; then the solvent was evaporated. The residue was absorbed onto silica, then subjected to column chromatography (cyclohexane) to give **7** as a solid (8.41 g, 98%). M.p. 67–69 °C (ref.[27] 67.4–67.8). IR (KBr): $\tilde{\nu}$ = 2949, 1247, 823 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, 2 H, J = 8.0 Hz, Ar-H), 7.43 (s, 1 H, Ar-H), 7.26 (d, 2 H, J = 8.0 Hz, Ar-H), 7.08 (s, 1 H, Ar-H), 2.37 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3), 0.29 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.2, 141.0, 139.0, 135.0, 134.6, 133.7 (CH), 133.1 (2 CH), 132.0 (CH), 128.3 (2 CH), 123.4, 22.3 (CH_3), 19.7 (CH_3), –1.1 [$Si(CH_3)_3$]. MS: *m*/*z* (%) = 333 (42) $[M]^+$, 317 (100), 178 (11).

2,5-Dimethyl-*p*-(4′-trimethylsilylphenyl)phenylboronic Acid (8): Following the procedure outlined for **4**,[25] compound **7** (1.65 g, 4.95 mmol) was treated with anhydrous THF (20 mL), *n*BuLi (3.40 mL, 5.45 mmol), and neat $B(OMe)_3$ (1.1 mL, 9.9 mmol). After acidic treatment with 1 M HCl (20 mL), the reaction mixture was extracted with EtOAc (2 × 30 mL), dried with anhydrous Na_2SO_4, and concentrated in vacuo. The residue was separated by column chromatography (cyclohexanes/EtOAc, 4:1 to 3:1) to obtain **8** as a white solid (1.48 g, 100%). M.p. 118–120 °C. IR (KBr): $\tilde{\nu}$ = 1395, 1333, 839, 823 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (s, 1 H, Ar-H), 7.59 (d, J = 8 Hz, 2 H, Ar-H), 7.36 (d, J = 7.6 Hz, 2H, Ar-H), 7.17 (s, 1 H, Ar-H), 2.82 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 0.31 [s, 9H, $Si(CH_3)_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.5 (C), 143.5 (C), 142.0 (C), 139.5 (CH), 139.0 (C), 136.0 (C), 133.1 (2 CH), 132.1 (CH), 131.8 (C), 128.3 (2 CH), 22.5 (CH_3), 20.1 (CH_3), –1.1 [$Si(CH_3)_3$] ppm. MS: *m*/*z* (%) = 298 (2) $[M]^+$, 254 (26), 239 (100).

Tri(2′,5′-dimethyl-4′′-trimethylsilyl[4,1′;4′,1′′]terphenyl)silanol (2a): A degassed solution of **6** (0.25 g, 0.40 mmol), **8** (0.40 g, 1.32 mmol), $Pd(PPh_3)_4$ (0.04 g, 0.03 mmol), $CsCO_3$ (0.08 g, 2.38 mmol) in H_2O (5 mL), and DME (20 mL) was heated at reflux for 12 h. After this period, the mixture was cooled to room temperature and then filtered and extracted with $CHCl_3$ (2 × 10 mL). The organic phase was dried with $MgSO_4$, and the solvent was removed in vacuo. The residue was purified by column chromatography (cyclohexanes/EtOAc, 9:1) to give **2a** as a yellowish syrup (92 mg, 24%). ^{1}H NMR

(400 MHz, $CDCl_3$): δ = 7.80 (d, J = 8.0 Hz, 6 H, Ar-H), 7.58 (d, J = 8.0 Hz, 6 H, Ar-H), 7.46 (d, J = 8.0 Hz, 6 H, Ar-H), 7.37 (d, J = 8 Hz, 6 H, Ar-H), 7.19 (s, 3 H, Ar-H), 7.16 (s, 3 H, Ar-H), 2.31 (s, 9 H, 3 CH_3), 2.30 (s, 9 H, 3 CH_3), 0.30 [s, 27 H, 3 Si(CH_3)$_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.4 (3 C), 142.0 (3 C), 140.9 (3 C), 140.6 (3 C), 138.6 (3 C), 135.2 (6 CH), 133.1 (6 CH), 132.7 (3 C), 132.6 (3 C), 132.1 (3 C), 132.0 (3 CH), 131.9 (3 CH), 128.8 (6 CH), 128.5 (6 CH), 20.0 (3 CH_3), 19.9 (3 CH_3), –1.0 [3 Si(CH_3)$_3$] ppm. MS: m/z (%) = 1035 (<1) [M]$^+$, 330 (63), 315 (100). HRMS (ESI): calcd. for $C_{69}H_{76}OSi_4Na$ 1055.4871; found 1055.4430.

