DOI: 10.1002/chem.200801939

Two-Dimensional Oligo(phenylene-ethynylene-butadiynylene)s: All-Covalent Nanoscale Spoked Wheels

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Dedicated to Professor Fritz Vögtle on the occasion of his 70th birthday

Abstract: The synthesis and characterization of a shape-persistent two-dimensional (2D) organic compound is described in detail. In a rational modular synthesis of a dodecaacetylene precursor and its subsequent template-aided cyclization, we obtained a molecularly defined, stable, C_6 -symmetric, rigid, spoked wheel. Peripheral tert-butyl groups and alkyl chains attached to the plane of the molecule provide sufficient solubility, so that the 2D oligomer can be fully characterized by MALDI-MS, GPC, and ¹H NMR, UV/Vis absorption, and fluorescence spectroscopy. Molecular mechanics and dynamics simulations indicate that the most

stable conformer of the molecule in vacuum is a shallow boat conformation with a small dihedral angle. Comparisons with the precursor as well as a ring-only structure clearly reveal the high rigidity of the title compound. Small-angle neutron scattering (SANS) experiments in $[D_8]$ THF and CDCl₃ affirm the rigid backbone structure in solution, that is, a radius of about 2.7 nm and a thickness of about

Keywords: molecular dynamics • molecular spoked wheels • scanning probe microscopy • neutron scattering • template synthesis 0.22 nm. STM investigations illustrate that the wheel molecules adsorb with their molecular plane parallel to the surface and can form hexagonal crystalline domains (unit cell parameters are $a=b=6.0\pm0.2$ nm and $\theta=60\pm2^\circ$), with the *tert*-butyl groups on the apexes staggered. Such staggering induces chirality in the organized domains. AFM investigations demonstrate that the wheel molecules inside overlayers organize in the same way as in the layer directly in contact with the surface. This indicates an epitaxial growth characteristic of the film.

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- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200801939.





Introduction

Large shape-persistent molecules of defined constitution, size, and shape have gained increasing importance in material science, both in fundamental research and various fields of application. Precise control of the structure and definite extensions rely on the molecules' internal order, which is achieved by the use of rigid building blocks and well-designed architecture. Apart from several supramolecular approaches that result in monodisperse organic or organometallic nanostructures, most synthetic monodisperse macromolecules are produced in a stepwise fashion by covalent bond-forming reactions provided by organic synthesis.^[1] Although oligomer synthesis is generally more tedious than the preparation of the corresponding polymers, linear oligomers are well investigated as models for the corresponding (polydisperse) polymers, since they can, in principle, be obtained free from defects. Physical, optical, and electronic properties can be correlated with the chain length and allow an estimation of a specific property of the pure polymer. In addition, thin-film deposition from the gas phase as well as lower intrinsic viscosities of oligomer solutions have opened up a particular field of applications for defined linear oligomers, mainly in optoelectronics.^[2]

Although the aforementioned criteria hold mostly for linear (1D) (and rarely for cyclic) oligomers, similar synthetic approaches lead to perfectly hyper-branched molecules, which can form three-dimensional (3D) structures. In the field of dendrimer chemistry, two synthetic strategies, convergent and divergent, are routinely used for compound preparation. Both approaches deploy multifunctional building blocks, either starting from a multifunctional core (spherical growth) or by attaching the ready-made modules (dendrons) to a multifunctional hub in the last step.^[3] If rigid building blocks such as phenylene or phenylene-ethynylene^[4] are used, the branches are prevented from backfolding. Therefore, stiff dendritic macromolecules are not only defined in constitution but also in macroconformation.^[5] Beside those aspects, concerning the importance of defined molecules, the share of aesthetics due to high symmetry should not be understated in this context.^[6]

As it holds for 1D and 3D representatives mentioned above, defined rigid two-dimensional (2D) structures are apt for purposes that require strict size- and shape regularity. Such 2D nano objects of defined size and shape are predominantly applied in the field of surface patterning and functionalization, in many cases involved with host-guest chemistry.^[7] Further areas of interest are defined layers for light emission and harvesting,^[8] the formation of discotic liquid crystals^[9] and the formulation of nanocomposite materials.^[10] Intensely explored oblate objects in the nanometer regime are disk-shaped synthetic clay platelets (e.g., Laponite RD° , $d \approx 25 \text{ nm}$) applied as rigid components in polymer-clay nanocomposites.^[11] Layered silicate polymer fillers enhance stiffness, strength, and thermal stability and reduce gas and liquid permeability of the resulting composite materials.^[10] More recently, nanoscopic disk-shaped synthetic clay platelets have been analyzed in order to understand fundamental physical and chemical aspects of polymer–clay composite materials. By nature, inorganic silicates are not compatible with nonpolar organic polymers and have therefore to be processed and made "organophilic" to prevent microphase separation.^[11]

Rigid 2D organic polymers and oligomers with similar lateral expansions could be employed as reinforcing components instead of inorganic platelets, be it as model compounds or even for the formulation of new composites.^[12] 2D polymers are highly intriguing systems, although only few of them were prepared with a defined structure.^[13-14] However, for these macromolecules defined structure does not necessarily mean defined size and shape, some of them behave rather like flexible membrane sheets than rigid disks.^[15] There have also been reports on single-lamella polyethylene crystallites, which are shape-persistent due to intramolecular interactions,^[16] but the problem of size control remains. By contrast, rigid, defined 2D oligomers offer several evident advantages over the inorganic counterparts. Beside better polymer compatibility, they are well characterizable, can be obtained in different, yet defined sizes, and are not limited to special structural motifs. Moreover, they allow the introduction of functionality at the perimeter as well as above and below the molecular plane. As also necessary for linear rigid oligomers, these structures require the attachment of flexible side groups in order to render them soluble and meltable (Figure 1).



Figure 1. Schematic drawing of a defined shape-persistent 2D oligomer: A rigid scaffold in the shape of a spoked wheel and flexible side groups attached within the molecular plane and at the periphery.

Although approaches towards oblate objects in a size range of the inorganic counterparts can be rarely found, some defined rigid 2D structures have already been described. Starting from the oldest carbon-based 2D functional material, graphite itself, research focussed on processable graphite cutouts like hexabenzocoronenes (HBCs), trinaphtho-HBCs, super-acenes, super-phenalenes and even C₂₂₂graphene.^[17] Moreover, artificial ethynylene and butadiynylene extensions of the graphite carbon network have been investigated. Although the all-carbon networks graphyne and graphdiyne have so far not been accomplished, a limited number of cutouts were synthesized and investigated. Such benzodehydroannulene systems include triangles, trefoils, bow ties, rhombi, and other edge- or angle-fused triangles,^[18]

phthalocyanine- and subphthalocyaninedehydroannulenes,^[19] as well as heterocycle-fused polycyclic aromatic hydrocarbons.^[20] These investigations also lead to the synthesis of macrocyclic and spoked wheel structures, that is, macrocycles with opposite apexes connected by rigid linear elements. Beside purely covalent examples,^[21] there are also supramolecular spoked-wheel structures known in literature with even larger size expansions. In those cases the noncovalent interior scaffold is either intended as a reinforcement of a flexible macrocycle^[22] or—more commonly—as a temporary template in order to facilitate cyclization.^[23]

We applied the benefits of covalent template synthesis by using a star-shaped precursor as molecule a template. Scheme 1 presents the straightforward synthetic pathway to all-covalent 2D oligo(phenylene-ethynylene-butadiynylene)s (2D-OPEBs) relying on a highyield template-directed sixfold acetylene dimerization in the final step.^[24] Our approach paves the way to molecularly defined 2D structures that are well characterizable, allow introduction of functionality at the rim as well as above and below the molecular plane, and can be obtained in different sizes. Unlike the abovementioned cutouts of graphite, graphyne, or graphdiyne, our approach is not restricted to structural ideals, but can be adapted to synthetic feasibility as well as improved solubility and surface patterning properties. Here we describe the detailed synthesis of 1 (Figure 2), the first member of this family of molecules, along with its characterization. Our aforementioned proposal on the shape-persistence of this 2D oli-



Scheme 1. Covalent-template principle: hub and rim modules (\mathbf{A}) undergoing a 1:6 coupling to form a star-shaped molecule (\mathbf{B}) and subsequent cyclization to a molecular spoked wheel (\mathbf{C}) .



Figure 2. Molecular spoked wheel: structure formula of shape-persistent 2D oligomer 1.

gomer is supported by molecular modeling simulations and small-angle neutron scattering in solution. The organization of these rigid structures at the solid/liquid and solid/air interface is investigated by means of STM and AFM.