Ethoxy Tri(2′,5′-dimethyl-4′′-trimethylsilyl[4,1′;4′,1′′]terphenyl)silane (2b): Following the procedure outlined for **1**, compound **6** (0.25 g, 0.4 mmol) was coupled with **8** (0.4 g, 1.32 mmol) in the presence of Cs_2CO_3 (0.07 g, 2.20 mmol) and $Pd(PPh_3)_4$ (0.04 g, 0.04 mmol) in toluene (15 mL) and absolute EtOH (12 mL). Compound **2b** was isolated by column chromatography (cyclohexanes/EtOAc, 9:1) to give a solid foam (254 mg, 60%). M.p. 139–142. IR (KBr): $\tilde{\nu}$ = 2917, 2849, 1248, 1116, 825 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 8.0 Hz, 6 H, Ar-H), 7.57 (d, J = 8.0 Hz, 6 H, Ar-H), 7.44 (d, J = 8.0 Hz, 6 H, Ar-H), 7.36 (d, J = 8 Hz, 6 H, Ar-H), 7.19 (s, 3 H, Ar-H), 7.16 (s, 3 H, Ar-H), 3.99 (q, J = 7.0 Hz, 2 H, OCH_2CH$_3$), 2.31 (s, 9 H, 3 CH_3), 2.29 (s, 9 H, 3 CH_3), 1.32 (t, J = 7.0 Hz, 3 H, OCH$_2$CH_3), 0.30 [s, 27 H, 3 Si(CH_3)$_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.3 (3 C), 142.0 (3 C), 140.9 (3 C), 140.6 (3 C), 138.6 (6 CH), 135.2 (6 CH), 133.1 (6 CH), 132.7 (3 C), 132.6 (3 C), 131.9 (6 CH), 131.8 (6 C), 128.7, (3 CH), 128.5 (9 CH), 59.9 (OCH$_2$CH$_3$), 20.0 (6 CH_3), 18.5 (OCH$_2$$CH_3$), –1.0 [3 Si($CH_3$)$_3$] ppm. MS: m/z (%) = 1060 (0) [M]$^+$, 330 (70), 315 (100). HRMS (ESI): calcd. for $C_{71}H_{80}OSi_4Na$ 1083.5184; found 1083.5184.

Ethoxy Tri(2′,5′-dimethyl-4′′-iodo[4,1′;4′,1′′]terphenyl)silane (2c): ICl (1 M in CH_2Cl_2, 0.16 mL, 0.16 mmol) was added dropwise to a solution of **2b** (0.14 g, 0.13 mmol) in dry CCl_4 (3 mL) at 0 °C under an argon atmosphere. The reaction mixture was warmed to room temperature and stirred for 1 h. A solution of sodium disulfide was added, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2, and the combined organic phase was washed with water. The organic phase was dried with $MgSO_4$, and then the solvent was removed in vacuo. Compound **2c** was isolated by column chromatography (cyclohexanes/EtOAc, 9:1) as a solid foam (71 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81–7.73 (m, 12 H, Ar-H), 7.46–7.41 (m, 6 H, Ar-H), 7.19–7.10 (m, 12 H, Ar-H), 4.00 (q, J = 6.8 Hz, 2 H, OCH_2CH$_3$), 2.32 (s, 9 H, 3 CH_3), 2.26 (s, 9 H, 3 CH_3), 1.33 (t, J = 6.8 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.1 (3 C), 141.1 (3 C), 141.0 (3 C), 139.7 (3 C), 137.2 (6 CH), 135.2 (6 CH), 132.8 (3 C), 132.5 (3 C), 132.4 (3 C), 131.9 (3 CH), 131.6 (3 CH), 131.2 (6 CH), 128.7 (6 CH), 92.5 (3 CI), 20.0 (3 CH_3), 19.8 (3 CH_3), 59.9 (OCH$_2$CH$_3$), 18.5 (OCH$_2$$CH_3$) ppm. HRMS (ESI): calcd. for $C_{62}H_{53}I_3OSiNa$ 1245.0897; found 1245.0899.