Results and Discussion

Synthesis of 2D oligo(phenylene-*co*-ethynylene-*co*-butadiynylene) (1): The synthesis of 2D oligomer 1 relies on two strategic disconnections. First, the cyclization of the open precursor **2** by sixfold Glaser coupling, in which the central "hub" acts as a template that guarantees a high yield due to the intramolecular nature of the reaction. Second, the formation of **2** from two reasonable modules functioning as "hub" and "rim" by 1:6 Sonogashira-Hagihara coupling. Scheme 2 displays the synthesis of **1**. The central "hub" module was prepared starting from commercially available hexaphenylbenzene. Hexabromination^[25] yielded **3**, which was radially extended with the silylated diethylphenylboron pinacolate **4**.^[26] In this sixfold Suzuki coupling reaction, we employed an activated NHC catalyst system^[27] in anhydrous THF and with KOH as base. If the reaction was performed



Scheme 2. TIPS = triisopropylsilyl, CPDMS = (3-cyanopropyl)dimethylsilyl. a) PEPPSI catalyst,^[27] KOH, THF, 2 d reflux, 35%; b) ICl, CHCl₃, 0–20°C, 24 h, 91%; c) Ac₂O, 150°C, 5 h, 70%; d) [Pd(PPh₃)₄], Cs₂CO₃, H₂O, THF, 3 d reflux, 26%; e) *n*BuLi, C₂H₄I₂, THF, -78°C, 2 h, 20°C; f) CPDMS acetylene, [PdCl₂(PPh₃)₂], CuI, PPh₃, THF, piperidine, 20°C, 24 h, 61% (2 steps); g) K₂CO₃, THF/MeOH (2:1), 20°C, 3 h, 98%; h) [PdCl₂(PPh₃)₂], CuI, PPh₃, THF, piperidine, 20°C, 24 h, 61% (2 steps); g) K₂CO₃, THF/MeOH (2:1), 20°C, 3 h, 98%; h) [PdCl₂(PPh₃)₂], CuI, PPh₃, THF, piperidine, 70°C, 3 d, 59%; k) excess TBAF = [NBu₄]F, 1.0 m in THF, 5% H₂O, 20°C, 3 d, 76%; l) CuCl, CuCl₂, pyridine, 50°C, 4 d, 59%.

Chem. Eur. J. 2009, 15, 2518-2535

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with nine equivalents of base, crude 5 was obtained in about 65% yield after stirring at 70°C for 5 h. However, the MALDI-TOF mass spectrum revealed up to 25% of fourand fivefold coupling products, which could not be separated by column chromatography. On the other hand, if the reaction was stirred at the same temperature for 48 h and up to 24 equivalents of base were added during the reaction, pure sixfold coupling product could be easily isolated in 35% yield after column chromatography (clean NMR spectra, single peak in MALDI-MS). Subsequently, the hexakis-(trimethylsilyl) compound 5 was transformed into the hexaiodo compound 6 by treating with iodine monochloride.^[25] Due to the twelve ethyl groups, its solubility was sufficient for recrystallization from chloroform. It is worth mentioning that in preliminary experiments the unsubstituted analogue of 5 could neither be properly characterized nor purified. However, purity is a prerequisite for the success of the following reaction sequence.

Pyrylium salt 7 was used as precursor for the corner piece 9 of the "rim" module.^[28] Condensation with ten equivalents of sodium (4-bromophenyl)acetate 8 in acetic anhydride gave the bromodiiodo compound 9 in 70% yield.^[29] In the next step we utilized the iodo selectivity of the Suzuki condensation protocol for the elongation of the *m*-terphenyl arms with two equivalents of pinacol boronic ester 10. However, chromatographic separation of compound 11 from its byproducts was tedious, resulting in mediocre yields. The bromo function of 11 was transformed into the more reactive iodide by lithiation with *n*-butyllithium and addition of diiodoethane. The crude iodination product 12 was coupled with (3-cyanopropyl)dimethylysilyl acetylene (CPDMS acetylene, 13) providing 14. Generally speaking, the CPDMS group is a polar analogue of the trimethylsilyl group, is readily available, and dramatically simplifies the chromatographic separation of coupling products, starting material, and dehalogenated side products.^[30] Base-catalyzed deprotection of 14 gave the free acetylene 15, which was coupled with 16. This building block appreciably enhanced the solubility of the "rim" module as well as of the final 2D oligomer 1. Here again, purification of 17 by column chromatography was straightforward even on a hundred-milligram scale due to the polar CPDMS group. After base-catalysed removal of the CPDMS group, 18 could be also obtained in high purity. As confirmed by GPC analysis, the consecutive polarity change of the products in the reaction sequence ensured that the ready "rim" module was not contaminated even with traces of side product, an absolute requirement for the next severalfold coupling steps.[31]

The assembly of the "hub" and "rim" subunits had to be achieved in a sixfold Sonogashira–Hagihara coupling under rather harsh conditions. In first experiments, the hexaiodide **6** was coupled with nine equivalents of **18** at 20-50 °C and 5 mol% Pd⁰ catalyst per reactive site (i.e. 0.3 equivalents based on **6**) for two days. While the homocoupled side product (diacetylene) could be removed from the mixture by silica gel chromatography, the separation of four-, five-, and sixfold coupling products was not possible at this point of

the synthesis. Since R_f values on TLC were similar, we first assumed exclusive sixfold coupling.^[32] However, the crude product composition of **19** could be depicted by MALDI-MS. The spectrum showed a distribution of four-, five-, and sixfold coupling products (and their corresponding matrix adduct peaks) of approximately 0.7:1:1. To our surprise, after the removal of the triisopropylsilyl (TIPS) groups with TBAF (TBAF=[NBu₄]F), the corresponding desilylated five- (and fourfold) coupling products have larger R_f values, thus **2** could be purified by radial chromatography. The fourand fivefold coupled side products were isolated and characterized by MALDI-MS, GPC analysis, and ¹H NMR spectroscopy.

This last method allows an easy distinction of the different species. As depicted in Figure 3, the two signals for the methylene moieties of the hub ethyl groups (δ =2.67 and 2.31 ppm in **6**) shift downfield upon the coupling reaction



Figure 3. ¹H NMR spectra (left) and cartoons (right) of the separated 1:6 (top), 1:5 (middle) and 1:4 (bottom) Sonogashira coupling products occurring in the reaction towards **2**. During the coupling reaction the ethyl CH₂ signals of **6** (2.67 and 2.31 ppm) shift to 2.85 and 2.39 ppm (b and c), respectively. The terminal acetylene signal (a, 3.16 ppm) is split into two or three signals, depending on the number of neighboring vacancies the acetylene protons "sense". Arrows indicate signals not present in the spectrum of the desired 1:6 coupling product.

(2.85 and 2.39 ppm in 2). While the desired sixfold coupling product 2 merely shows shifted signals (Figure 3 top, b and c), integration of shifted and non-shifted signals gives a 5:1 ratio for the fivefold- (middle) and a 4:2 ratio for the fourfold-coupled species (bottom). Surprisingly, the terminal acetylene protons (solid circles in the cartoons) turn out to be very sensitive to their chemical environment, so they make an even better monitor. Given unhindered rotation around the spokes, all alkyne protons in the 1:6 coupling product experience the same environment, resulting in one singlet signal "a" (δ =3.16 ppm). In the 1:5 species, there are four acetylene protons (rotation!) close-by to a vacancy, while only six protons are adjacent to other "corner pieces" as in the 1:6 coupling product. This results in a shifted second signal. The situation becomes even more complex

for the 1:4 species, that is, with two vacant sites. Depending on the position of the vacancies (three permutations, see cartoons in Figure 3), the alkyne hydrogen atoms can experience two, one, or no neighboring vacancies at all, resulting in three distinct singlets. Their intensity distribution can be approximated by simple statistics that support the above interpretation.^[33] In successive coupling experiments we were able to optimize the sixfold Sonogashira reaction towards **19**. Doubling the catalyst load (0.6 equiv), increasing the overall concentration of the reaction partners and stirring at 70 °C for three days gave good yields of the sixfold coupling product (70% after desilylation towards **2**).

The attachment of the six corner pieces to the central hub leads to a high local acetylene concentration. When **2** was added slowly to a suspension of CuCl/CuCl₂ (10:1, 500 molar equiv of CuCl) in pyridine, an oxidative acetylene coupling took place.^[34] Due to the linkage of the acetylenes at the hub ("covalent template"), the intramolecular coupling is strongly favored over the intermolecular reaction.^[30b,35] However, GPC analysis of the crude product reveals that the reaction does not run completely intramolecular at room temperature and the formation of the dimer of **1** could be observed (ca. 16000 gmol⁻¹, Figure 4). The mono-



Figure 4. GPC analysis of 2D oligomer **1** (black) and open precursor **2** (gray) versus PS standard in THF. The dotted line shows a typical crude product composition with dimer signal around 16000 g mol^{-1} . Intensity signals were obtained from UV absorption at $\lambda = 254 \text{ nm}$.

mer–dimer ratio estimated from GPC data of the crude cyclization product was 5:1 (UV detector signals, relative absorption at $\lambda = 254$ nm). As we have shown previously on other systems,^[36] slightly elevated reaction temperatures (50 °C) favor the intramolecular reaction resulting in a product distribution of about 12:1 under otherwise identical conditions. Assuming that the extinction coefficient of the side product is twice as large as that of **1**, less than 5% of dimer was produced under these conditions. Purification of **1** by column chromatography (to remove low molecular weight impurities) and subsequent purification by preparative GPC yielded **1** in 59%.

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Figure 4 also displays the molecular weight distributions of pure 1 (black curve) and the open precursor molecule 2 (gray curve). Although both species only differ by about 12 units in molecular mass, a clear shift of the maxima can be observed. This nicely illustrates the decrease of the hydrodynamic volume: in the course of cyclization the star-shaped precursor's twigs become coplanar and lose their rotational degrees of freedom around the spoke axes. According to GPC interpretation in terms of molecular weight, 1 and 2 should differ by approximately 500 g mol⁻¹. Evidently this difference is a gross overestimation; we also have to be cautious with absolute molecular mass values obtained from GPC analysis as we used common polystyrene calibration as a reference. However, PPE and PS fundamentally differ in rigidity, as expressed by the persistence length.^[37] Previously, linear PPEs have been examined regarding the overestimation of their molar mass by established methods such as GPC and end group analysis.^[38] Several groups were in search of an empirical PPE-PS conversion factor, which turned out to depend on sample properties and determination method and hence spread from 1.5 to 3. Astonishingly, on our 2D-OPEB system, the molecular weight measured by GPC in THF matches better with the absolute molecular mass than for linear PPEs. We find a molar mass overestimation of less than 10%, that is, our conversion factor is smaller than 1.1. In the case of 1, the second dimension apparently compensates the difference in persistence length, so that the molecule has only a slightly larger hydrodynamic volume than a 3D polystyrene random coil of the same molecular mass.[39]

By far the most powerful method to prove complete cyclization towards **1** is MALDI-TOF mass spectrometry. The mass difference between **1** and **2** of about 12 amu is clearly resolved in the mass spectra as shown in Figure 5 (non highresolution spectra). In addition to matrix adduct peaks that are shifted by 250 and 500 m/z units, the spectra display distinct molecule peaks at m/z 8779.5 (**2**, calcd.: 8779.7) and



Figure 5. Cut-outs of MALDI-TOF mass spectra of 2D oligomer 1 and open precursor molecule 2 (m/z values indicated). Minor peaks at higher m/z ratios originate from matrix adducts (DCTB, 250.34 gmol⁻¹). See Supporting Information for full spectra.

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m/z 8767.2 (1, calcd.: 8767.6). The difference between the two distribution maxima of 12.3 (± 0.5) m/z units indicates the loss of twelve acetylene protons in the course of cyclization. Minor peaks in the mass spectrum of 1, which are not shown in Figure 5, originate from doubly charged molecules $(m/z \ 4383.9)$ as well as dimers and trimers (see Supporting Information).^[40]

 1 H NMR measurements of **1** were performed on a 500 MHz spectrometer (Figure 6). At ambient temperature we obtained a spectrum of broadened signals, even in good



Figure 6. ¹H NMR spectra of **1** showing the aromatic region at 25 °C and 120 °C. The corresponding assignment of signals is illustrated on top. In both spectra deuterated TCE was used as solvent and reference peak ($\delta = 6.00$ ppm). See Supporting Information for full spectra.

solvents such as deuterated TCE (Figure 6 bottom). This finding is good evidence for the 2D oligomer rigidity and can be ascribed most probably to hindered rotation of the *p*-phenylene units, especially the units close to the hub and the corners of the wheel (signals a and d, respectively).^[41] To a smaller extent, this effect can already be observed in the spectrum of **2** (Supporting Information), although the molecule conformational strain is expected to be far less (see molecular modeling).

High-temperature experiments in TCE were carried out in order to overcome these rotation barriers. Measurements of 1 at 90 °C gave a resolution comparable to the room-temperature experiments of 2, that is, the doublet signals of pphenylene units a and d were merged. Good resolution of all signals was achieved at 120°C (Figure 6 middle). Though we observed a temperature shift of the solvent signal, we set it as reference in both spectra. For that reason the spectra at 25 and 120°C also vary in chemical shift. By comparison with NMR measurements of several precursor moleculesincluding DEPT and 2D techniques-we were able to assign the signals. The aromatic region of the high-temperature spectrum consists of only 14 partly overlapping signal groups, which correspond to different phenylene moieties (Figure 6 top, a-h). Actually the molecule bears 204 aromatic hydrogen atoms, so this feature reflects its high symmetry, as expected for a perfect wheel structure. Furthermore, the precursor characteristic signal at $\delta = 3.2 \text{ ppm}$ (terminal alkyne units) is absent in the full spectrum of 1 (Supporting Information). Both results support our assumption that the cyclization is complete. We decided against measuring ¹³C NMR spectra at 120°C for reasons of low sensitivity at elevated temperatures, limited substance quantity, and a resulting long-term high-temperature strain of the measuring head.

The 2D oligomer 1 is a stable, slightly yellow solid that does not melt below 250 °C (decomp). Due to solubility-enhancing alkyl groups at the rim and inside the molecular plane, the molecule can be handled and processed in toluene (solubility $\approx 0.1 \text{ mgmL}^{-1}$), THF ($\approx 1.5 \text{ mgmL}^{-1}$), chloroform (\approx 7.5 mgmL⁻¹), and tetrachlororethane (TCE; $>15 \text{ mgmL}^{-1}$). As illustrated in Figure 7 for measurements in dichloromethane, 2D oligomer 1 displays a broad and structured absorption band stretching from 290 nm to about 415 nm. Beside two maxima at 324 nm $(\varepsilon_{\lambda}$ $\approx 764\,000\,\mathrm{L\,mol^{-1}\,cm^{-1}})$ and 347 nm (ε_{λ})



Figure 7. Normalized UV/Vis absorption (full lines) and emission (dashed lines) spectra of 1 (black curves) and 2 (gray curves) measured in CH₂Cl₂. The emission spectra for 1 (λ_{exc} =350 nm) and 2 (λ_{exc} = 379 nm) are very similar in shape and spectral range.

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 \approx 729 000 L mol⁻¹ cm⁻¹), there are two shoulders at larger wavelengths. Oligomers **1** and **2** can be easily distinguished by their absorption spectra, but upon excitation (**1**: λ_{exc} = 350 nm, **2**: λ_{exc} =379 nm) both species exhibit a violet–blue fluorescence that originates from a relatively sharp emission band at 417 nm and vibronic progression. While the absorption spectra of **1** and **2** are merely comparable, the emission spectra are nearly identical. Hence, the chromophore from which radiant relaxation emanates must already be present in **2**, that is, before cyclization.^[42]

Molecular modeling: Molecular mecahnics (MM) and molecular dynamics (MD) simulations can provide information on the individual molecule level, such as conformation analysis and bond strain. Extensive simulations have been carried out for shape-persistent macrocycles based on phenylene, phenylene–ethynylene, or phenylene–butadiynylene backbones.^[35g] These calculations indicate that, despite the rigid building blocks, these macrocycles adopt various macroconformations and are merely shape-persistent in the sense, that they do not fold or collapse.^[43]

To focus on the structure of the π -conjugated wheel (hub, spokes, and rim) the long hexadecyloxy chains on the spokes were replaced by methoxy groups. The MD run reveals a rigid structure, with no change in the hexagonal shape of the molecule (Figure 8, right). The distance between opposite atoms 1–4 (or 2–5 or 3–6; Figure 8, left) only slightly fluctuates between 48 and 50 Å during the MD run, and the distance between two opposite, most far apart hydrogen atoms of the *tert*-butyl groups is on average 68 Å.

The molecule shape can fluctuate close to the fully planar conformation, the angle (atoms 1-7-4) typically evolves between 180° and 160°, that is, between the planar and a shallow boat conformation. The most stable conformations are those showing a boat-type structure (Figure 8, right), but the energy difference between the boat conformation and the planar conformation is small, that is, around 2.3 kcalmol⁻¹. This conformation shows a small dihedral angle (atoms 5-6-

1-2) around 12° (5 and 2 are the "bow" and "stern" atoms, to remain in the marine lexicon). This dihedral angle is comparable to the boat conformations of other unsubstituted phenylene-ethynylene macrocycles.[35g] Notably for the wheel, we find no stable chair conformation, while it is the most stable conformer for an unsubstituted phenylene-ethynylene macrocycle.^[44] The size of the hexagonal frame of the wheel imposes that the spokes are not strictly linear, because they are slightly too long for that frame in their fullyextended linear conformation. In Figure 9, we compare the behavior of the entire wheel with that of the open precursor, that is, the same wheel "cut" in the middle of the hexagon segments (Figure 8, left). Starting from a relatively planar conformation, the spokes are revealed to be much more flexible than the wheel. This is illustrated in Figure 9, showing the evolution of geometric features for the wagon wheel 1 (blue line) and the open precursor (red line). In the former, the distance between opposite atoms (e.g. atoms 2 and 5) remains constant, between 48 and 50 Å, while for the latter this distance shows large variations between 50 Å and 36 Å. This is also found for the angle 1-7-4, showing large variations in the case of the precursor (between 120° and 180°), while in the wheel it only evolves from boat (160°) to planar (180°) conformations. This difference in flexibility can also be illustrated by the self-diffusion coefficient^[45] (D)for all the atoms during the MD: $D = 0.5 \times 10^{-3} \text{ Å}^2 \text{ ps atom}^{-1}$ for the wheel versus $D = 0.3 \times 10^{-1} \text{ Å}^2 \text{ ps} \text{ atom}^{-1}$ for the precursor. This difference of two orders of magnitude clearly indicates that the wheel is very rigid compared to the open precursor.