Ethoxy Tri(2′,5′-dimethyl-4′′′-carboxy[4,1′;4′,1′′;4′′,1′′′]tetraphenyl)silane (2d): Following the procedure outlined for **1**, compound **2c** (0.05 g, 0.04 mmol) was coupled with *p*-carboxyphenylboronic acid (0.04 g, 0.14 mmol) in the presence of Cs_2CO_3 (8.0 mg, 0.2 mmol) and $Pd(PPh_3)_4$ (14 mg, 0.0123 mmol) in toluene (3 mL) and absolute EtOH (2 mL). Compound **2d** was isolated by column chromatography (cyclohexanes/EtOAc, 9:1) to give a yellowish syrup (26 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, J = 7.9 Hz, 6 H, Ar-H), 7.89–7.70 (m, 18 H, Ar-H), 7.50–7.40 (m, 6 H, Ar-H), 7.21–7.10 (m, 12 H, Ar-H), 3.98 (q, J = 6.8 Hz, 2 H, OCH_2CH$_3$), 2.34 (s, 9 H, 3 CH_3), 2.29 (s, 9 H, 3 CH_3), 1.30 (t, J = 6.8 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.0 (3 C=O), 143.2 (3 C), 143.3 (3 C), 141.1 (3 C), 141.1 (3 C), 139.7 (3 C), 137.3 (6 CH), 135.5 (6 CH), 132.9 (3 C), 132.1 (3 C), 132.0 (3 C), 131.9 (3 CH), 131.6 (3 CH), 131.3 (6 CH), 130.0 (6 CH), 129.0 (3 C), 128.6 (6 CH), 128.5 (6 CH), 21.1 (3 CH_3), 20.1 (3 CH_3), 59.9 (OCH$_2$CH$_3$), 19.5 (OCH$_2$$CH_3$) ppm. HRMS (ESI): calcd. for $C_{83}H_{68}O_7SiNa$ 1227.4632; found 1227.4651.

Tripods 3

[4′-Bromo-2′,5′-bis(bromomethyl)biphenyl-4-yl]trimethylsilane (9): Under an argon atmosphere, over a solution of **7** (4.88 g, 14.65 mmol) and AIBN (100 mg) in carbon tetrachloride (200 mL) was added NBS (5.22 g, 29.31 mmol). The reaction mixture was heated at reflux for 12 h. After this period, the mixture was filtered while hot and then the solvent was removed in vacuo. The solid residue was purified by column chromatography (cyclohexanes) to give **9** as a white solid (3.73 g, 52%). M.p. 100–102 °C. IR (KBr): $\tilde{\nu}$ = 1248, 1215, 1051, 838, 823 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (s, 1 H, Ar-H), 7.60 (d, J = 8.4 Hz, 2 H, Ar-H), 7.39 (d, J = 8 Hz, 2 H, Ar-H), 7.33 (s, 1 H, Ar-H), 4.57 (s, 2 H, CH_2), 4.36 (s, 2 H, CH_2), 0.30 [s, 9 H, Si(CH_3)$_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.8 (C), 140.4 (C), 138.7 (C), 137.4 (C), 137.1 (C), 135.4 (CH), 133.5 (2 CH), 133.0 (CH), 128.0 (2 CH), 123.4 (C), 32.6 (CH_2), 30.3 (CH_2), –1.1 [Si(CH_3)$_3$] ppm. MS: m/z (%) = 490 (25) [M]$^+$, 411 (26), 317 (8), 257 (100), 178 (59), 73 (27). HRMS (ESI): calcd. for $C_{17}H_{19}Br_3Si$ 487.8806; found 487.8810.