MD of a hypothetical ring structure (Figure 8, right) reveals a relatively flexible structure. The self-diffusion coefficient during the MD run is $D = 0.1 \times 10^{-1} \text{ Å}^2 \text{ ps atom}^{-1}$, to be compared with $0.5 \times 10^{-3} \text{ Å}^2 \text{ ps atom}^{-1}$ for the wheel and $0.3 \times 10^{-1} \text{ Å}^2 \text{ ps atom}^{-1}$ for the open precursor. The "flexibility" of the ring is therefore comparable to that of the open precursor, while for the wheel the spokes maintain a rigid conformation. This is also illustrated in Figure 9, showing



Figure 8. Left: Structure formulas of the three models used for MD simulations. The "wheel" (blue) corresponds to **1** bearing methoxy instead of hexadecyloxy groups, while the "open precursor" is derived from **2**. The "ring" represents a hypothetical macrocyclic compound consisting of the same phenylene-butadiynylene frame as **1**. Right: CPK models of the boat conformer of the wheel, with the hexagonal rim shown parallel (top) and perpendicular (bottom) to the view.

Chem. Eur. J. 2009, 15, 2518-2535

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Figure 9. Graphs showing the evolution of geometrical features (see labeled atoms in Figure 8, left) during the MD run. Blue line: wheel 1; red line: open precursor 2; green line: ring.

the evolution of the distance between opposite atoms (e.g. 2 and 5). For the ring (green line) that distance shows large variations, from 35 to almost 55 Å. The energy-minimized structures of several conformations extracted from the MD show relatively planar conformations. Boat and fully planar hexagonal conformations are two stable conformers, with a very small energy difference (few tenths of kcalmol⁻¹). The

boat conformation is very similar to that of the wheel: the distance between atoms 2 and 5 (between bow and stern atoms) is around 49 Å and the dihedral angle (5-6-1-2) is around 7°. This is similar to the behavior of the wheel described above. Therefore, the ring, though being much more flexible than the spoked wheel, exhibits the same stable conformers. This suggests that the phenylene-butadiynylene frame plays а

major role in the formation of a stable rigid conformation. The high flexibilities of the open precursor and the hypothetical ring are not surprising if we take into account the compounds' size and the relatively small persistence length of phenylene–ethynylene structures in general.^[37] Even single-crystal X-ray structures of phenylene–acetylene rings exhibit considerable deviations from linear phenylene–acetylene bonds.^[46]

Small-angle neutron scattering (SANS) investigations: To get an experimental insight into the structure of the compound **1**, SANS investigations were performed. Coherent elastic neutron scattering provides information on the spatial structure of dissolved species with a typical size range of 1–200 nm.^[47] Molecules that locally vary in scattering length density can be investigated in different solvents or solvent mixtures, resulting in different scattering contrasts.^[47a,48] SANS data taken at high contrast between the solvent and the solute can be used to explore the shape of the entire molecule. At intermediate contrast the details of the molecule can be detected. Scattering intensities can be fitted by applying models with appropriate geometry and scattering length density distribution.^[11b,16,47,49]

Small-angle neutron scattering was performed on several samples of **1** in CDCl_3 and in a contrast series of THF/ $[D_8]$ THF mixtures. As a result of the limited solubility of **1**, the investigations were restricted to low concentrations. For the evaluation, any scattering contribution due to interparticular interaction was neglected; hence, any concentration influence was disregarded. Due to the restricted resolution of SANS, the experimental data are described by using the simple model of a stack of three disks ("hamburger model", Figure 10).^[16]

The inner disk corresponds to the backbone that determines the molecule radius. The outer dimension of the hamburger is given by the overall thickness of the attached alkyl chains. At high contrast, neutron scattering is most sensitive to the outer dimensions (the radius *R* and the thickness *L*1). The best description of the experimental data was obtained using a radius of 2.7 nm. However, the overall thickness of the molecule is governed by the hexadecyloxy chains, the conformation of which depends on the solvent: we found L1=2.5 nm in CDCl₃ and L1=1.2 nm in [D₈]THF. This dif-



Figure 10. Schematic drawing of 2D oligomer 1 illustrating the rigid backbone with orthogonal alkyl chains (left). The molecule can be modelled as "hamburger", that is, a hard disk between two soft layers (right), since the rigid backbone and the orthogonal alkyl chains inside the plane differ in scattering length density. Varying the ratio of protonated to deuterated solvent changes the scattering contrast of the hamburger. The hamburger model requires only three parameters: radius R, overall thickness L1 and rigid disk thickness L2.

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ference can be ascribed to the solubility of the side chains in the different solvents. At intermediate contrast, the scattering intensity is also sensitive to the variation of the scattering length density distribution. Thus, by fitting different contrasts, the thickness of the backbone L2 is available. From the contrast variation and model calculations using the experimental contrasts, the radius of 2.7 nm, and the determined overall dimension L1 gave a thickness of the inner disk of approximately 0.22 nm, underlining the rigidity of the backbone (see Supporting Information). In Figure 11,



Figure 11. Measured coherent scattering intensities at highest contrast (symbols) and theoretical scattering intensities based on the hamburger model (lines) of two samples of **1** in $[D_8]$ THF (circles) and CDCl₃ (squares). Fit parameters in $[D_8]$ THF: R=2.7 nm, L1=1.2 nm, L2=0.22 nm. Fit parameters in CDCl₃: R=2.7 nm, L1=2.5 nm, L2=0.22 nm.

the scattering intensities of the 2D oligomer at highest contrast are compared with theoretical intensities. For the sample in $[D_8]$ THF the upturn of the scattering intensities at scattering vectors q < 0.35 nm⁻¹ is attributed to a small fraction of aggregates.^[16,50] The coherent scattering intensities could be successfully fitted by theoretical scattering curves obtained from the hamburger model.

Evidently, the radius found in solution compares well to the value obtained from STM investigations (see below). Furthermore, the small thickness found for the central disk implies a rigid framework with a planar geometry. Considering that 1) the shallow boat conformation shown in Figure 8 has an effective atomic-density-weighted thickness of 0.33 nm,^[51] 2) the actual structure is expected to fluctuate between the boat and the fully planar conformation due to the very small energy difference $(2.3 \text{ kcalmol}^{-1})$, and 3) SANS probes the position of the nuclei, while the molecular representation in MD simulation comprises the electronic cloud, the results of the simulations and the SANS data are reasonably consistent with each other. Consequently, the 2D oligomer 1 morphology can be well described by the hamburger model. Due to SANS evaluation, the first information concerning the structure of the spoked wheel 1 in solution is now available. We can state that SANS is an appropriate method to investigate the particle morphology in solution and to prove the rigidity of the backbone experimentally. The conformation of the hexadeyloxy chains determines the thickness of the soft shell and therefore the overall dimension of the molecule in solution.

Scanning tunelling microscopy (STM) and atomic force microscopy (AFM) investigations: To gain insight into the adsorption bahavior of 1 on atomically flat solid surfaces, STM is an extremely powerful tool, either under ambient conditions or at a liquid–solid interface.^[52] At present, interest is directed towards the development of an understanding of the dynamic and static problems associated with the formation of 2D crystals of these large and well-defined molecules. This aspect relates to the wide area of epitaxial growth, with all its implications for material science. Information on 3D multilayer formation, be it random stacking or crystal growth, can be obtained by AFM investigations. This method does not depend on substrate or surface conductivity, which makes it suitable to study the topology of blank and patterned surfaces.

Molecule 1 can form close-packed 2D assemblies both at the air-solid (deposited from toluene) or liquid-solid (deposited from octanoic acid) interface. The structure of the assemblies is identical in both environments, indicating that the solvent has a negligible influence on the assembling of this spoked wheel molecule. The ordered 2D assembly could only be imaged at large tip-sample distances (high bias voltage and low current) and was easily destroyed with decreased tip-sample distance. This highlights the weak interaction between molecule and substrate. Figure 12a-c shows a well-ordered 2D crystalline domain formed by 1 at the octanoic acid/graphite interface. In high-resolution images, the internal structure of the molecule, the hub, spoke, and rim subunits could be clearly revealed. The spokes normally appear with a much higher contrast than the rim. The clear sixfold symmetry and 5.7 nm distance between two opposite apexes matches well the optimized molecular model of a molecule lying flat on the surface. The six edges as well as the spokes appear with equal contrast in the STM image, indicating that the molecule is adsorbed with its molecular plane parallel to the surface. The STM observations provide clear evidence for the rigidity and shape-persistence of this giant molecular spoked wheel. The spokes play a crucial role in maintaining the rigidity of the monolayer. Interestingly, sometimes a different contrast could be observed with the hub and six apexes appearing brighter than the spoke and rim subunits (Figure 12c). In this case, a cross composed by four bright spots is revealed for each apex. These bright spots could possibly be attributed to the phenylene rings connected to the apex.