{4′-Bromo-2′,5′-bis[(2-methoxyethoxy)methyl]biphenyl-4-yl}trimethylsilane (10): Under an argon atmosphere, over tri(ethylene glycol)monomethyl ether (38.60 mL, 241.24 mmol) at 0 °C was added Na (0.63 g, 27.38 mmol) in small portions. The reaction mixture was stirred for 30 min at 0 °C and then was left to reach room temperature till complete Na dissolution. Then, a solution of **9** (3.63 g, 7.40 mmol) in dry benzene (50 mL) was added by cannula. The reaction mixture was stirred and heated at 70 °C for 3 h. After this period, the mixture was cooled and Et_2O (100 mL) was added. The ethereal solution was washed with H_2O (3 × 20 mL), dried with $CaCl_2$, and concentrated to dryness. Compound **10** was isolated by column chromatography (cyclohexane/EtOAc, 6:4) as a yellowish syrup (2.85 g, 59%). IR (KBr): $\tilde{\nu}$ = 3325, 2874, 1248, 1097, 1046, 840, 827 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (s, 1 H, Ar-H), 7.52 (d, J = 7.8 Hz, 2 H, Ar-H), 7.36 (s, 1 H, Ar-H), 7.28 (d, J = 7.8 Hz, 2 H, Ar-H), 4.60 (s, 2 H, PhCH_2), 4.38 (s, 2 H, PhCH_2), 3.67–3.46 (m, 24 H, 12 CH_2O), 3.32 (s, 3 H, OCH_3), 3.31 (s, 3 H, OCH_3), 0.27 [s, 9 H, Si(CH_3)$_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.5 (C), 139.9 (C), 139.3 (C), 136.6 (C), 133.0 (C), 132.5 (2 CH), 130.2 (CH), 128.2 (CH), 121.4 (2 CH), 72.1 (CH_2O), 71.8 (CH_2O), 70.5 (4 CH_2O), 70.44 (2 CH_2O), 70.36 (4 CH_2), 70.0 (CH_2O), 69.6 (CH_2O), 58.8 (2 OCH_3), –1.2 [Si(CH_3)$_3$] ppm. MS: m/z (%) = 656 (<1) [M]$^+$, 166 (67), 161 (30), 117 (76), 103 (31), 83 (42), 82 (100), 73 (77), 67 (71). HRMS (ESI): calcd. for $C_{31}H_{49}BrO_8SiNa$ 679.2278; found 679.2276.

{2′,5′-Bis[(2-methoxyethoxy)methyl]-4′-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl-4-yl}trimethylsilane (11): Under an argon atmosphere, a degassed solution of **10** (1.14 g, 1.73 mmol), bis(pinacolato)diboron (0.53 mg, 2.08 mmol), $Pd(dppf)_2Cl_2$ (0.30 g, 0.35 mmol), and KOAc (0.51 g, 5.19 mmol) in dry DME (20 mL) was heated at reflux for 12 h. After this period, the reaction was cooled to room temperature, filtered, and diluted with CH_2Cl_2 (15 mL). The organic solution was washed with H_2O (2 × 10 mL) and brine, then dried with $MgSO_4$, and concentrated to dryness. The residue was separated by column chromatography (EtOAc/cyclohexanes, 8:2) to give compound **11** as a yellowish syrup (675 mg, 55%). IR (KBr): $\tilde{\nu}$ = 2870, 1337, 1142, 1098, 1068, 839 cm^{-1}. ^{1}H

NMR (400 MHz, $CDCl_3$): δ = 7.91 (s, 1 H, Ar-H), 7.53 (d, J = 8.0 Hz, 2 H, Ar-H), 7.40 (s, 1 H, Ar-H), 7.39 (d, J = 8.0 Hz, 2 H, Ar-H), 4.81 (s, 2 H, PhCH_2), 4.40 (s, 2 H, PhCH_2), 3.65–3.46 (m, 24 H, 12 CH_2O), 3.34 (s, 3 H, OCH_3), 3.33 (s, 3 H, OCH_3), 1.33 (s, 12 H, 4 CH_3), 0.28 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.6 (C), 144.4 (C), 141.1 (C), 139.1 (C), 137.8 (C), 133.3 (CH), 133.0 (2 CH), 129.2 (C), 128.6 (2 CH), 83.6 (2 C-O), 72.1 (CH_2O), 71.89 (CH_2O), 71.88 (CH_2O), 70.9 (CH_2O), 70.62 (CH_2O), 70.56 (4 CH_2O), 70.50 (2 CH_2O), 70.47 (CH_2O), 69.6 (CH_2O), 69.5 (CH_2O), 59.0 (2 CH_3O), 24.9 (4 CH_3), –1.1 [$Si(CH_3)_3$] ppm. MS: m/z (%) = 704 (<1) $[M]^+$, 540 (24), 376 (26), 147 (42), 103 (36), 73 (58), 59 (100). HRMS (ESI): calcd. for $C_{37}H_{61}BO_{10}SiNa$ 727.4025; found 727.4017.