The unit cell contains one molecule (Figure 12a). Using the graphite lattice as a calibration grid, the unit cell parameters of the ordered domains could be determined as a=b= 6.0 ± 0.2 nm and $\theta=60\pm2^{\circ}$, which indicates C_6 symmetry. On the basis of these parameters, a molecular model was built reflecting the packing of **1** in ordered domains. In the



Figure 12. STM images of the 2D organization of **1** at the octanoic acid/ graphite interface. a) A unit cell is indicated in white. b) and c) reveal a different contrast of the molecule in the 2D lattice. Tunneling parameters: a) $V_{\text{bias}} = -1.50$ V, $I_{\text{set}} = 10$ pA, b) and c) $V_{\text{bias}} = -1.75$ V, $I_{\text{set}} = 16$ pA. d) STM image revealing clearly the formation of a multilayer structure of **1** ($V_{\text{bias}} = -1.50$ V, $I_{\text{set}} = 11$ pA). In the upper part of the image an ordered multilayer is observed, while in the lower part the molecules in the top layer are disordered. e) A tentative model reflecting the random position/orientation of molecules on top of a well-ordered bottom layer.

model, the giant wheel molecules are aligned side-by-side with their molecular plane parallel to the surface. Adjacent

molecules are slightly shifted to allow staggering of the tertbutyl groups. This results in an intermolecular distance of 6.0 nm, in agreement with that determined experimentally, but slightly smaller than the 6.8 nm distance between two farthest apart hydrogen atoms determined by molecular modeling. Therefore, the wheels must pack tightly, with staggered tertbutyl groups as deduced from the STM data. By imaging the graphite lattice underneath, the epitaxial orientation of these chiral domains could be determined. Our observation indicates that the unit cell vectors of the chiral domain are oriented either clockwise or counterclockwise by $18\pm3^{\circ}$ with respect to the $\langle 11\bar{2}0 \rangle$ direction of graphite (see Supporting Information).

Occasionally, multilayers could be revealed by STM. Figure 12d shows a typical image of such a multilayer structure.

In the lower part of the image isolated giant wheel molecules are located randomly on top of the bottom crystalline layer, while in the upper part of the image the molecules in the top layer also form crystalline domains. Those molecules, which are also resolved with submolecular resolution, sit exactly on top of the molecules in the bottom layer without any significant shift. In contrast, the isolated giant wheel molecules in the lower part of the image appear more like an "O" ring: only the rim is clearly visible, while the spoke and hub units are hardly visible. The sixfold symmetry is not pronounced. This suggests that the isolated giant wheel molecules are more mobile in comparison with those forming a 2D lattice. Nevertheless, since some congruent stacking occurs, the multilayer formation reveals the possibility of the giant wheel molecule to form 3D crystals at the interface through epitaxial growth. However, the role in the assembly process and the actual position of the alkyl chains in the crystal remains unclear. There are two possibilities: the alkyl chains fill the voids between the spokes of their own wheel or extend out of the plane and point into the voids of neighboring wheels. The STM contrast is known to be a combination of both topographic and electronic contributions,^[53] and thus the height measured by STM is not reliable to distinguish between those two cases. For this purpose AFM is a better tool.

Figure 13 shows typical AFM topography and phase images obtained on the epitaxial crystalline film of **1** on the graphite surface. The topography image indicates that **1**



Figure 13. a) Large-scale and b) high-resolution AFM topography and phase images (c, corresponding to b) of the as-prepared crystalline film of the giant molecular wheel, revealing the 3D crystallization on the graphite surface. Domains of different orientations could be clearly revealed and the angle between these domains is determined to be 30° . d) Large-scale and e) and f) high-resolution AFM images of the film after annealing at 50° C for 45 min. Height profiles in the topography images allow the determination of the film and terraces thickness. The total thickness of the film is about 7 nm, corresponding to more than ten layers. The phase image in f) clearly demonstrates the single-crystal nature of the area probed, which is confirmed by the Fourier transform shown in g). h) Zoom of the area marked in f) with the white rectangle, the same area is also marked in e). The two white lines indicate the orientation of the molecular rows in the top layer and the layer underneath: the molecules in the top layer sit on top of the molecules in the second layer without any notice-able shift.

forms a layered structure. However, in some parts of the film, triangular shapes are revealed (Figure 13a), in line with the threefold symmetry of the crystalline film. The molecularly resolved phase and topography images highlight the crystalline characteristics of the film: each molecule appears as a disk with a diameter of about 6 nm, which is in line with the model that the giant wheel molecules are lying with their molecular plane parallel to the surface, in agreement with STM results. The films are polycrystalline in nature with domain sizes ranging from several tens to hundreds of nanometers. From the analysis of the high-resolution topography images, the molecular height is estimated to range from 0.5 to 0.7 nm (see also Figure 13d-h). Considering the thickness of the aromatic rigid backbone (≈ 0.3 nm) and the alkyl chains (≈ 0.4 nm), the 0.5 to 0.7 nm thickness of the molecular layer indicates that some alkyl chains stay within or close to the molecular plane. More probably they fill the voids or lie parallel on top of the backbone, rather than extending away from the plane. As discussed before, SANS characterization indicates that the conformation of alkyl chains depends heavily on the solvent (L1=2.5 nm in)chloroform, L1 = 1.2 nm in THF). Thus the 0.5 to 0.7 nm thickness seems in line with the SANS data. Considering there is no solvent anymore in the crystalline layer, an even smaller L1 value is expected in comparison with 1 in THF.

The domain symmetry directions do not always follow the three main symmetry directions of the substrate: domains are often rotated with respect to each other by about 30°, which is in line with the STM observation of chiral domains within the monolayers. The existence of chiral domains in the upper layers highlights the epitaxial growth characteristics of the film: the in-plane ordering in 3D crystals is identical to and directed by the 2D monolayer assembly. Annealing of the film at 50°C for about 45 min significantly increases the domain size. Single crystalline domains of more than 500 nm are commonly observed. The height differences between terraces, as revealed by height profiles is typically 1.1 and 1.6 nm, so approximately two and three times the height of an individual molecule, indicating the tendency of the giant wheel to form double and triple layers. The triple layer always forms large islands (Figure 13d), while the double layer structure most frequently appears as small islands on top of the triple layer. Occasionally, at the site at which a double layer joins a triple layer island, single molecular steps are observed with a height difference around 0.5 nm (Figure 13d). Figure 13e and f show molecular resolution topography and phase images. The unit cell parameters ($a=b=6.0\pm0.2$ nm, and $\theta=60\pm2^{\circ}$) are in good agreement with the STM and SANS results, again indicating that the structure of 2D giant wheel layers (in the bulk) is independent of the film thickness.

From the molecular modeling simulations we know that the dihedral angle of the boat conformer is rather small. Moreover, the energy difference between the planar and boat conformation is around 2.3 kcalmol⁻¹. It is very likely that the wheel planarizes when adsorbing on a graphite surface to maximize the π -stacking with the surface, as in other phenylene–ethynylene macrocycles.^[44] This has also been confirmed by our STM observations, in which the six rim segments as well as the spokes show equal contrast in the image. However, it is not clear whether the long alkoxy groups on the spokes ($OC_{16}H_{33}$) will entirely adsorb on the surface, within a triangle formed by two spokes and a segment of the rim (e.g., triangle formed by atoms 1, 2, 7 in Figure 8, left). Calculations show that, due to the restricted dihedral angles in alkoxy chains, it is not possible to have all the methylene groups of two $OC_{16}H_{33}$ chains in the plane of the cavity. Figure 14 illustrates that the available van der



Figure 14. Model showing the van der Waals volume of atoms (dotted spheres) in a triangle formed between two spokes, with *n*-octyloxy groups at the substitution position.

Waals surface is already filled by two octyloxy (OC_8H_{17}) groups (note that one $OC_{0}H_{19}$ plus one $OC_{8}H_{17}$ group can still fit in this cavity). This shows that at least half of the whole hexadecyloxy chain is not adsorbed on graphite in the plane of the cavity, but either on top of the wheel and/or at the periphery, outside of the rim. In a multilayer film, in which the molecular planes are parallel to the surface, both arrangements would increase the stacking distance between the wheels compared to a typical π -stacking distance. If part of the alkoxy groups were located on top of the wheel, considering the van der Waals radius of a methylene group, that is, 1.85 Å, this would lead to an increased thickness of at most 0.3-0.4 nm. This is consistent with the fact that the thickness of the layers, as observed by AFM on multilayer films, ranges between 0.5-0.7 nm, slightly larger than the typical π -stacking distance (0.4 nm).

Thus, the 2D assembly is stabilized solely by the staggering of the *tert*-butyl groups and the interaction with the substrate. This implies that the intermolecular interaction is weak, which has been confirmed both by the STM and AFM observations. The assembly is easily affected by the tip scanning. Nevertheless, the molecule is so big that its diffusion on the surface is quite slow at room temperature, and even isolated molecules could be observed by STM with reasonable resolution.^[24]

Conclusion

In summary, we described a representative of a novel family of shape-persistent two-dimensional oligomers in detail. In a rational modular synthesis and subsequent template-aided cyclization, we obtained a molecularly defined, stable, highly symmetrical, rigid, wheel-shaped compound. Peripheral tert-butyl groups and alkyl chains attached to the planes of the molecule provide sufficient solubility such that the compound can be fully characterized. We were able to accomplish the critical steps with respect to the covalent-template synthesis principle, such as sixfold Suzuki and Sonogashira-Hagihara couplings and the final Glaser-Eglinton coupling in good yields. Molecular masses of the target molecule and its free acetylene precursor could be determined by MALDI-MS with perfect match. Other than for linear OPEs, polystyrene calibrated GPC analysis in THF gave a good estimation of the molecular weight. As expected, the molecule conformational constraint observed in ¹H NMR spectra at ambient temperature could be overcome by heating. At 120°C a good resolution is obtained, as illustrated for the aromatic region.