Tri{2′,5′-bis[(2-methoxyethoxy)methyl]-4′′-trimethylsilyl-[4,1′;4′,1′′]}terphenylsilanol (3a): Following the procedure outlined for **2a**, compound **6** (0.13 g, 0.20 mmol) was coupled with **11** (0.43 g, 0.66 mmol) in the presence of Cs_2CO_3 (0.04 g, 1.19 mmol) and $Pd(PPh_3)_4$ (0.02 g, 0.02 mmol) in H_2O (3 mL) and DME (10 mL). Compound **3a** was isolated by column chromatography (cyclohexanes/EtOAc, 9:1) to give a colorless syrup (172 mg, 43%). IR (KBr): $\tilde{\nu}$ = 2870, 1092, 836 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, J = 8.0 Hz, 6 H, Ar-H), 7.60–7.48 (m, 18 H, Ar-H), 7.42 (d, J = 8.0 Hz, 6 H, Ar-H), 4.51 (s, 6 H, 3 PhCH_2), 4.47 (s, 6 H, 3 $PhCH_2$), 3.8–3.4 (m, 72 H, 36 CH_2O), 3.31 (s, 9 H, 3 OCH_3), 3.30 (s, 9 H, 3 OCH_3), 0.30 [s, 27 H, 3 $Si(CH_3)_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.2 (3 C), 141.1 (3 C), 140.7 (3 C), 140.5 (3 C), 139.1 (3 C), 135.2 (6 CH), 134.8 (3 C), 134.7 (3 C), 133.1 (6 CH), 132.4 (3 C), 131.1 (3 CH), 130.9 (3 CH), 128.9 (6 CH), 128.6 (6 CH), 71.8 (6 CH_2O), 70.9 (3 PhCH_2), 70.8 (3 PhCH_2), 70.6 (12 CH_2O), 70.5 (12 CH_2O), 69.6 (6 CH_2O), 59.0 (6 OCH_3), –1.1 [3 $Si(CH_3)_3$] ppm. HRMS (ESI): calcd. for $C_{111}H_{160}O_{25}Si_4Na$ 2028.0224; found 2028.0750.

Ethoxy Tri{2′,5′-bis[(2-methoxyethoxy)methyl]-4′′-trimethylsilyl-[4,1′;4′,1′′]}terphenylsilane (3b): Following the procedure outlined for **1**, compound **6** (0.08 g, 0.12 mmol) was coupled with **11** (0.25 g, 0.40 mmol) in presence the of Cs_2CO_3 (0.02 g, 0.60 mmol), $Pd(PPh_3)_4$ (0.01 g, 0.01 mmol), toluene (5 mL), and absolute EtOH (4 mL). Compound **3b** was isolated by column chromatography (cyclohexanes/EtOAc, 9:1) as a colorless syrup (39 mg, 16%). IR (KBr): $\tilde{\nu}$ = 2868, 1097, 837 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 8.0 Hz, 6 H, Ar-H), 7.57 (d, J = 8.0 Hz, 6 H, Ar-H), 7.51 (d, J = 8.0 Hz, 6 H, Ar-H), 7.50 (s, 6 H, Ar-H), 7.43 (d, J = 8.0 Hz, 6 H, Ar-H), 4.53 (s, 6 H, 3 PhCH_2), 4.48 (s, 6 H, 3 PhCH_2), 3.99 (q, J = 7.2, 7.2 Hz, 2 H, OC$H_2$$CH_3$), 3.63–3.45 (m, 72 H, 36 CH_2O), 3.31 (s, 9 H, 3 OCH_3), 3.30 (s, 9 H, 3 OCH_3), 1.34 (t, J = 7.2 Hz, 3 H, OCH_2CH_3), 0.31 [s, 27 H, 3 $Si(CH_3)_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.0 (3 C), 141.0 (3 C), 140.7 (3 C), 140.4 (3 C), 139.0 (3 C), 135.1 (6 CH), 134.7 (3 C), 134.6 (3 C), 133.0 (6 CH), 132.9 (3 C), 131.0 (3 CH), 130.8 (3 CH), 128.8 (6 CH), 128.6 (6 CH), 71.77 (3 CH_2O), 71.75 (3 CH_2O), 70.8 (3 PhCH_2), 70.7 (3 PhCH_2), 70.48, 70.45, 70.42, 70.38, 70.36 (24 CH_2O), 69.56 (3 CH_2O), 69.52 (3 CH_2O), 59.8 (OCH_2CH_3), 58.87 (3 OCH_3), 58.85 (3 OCH_3), 18.4 (OCH_2CH_3), –1.1 [3 $Si(CH_3)_3$] ppm. HRMS (ESI): calcd. for $C_{113}H_{164}O_{25}Si_4Na$ 2056.0536; found 2056.0530.