Molecular mechanics and molecular dynamics simulations indicate that the most stable conformer of the molecule is a nearly planar boat conformation with a small dihedral angle (12°). During the simulation the distance between "bow" and "stern" atoms only fluctuates about 0.2 nm. Compared to the open precursor and a hypothetical void macrocycle of the same size and structure, the wheel-shaped compound is utterly constrained in its macroconformations. Upon adsorption on the surface, the molecule is very likely to planarize, which has already been observed for other phenylene-ethvnylene macrocycles. The simulations also demonstrate that at least half of the hexadecyloxy chains cannot be accommodated within the triangle cavity formed by the spokes and rim. Therefore they have to arrange above the molecular plane, resulting in an increased thickness of the molecule, consistent with the SANS, STM, and AFM observations.

Small-angle neutron scattering (SANS) experiments affirm the rigidity of the molecule in solution. Observed scattering intensities could be described by a theoretical hamburger model, which assigns a radius of about 2.7 nm and a thickness of about 0.22 nm to the rigid backbone. The thickness of the soft shell, that is, the conformation of the orthogonal hexadecyloxy chains, depends on the solvent.

The supramolecular organization of the compound has been investigated both at the solid/liquid interface and in thin films with STM and AFM. STM characterization demonstrates that the wheel molecules adsorb with their molecular plane parallel to the surface and organize into hexagonal crystalline domains both at the octanoic acid/graphite and air/graphite interface with the *tert*-butyl groups on the apexes staggered with those of neighboring molecules. The staggering characteristic induces chirality to the organized domains: the *tert*-butyl groups staggered either clockwise or counterclockwise on the surface. AFM investigations of a thin film grown from toluene demonstrate that the wheel molecules inside the top layer organize in the same way as in the layer directly in contact with the surface. This indicates an epitaxial growth characteristic of the film.

Since the covalent-template synthesis principles have now been verified, the synthetic scope of the 2D oligomer at hand enables us to introduce functional groups onto the wheel, either on the spokes or on the rim. Thus, the assembly of these molecules on surfaces does not only lead to nanopatterned surfaces, but can also be enhanced to functionalized surfaces. These 2D functionalized assemblies could be used as platform for the directed growth of supramolecular 3D structures.^[54] Investigations using the self-organized 2D crystalline adsorption layer at the interface as template to guide the assembly of guest molecules are ongoing.[55] Functionalization of the rim with dendrons should pave the way to meltable or even mesomorphic derivatives of 1. Alternatively, the rim can be reserved for the construction of the next generation in a repetitive approach leading to spider web topologies. Ongoing synthetic efforts towards more efficient routes to rigid 2D oligomers will also enable us to investigate high-performance composite materials.

Experimental Section

Molecular mechanics (MM) and molecular dynamics (MD) simulations: Simulations and analysis of the results were performed using the Materials Studio 4.0 and Cerius² packages from Accelrys. We used the same methodology as that applied for a previous phenylene-ethynylene macrocycle,^[35g] using the COMPASS force field as it provides an accurate description of the geometry and the torsion barriers of phenylene-ethynylene oligomers and saturated chains, such as alkoxy or alkyl groups.^[56] The simulations were carried out on an isolated molecule, with methoxy instead of the long OC16H33 groups except when stated. The core was first built planar and a preliminary molecular mechanics (MM) minimization was performed. The nonbonded van der Waals and electrostatic terms are described using a spline function, with a cut-off at 14.0 Å (spline width: 3 Å). For MM energy minimization, we used the conjugate gradient algorithm with an RMS force convergence parameter set to 10⁻³ kcalmol⁻¹ Å. A molecular dynamics (MD) procedure was then applied to the system using the canonical ensemble (N,V,T) at 298 K with a Nosé-Hoover thermostat. The time step was set to 1 fs and the duration of the run was 500 ps, with an output frame every 200 fs. A few minima of the potential energy during the whole MD run were picked from the trajectory file, and a final MM procedure was applied to those structures. SANS measurements: 2D oligomer 1, protonated (THF, p.a., Riedel-de Haën) and deuterated solvents ([D₈]THF, 99.5%, CDCl₃, 99.8%, Deutero GmbH) were used as received. The investigations were restricted to low concentrations (ca. 1 gL^{-1} in THF and ca. 7 gL^{-1} in chloroform) due to the limited solubility of the compound in these solvents. The solvents used have high vapor pressures, leading to a marked loss of the solvent during SANS measurements. This resulted in high concentration errors. Therefore, the number density of the particles was a free fitting parameter during evaluation of the data. The specific volume of 2D oligomer 1 was measured by using a DMA-60-densitometer (Paar, Graz, Austria). The specific volume of 1 was determined to be 1.0 cm^3 g in chloroform. Due to limited amount of 1, we assumed the equal value in THF. All SANS data were obtained using the instrument D11 of the Institut Laue-Langevin in Grenoble.^[57] To obtain the absolute intensities, the data were corrected by the use of the software provided at the instrument. For all data sets, the rates of incoherent scattering caused by the protons were determined at high scattering vector, set as a constant and subtracted

from the crude data. Further data treatment was carried out according to literature procedures. $^{\left[58\right] }$

STM and AFM characterization: The compound was either dissolved in octanoic acid or toluene with a concentration of about 0.1 mg g^{-1} . Samples for STM and AFM characterizations are prepared by drop casting a solution (1 to 3 µL) on a freshly cleaved graphite substrate (HOPG, grade ZYB, Advanced Ceramics Inc., Cleveland, OH). All STM experiments were performed at 20 to 22 °C using a PicoSPM (Agilent Technologies, Santa Clara, CA). Pt/Ir (80%/20%, diameter 0.2 mm) STM tips were prepared by mechanical cutting. The STM images were acquired in the constant-current mode. The experiments were repeated in several sessions by using several tips to check for reproducibility and to avoid artifacts. The molecules could be imaged both under positive and negative bias voltage with submolecular resolution, both under ambient conditions (from toluene) and at the liquid-solid interface (from octanoic acid). For analysis purposes, the graphite substrate was used as a calibration grid. The images were processed by scanning probe image processor (SPIP) software (Image Metrology ApS). The imaging parameters (bias voltage and set point of the tunnelling current) are indicated in the figure captions. The STM sample prepared from toluene was also used for AFM characterization on a Nanoscope IV (Veeco Metrology, USA) operating in tapping mode. A J scanner was used for large scale imaging and an A scanner for high-resolution imaging.

Synthesis and characterization: The syntheses of compounds 3, 4, 7, 8, 10, 13, and 16 as well as their precursors were carried out according to literature methods and will be described in the Supporting Information. The syntheses of compounds 1, 2, 5, 6, 9, 11, 12, 14, 15, 17, 18 and 19 are described below. For synthesis, all experiments were performed under strict exclusion of air and humidity. Therefore all glassware was evacuated, heated, and cooled down in a flow of argon. Unless otherwise indicated, commercially available chemicals were used as received. All solvents were at least "p.a." quality. Dry solvents were either purchased in <50 ppm quality (toluene, dichloromethane) or dried, distilled, and stored under argon according to standard methods (THF, piperidine, pyridine). Prior to characterization and further processing, all solids and oils were dried overnight at RT under vacuum. ${}^{1}\!\dot{H}$ and ${}^{13}\!\dot{C}\,NMR$ spectra were recorded on a Bruker DPX 300, DPX 400, and DRX 500 (300, 400, and 500 for ¹H and 75, 100 and 125 MHz for ¹³C, respectively). Chemical shifts are given in parts per million (ppm) referring to tetramethylsilane (TMS). Mass spectra were measured on a Finnigan ThermoOuest MAT 95 XL (EI-MS), Kratos Concept 1H (FAB-MS; matrix material: 3-nitrobenzyl alcohol, no salts added) and a Bruker Daltronics autoflex TOF/ TOF, (MALDI-MS; matrix material: DCTB, no salts added). m/z peaks smaller than 10% (compared with the most intensive signal) are not reported. UV/Vis spectra were recorded on a Shimadzu UV-2100 spectrophotometer. Unless otherwise indicated, solutions were prepared with indefinite concentration of the sample in dichloromethane. Quartz cuvettes measuring 1 cm in diameter were used for sample solutions as well as solvent references (dual-beam measurements). Fluorescence experiments were run on a Horiba Jobin Yvon FluoroMax-4 spectofluorometer in alltransparent quartz cuvettes and by monochromatic excitation at the indicated wavelength. Melting points were determined using a Leica DMLB microscope with resistive heating socket controlled by a Leica LMW transformator and a Testo 925 digital thermometer. Thin-layer chromatography was conducted on silica gel coated aluminium plates (Macherey-Nagel, Alugramm SIL G/UV 0.25 mm, silica gel with fluorescence indicator); detection either by fluorescence quenching of the luminous indicator ($\lambda = 254$ nm) or autofluorescence of substance spots ($\lambda =$ 366 nm). For column chromatography, silica gel 60 (40-63 µm) from Merck was used as stationary phase, suspended in the respective solvent. Radial thin-layer chromatography was performed with a "chromatotron" (Harrison Research) with silica gel 60 PF254 containing gypsum and fluorescence indicator (designed for preparative thin layer chromatography) as stationary phase. Gel permeation chromatograms (GPC) were measured in THF (stabilized with 2.5 ppm BHT) at RT using a UV detector operating at $\lambda = 254$ nm (flow rate: 1 mLmin⁻¹ in the analytical mode; 4 mLmin⁻¹ for preparative separations). The molecular weight was obtained from polystyrene-calibrated SEC columns (porosity 10², 10³, 10⁵ and 106 Å for analytical measurements and 103 Å for preparative separations). Data integration was undertaken of the UV absorbance at $\lambda = 254$ nm.

Synthesis of 5: A mixture of 4 (1.90 g, 5.72 mmol), 3 (0.480 g, 0.48 mmol), PEPPSI catalyst $^{[27]}$ (39.0 mg, 57.2 $\mu mol),$ and KOH (321 mg, 5.72 mmol, 12.0 equiv) were placed in a Schlenk flask and then evacuated and purged with Ar three times. After adding dry THF (6 mL), the reaction mixture was stirred at 70°C for 24 h. Additional powdered KOH (12.0 equiv) was added and the reaction was stirred on for additional 24 h under argon. The ochre suspension was transferred into a round flask with THF (10 mL) and dried under reduced pressure. Column chromatography (PE/CH₂Cl₂=5:1, $R_{\rm f}$ =0.60) yielded a pure white powder (0.296 g, 0.168 mmol, 35 %). M.p. > 300 °C; ¹H NMR (400 MHz, CD₂Cl₂, 25°C, TMS): $\delta = 7.26$ (s, 6 H), 7.02 (d, ${}^{3}J(H,H) = 8.2$ Hz, 12 H), 6.90 (d, ${}^{3}J_{-}$ $(H,H) = 8.2 Hz, 12 H), 6.86 (s, 6 H), 2.69 (q, {}^{3}J(H,H) = 7.5 Hz, 12 H), 2.39$ (q, ${}^{3}J(H,H) = 7.5$ Hz, 12H), 1.17 (t, 18H, ${}^{3}J(H,H) = 7.5$ Hz), 0.84 (t, ${}^{3}J$ -(H,H) = 7.5 Hz, 18H), 0.33 ppm (s, 54H); ¹³C NMR (75 MHz, CD₂Cl₂, 25°C, TMS): δ=147.20, 142.65, 140.59, 139.44, 139.17, 138.09, 136.45, 134.99, 131.42, 129.47, 127.47, 28.63, 26.03, 16.62, 15.77, 0.25 ppm; MS (MALDI-TOF) C₁₂₀H₁₅₀Si₆ (1759.04): *m*/*z*: 1760.1 [*M*⁺].

Synthesis of 6: Compound 5 (230 mg, 0.131 mmol) was placed in a heated and Ar-flushed flask, dissolved in CHCl₃ (75 mL, degassed with Ar), and cooled down to 0°C. Under strict exclusion of light, a 0.1 M solution of ICl in CH₂Cl₂ (23.5 mL, 2.35 mmol) was added over 30 min. The dark solution was allowed to warm to RT and stirred overnight. Excess halogen was decomposed by adding aqueous $Na_2S_2O_5$ (40 mL, 10%). The aqueous phase was extracted three times with CHCl₃, and the combined organic layers were washed with water and brine, and dried over MgSO₄. Removal of the solvent under reduced pressure yielded the crude product, which was purified by recrystallization from CHCl3. Compound 6 was obtained as white powder in several precipitations (249 mg, 0.120 mmol, 91%). M.p. > 300°C; ¹H NMR (400 MHz, CD₂Cl₂, 25°C, TMS): $\delta = 7.64$ (s, 6 H), 7.01 (d, ${}^{3}J(H,H) = 8.1$ Hz, 12 H), 6.87 (s, 6 H), 6.85 (d, ${}^{3}J(H,H) = 8.1$ Hz, 12 H), 2.65 (q, ${}^{3}J(H,H) = 7.5$ Hz, 12 H), 2.29 (q, ${}^{3}J(H,H) = 7.5$ Hz, 12 H), 1.14 (t, 18 H, ${}^{3}J(H,H) = 7.5$ Hz), 0.81 ppm (t, 18 H, $^{3}J(H,H) = 7.5 \text{ Hz}$; $^{13}C \text{ NMR}$ (100 MHz, $C_2D_2Cl_4$, 25 °C, TMS): $\delta = 143.51$, 142.19, 141.40, 140.16, 139.58, 139.20, 137.77, 131.43, 129.80, 127.29, 98.98, 33.71, 25.60, 15.47, 14.91 ppm; MS (MALDI-TOF) C₁₀₂H₉₆I₆ (2082.18): m/z (%): 2206.5 (12), 2082.3 (100) [M^+], 1957.4 (18).

Synthesis of 9: Compounds 7 (17.63 g, 25.04 mmol) and 8 (58.29 g, 0.246 mol) were ground in a mortar, then suspended in Ac₂O (210 mL) and heated to reflux for 5 h at 150 °C bath temperature (no more CO2 developing). The reaction mixture was allowed to cool down and stirred overnight at RT. The precipitated solid was filtered, washed with distilled water and MeOH, recrystallized from CHCl3 (90 mL), and dried in vacuo. The product was obtained as white powder in several precipitations (13.48 g, 17.52 mmol, 70%). M.p. > 250°C; ¹H NMR (250 MHz, $C_2D_2Cl_4$, 25°C, TMS): $\delta = 7.63$ (d, ${}^{3}J(H,H) = 8.5$ Hz, 2H), 7.63 (s, 2H), 7.56 (d, ${}^{3}J(H,H) = 8.4$ Hz, 4H), 7.49 (d, ${}^{3}J(H,H) = 8.5$ Hz, 2H), 7.21 (d, ${}^{3}J_{-}$ $(H,H) = 8.4 \text{ Hz}, 2H), 6.86 \text{ (d, } {}^{3}J(H,H) = 8.4 \text{ Hz}, 4H), 6.73 \text{ (d, } {}^{3}J(H,H) =$ 8.4 Hz, 2H), 1.37 ppm (s, 9H); ¹³C NMR (100 MHz, C₂D₂Cl₄, 25 °C, TMS): $\delta = 151.06$, 141.20, 141.06, 140.39, 137.72, 137.04, 136.64, 136.05, 133.23, 131.84, 131.77, 130.94, 128.32, 126.78, 126.03, 120.63, 92.72, 34.62, 31.46 ppm; MS (EI) $C_{34}H_{27}BrI_2$ (767.94): m/z (%): 770.0 (100) [⁸¹M⁺], 768.0 (100) $[^{79}M^+]$, 755.0 (50) $[^{81}M^+-CH_3]$, 753.0 (50) $[^{79}M^+-CH_3]$.

Synthesis of 11: Compounds 9 (1.70 g, 2.20 mmol) and 10 (1.69 g, 4.40 mmol), Cs₂CO₃ (2.50 g, 7.67 mmol), THF (10 mL) and distilled water (4 mL) were mixed and the suspension was degassed three times ("pump and freeze"), [Pd(PPh₃)₄] (40 mg, 35 µmol) was added and the mixture was degassed once again. The reaction was stirred at 70 °C for three days before it was diluted with water (50 mL) and Et₂O (100 mL). The organic layer was separated and the aqueous phase was extracted with Et₂O. The combined organic layers were washed with diluted HCl and brine, and dried over MgSO₄. Removal of the solvent in vacuo gave the crude product, which was purified by column chromatography (PE/CH₂Cl₂=15:1; TLC in 5:1, R_f =0.32). Compound 11 was obtained as white solid (0.580 g, 0.56 mmol, 26%). M.p. 171–174°C; ¹H NMR (250 MHz, CD₂Cl₂, 25°C, TMS): δ =7.71–7.62 (m, 4H); δ =7.72 (s, 2H), 7.68 (d, ³*J*(H,H)= 8.5 Hz, 2H), 7.56 (s, 4H), 7.55 (s, 4H), 7.52 (d, ³*J*(H,H)=8.5 Hz, 2H),

Chem. Eur. J. 2009, 15, 2518-2535

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7.49 (d, ${}^{3}J(\text{H},\text{H}) = 8.4 \text{ Hz}$, 4 H), 7.23 (d, ${}^{3}J(\text{H},\text{H}) = 8.4 \text{ Hz}$, 4 H), 7.20 (d, ${}^{3}J(\text{H},\text{H}) = 8.5 \text{ Hz}$, 2 H), 6.87 (d, ${}^{3}J(\text{H},\text{H}) = 8.5 \text{ Hz}$, 2 H), 1,37 (s, 9 H), 1.16 ppm (s, 42 H); ${}^{13}\text{C}$ NMR (100 MHz, C₂D₂Cl₄, 25 °C, TMS): $\delta =$ 151.04, 142.01, 141.22, 140.42, 140.36, 138.60, 137.21, 136.53, 133.50, 132.43, 130.69, 130.55, 128.35, 126.76, 126.70, 126.31, 126.01, 122.48, 120.43, 106.97, 91.47, 34.56, 31.15, 18.53, 11.57 ppm; MS (EI) C₆₈H₇₇BrSi₂ (1028.47): m/z (%): 1029.6 (100), 1028.5 (75) [M^+], 766.4 (100).