Tri{2′,5′-bis[(2-methoxyethoxy)methyl]-4′′-iodo[4,1′;4′,1′′]}-terphenyl)silanol (3c): Following the procedure outlined for **2c**, from **3a** (0.10 g, 0.05 mmol), ICl (1 M in CH_2Cl_2, 0.065 mL, 0.064 mmol), dry CCl_4 (2 mL), and column chromatography (cyclohexanes/EtOAc, 9:1) compound **3c** was obtained as a yellowish syrup (29 mg, 27%). IR (KBr): $\tilde{\nu}$ = 2870, 1090, 1060, 837 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 8.4 Hz, 6 H, Ar-H), 7.74 (d, J = 8.4 Hz, 6 H, Ar-H), 7.48 (d, J = 8.2 Hz, 6 H, Ar-H), 7.47 (s, 3 H, Ar-H), 7.24 (s, 3 H, Ar-H), 7.21 (d, J = 8.2 Hz, 6 H, Ar-H), 4.50 (s, 6 H, 3 PhCH_2), 4.47 (s, 6 H, 3 PhCH_2), 3.7–3.4 (m, 72 H, 36 CH_2O), 3.32 (s, 9 H, 3 OCH_3), 3.31 (s, 9 H, 3 OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.8 (3 C), 140.9 (3 C), 140.1 (3 C), 139.9 (3 C), 137.2 (6 CH), 135.1 (3 C), 134.9 (6 CH), 134.5 (3 C), 134.4 (3 C), 131.4 (3 CH), 131.3 (6 CH), 130.7 (3 CH), 128.8 (6 CH), 93.1 (3 C-I), 71.8 (6 CH_2O), 70.9 (3 PhCH_2), 70.7 (3 PhCH_2), 70.51 (12 CH_2O), 70.48 (12 CH_2O), 69.7 (6 CH_2O), 58.99 (3 OCH_3), 58.96 (3 OCH_3) ppm. HRMS (ESI): calcd. for $C_{102}H_{133}I_3O_{25}SiNa$ 2189.5937; found 2189.5962.

Tripod 12

Ethoxy Tri(4′-trimethylsilyl[4,1′]biphenyl)silane (12): Following the procedure outlined for **1**, compound **6** (0.10 g, 0.15 mmol) was coupled with *p*-(carboxymethyl)phenylboronic acid pinacol ester (0.14 g, 0.50 mmol) in the presence of Ag_2CO_3 (0.50 g, 0.90 mmol) and $Pd(PPh_3)_4$ (0.02 g, 0.02 mmol) in refluxing THF (20 mL) for 12 h. Compound **12** was isolated by column chromatography (cyclohexanes/CH_2Cl_2, 9:1) to give a white solid (50 mg, 47%). M.p. 158–160 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, J = 7.8 Hz, 6 H, Ar-H), 7.77 (d, J = 7.8 Hz, 6 H, Ar-H), 7.69–7.65 (m, 12 H, Ar-H), 3.94 (q, J = 7 Hz, 2 H, OCH_2CH_3), 3.90 (s, 9 H, 3 OCH_3), 1.28 (t, J = 7 Hz, 3 H, OCH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9 (3 C=O), 145.2 (3 C), 141.6 (3 C), 135.9 (6 CH), 134.0 (6 CH), 130.1 (3 C), 129.2 (3 C), 127.1 (6 CH), 126.8 (6 CH), 59.9 (OCH_2CH_3), 52.1 (3 OCH_3), 18.4 (OCH_2CH_3). MS: m/z (%) = 706 $[M]^+$, 683 (18), 682 (65) $[M]^+$, 555 (28), 479 (84), 435 (100), 324 (25). HRMS (ESI): calcd. for $C_{44}H_{38}O_7SiNa$ 729.2284; found 729.2286.

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