Synthesis of 14: At -78°C, nBuLi (0.56 mL, 1.6 M in hexane) was added dropwise to a stirred solution of 11 (910 mg, 0.88 mmol) in THF (10 mL) and stirred for 15 min. Then a solution of diiodoethane (250 mg) in THF (10 mL) was added slowly. The reaction mixture was stirred for 1 h at -78°C, the cooling bath was removed, and the mixture was allowed to warm to RT. After stirring for another 30 min the reaction was diluted with Et2O (100 mL), washed twice with sodium thiosulfate solution (10%) and brine, and dried over ${\rm MgSO_{4}}.$ Removal of the solvent under reduced pressure gave crude 12 as a white solid (0.890 g, 0.83 mmol) that was used without further purification. Under Ar, a dry Schlenk flask was charged with the crude product 12 (0.502 g, 0.47 mmol), CuI (10 mg, 52.5 umol), PPh₃ (20 mg, 76 µmol), [PdCl₂(PPh₃)₂] (20 mg, 28.5 µmol) and 13 (0.106 g, 0.70 mmol). The reagents were dissolved in THF (8 mL) and piperidine (4 mL) and stirred for 24 h at RT. CH₂Cl₂ (70 mL) and water were poured into the cooled-down reaction mixture, the separating organic layer was washed with diluted HOAc, water, NaOH solution (10%), water, and brine. The crude product was obtained after drying over MgSO4 and removing the solvent in vacuo. Purification by column chromatography (PE/CH₂Cl₂=4:1, $R_{\rm f}$ =0.07) yielded **14** (0.330 g, 0.30 mmol, 61% for both steps). M.p. 153-156°C; ¹H NMR (250 MHz, CD₂Cl₂, 25°C, TMS): $\delta = 7.72$ (s, 2H), 7.67 (d, ³J(H,H) = 8.5 Hz, 2H), 7.56 (s, 4H), 7.54 (s, 4H), 7.51 (d, ${}^{3}J(H,H) = 8.6$ Hz, 2H), 7.48 (d, ${}^{3}J$ - $(H,H) = 8.4 Hz, 4H), 7.22 (d, {}^{3}J(H,H) = 8.3 Hz, 4H), 7.16 (d, {}^{3}J(H,H) =$ 8.4 Hz, 2H), 6.94 (d, ${}^{3}J(H,H) = 8.4$ Hz, 2H), 2.38 (t, ${}^{3}J(H,H) = 7.0$ Hz, 2H), 1.81-1.69 (m, 2H), 1.37 (s, 9H), 1.15 (s, 42H), 0.81-0.74 (m, 2H), 0.19 ppm (s, 6H); 13 C NMR (100 MHz, CD₂Cl₂, 25 °C, TMS): $\delta = 151.04$, 141.98, 141.26, 140.41, 140.38, 140.34, 138.18, 137.21, 137.05, 132.42, 131.85, 131.10, 130.54, 128.32, 126.75, 126.68, 126.25, 126.00, 122.47, 120.54, 119.80, 106.95, 106.23, 92.58, 91.47, 34.55, 31.14, 20.66, 20.43, 18.15, 15.62, 11.41, -2.17 ppm; MS (MALDI-TOF) C₇₆H₈₉NSi₃ (1099.63): m/z (%): 1313.8, 1099.6 [M^+], 1065.2, 1056.6 (100) [$M^+-C_3H_7$].

Synthesis of 15: Compound 14 (0.489 g, 0.44 mmol) was dissolved in THF/MeOH (2:1; 15 mL, purged for 15 min with Ar). In a flow of Ar, anhydrous powdered K₂CO₃ (0.607 g, 4.4 mmol) was added in small portions and the resulting suspension was vigorously stirred for 3 h under Ar. The reaction was diluted with water (50 mL) and Et₂O (100 mL). The aqueous phase was extracted with Et₂O, the combined organic layers were washed with water and brine, and were dried over MgSO₄. After removing the solvents under reduced pressure, the crude product was dissolved in CH₂Cl₂ (3 mL) and precipitated by the addition of MeOH (15 mL). The white solid was filtered and dried in vacuo (0.420 g, 0.43 mmol, 98%). M.p. 240°C (decomp); ¹H NMR (250 MHz, CD₂Cl₂, 25°C, TMS): $\delta = 7.72$ (s, 2H), 7.68 (d, ${}^{3}J(H,H) = 8.5$ Hz, 2H), 7.55 (s, 4H), 7.54 (s, 4H), 7.51 (d, ${}^{3}J(H,H) = 8.3$ Hz, 2H), 7.48 (d, {}^{3}J(H,H) = 8.3 Hz, 2H), 7.48 (d, {}^{3}J(H,H) = 8.3 Hz, 2H), 7.48 (d, {}^{3}J(H,H) = 8.3 8.3 Hz, 4H), 7.22 (d, ${}^{3}J(H,H) = 8.4$ Hz, 4H), 7.18 (d, ${}^{3}J(H,H) = 8.3$ Hz, 2H), 6.96 (d, ³*J*(H,H) = 8.3 Hz, 2H), 3.05 (s, 1H), 1.37 (s, 9H), 1.15 ppm (s, 42H); ¹³C NMR (100 MHz, CD₂Cl₂, 25 °C, TMS): $\delta = 151.05$, 142.00, 141.23, 140.49, 140.44, 140.38, 138.23, 137.23, 137.04, 132.41, 131.87, 131.28, 130.54, 128.32, 126.77, 126.70, 126.27, 126.00, 122.47, 119.80, 106.99, 91.46, 83.59, 77.21, 34.57, 31.16, 18.52, 11.44 ppm; MS (ESI) $C_{70}H_{78}Si_2$ (974.56): m/z: 1013.5 [M^++K].

Synthesis of 17: Compounds 15 (0.395 g, 0.405 mmol) and 16 (0.370 g, 0.44 mmol), CuI (7 mg, 37 µmol), PPh₃ (15 mg, 57 µmol), and [PdCl₂-(PPh₃)₂] (15 mg, 21 µmol) were dissolved in THF (10 mL) and piperidine (5 mL) and stirred for 4 h at RT under Ar. The reaction was diluted with Et₂O (70 mL) and water (50 mL) and the separated aqueous layer was extracted several times with Et₂O. The combined organic layers were washed with diluted HOAc, water, NaOH solution (10%), water, and brine. After drying over MgSO₄ and removing the solvent in vacuo the crude product was purified by column chromatography (PE/CH₂Cl₂= 5:2; TLC in 3:2, R_f =0.49) to give 17 as a yellow solid (0.444 g,

0.264 mmol, 64%). ¹H NMR (400 MHz, CDCl₃, 25°C, TMS): δ =7.72 (s, 2H), 7.65 (d, ³*J*(H,H)=8.5 Hz, 2H), 7.52 (s, 8H), 7.50 (d, ³*J*(H,H)=8.4 Hz, 2H), 7.44 (d, ³*J*(H,H)=8.3 Hz, 4H), 7.22 (d, ³*J*(H,H)=8.3 Hz, 2H), 7.21 (d, ³*J*(H,H)=8.3 Hz, 4H), 6.93 (d, ³*J*(H,H)=8.3 Hz, 2H), 7.21 (d, ³*J*(H,H)=8.3 Hz, 4H), 2.43 (t, ³*J*(H,H)=7.1 Hz, 2H), 1.90–1.73 (m, 6H), 1.52–1.41 (m, 4H), 1.38 (s, 9H), 1.37–1.19 (m, 48H), 1.14 (s, 42H), 0.90–0.82 (m, 8H), 0.26 ppm (s, 6H); ¹³C NMR (100 MHz, CD₂Cl₂, 25°C, TMS): δ =154.18, 153.41, 151.03, 142.01, 141.27, 140.42, 140.39, 140.04, 138.24, 137.26, 137.17, 132.40, 131.95, 130.71, 130.57, 128.34, 126.76, 126.70, 126.28, 126.00, 122.45, 121.07, 119.78, 117.14, 116.68, 114.37, 113.25, 106.99, 102.48, 97.99, 95.00, 91.43, 86.15, 69.63, 69.45, 34.57, 32.02, 31.16, 29.79, 29.74, 29.66, 29.47, 29.45, 29.40, 29.35, 69.45, 34.57, 32.02, 31.16, 29.79, 29.74, 29.66, 29.47, 29.45, 29.40, 29.35, 29.27, 26.07, 26.05, 22.78, 20.75, 20.45, 18.52, 15.71, 13.96, 11.44, -2.05 ppm; MS (MALDI-TOF) C₁₁₆H₁₅₇NO₂Si₃ (1680.15): *m/z*: 1681.1 [*M*⁺+H].

Synthesis of 18: The compound was synthesized by the same procedure described for 15 from 17 and purified by column chromatography (PE/ $CH_2Cl_2=2:1, R_f \approx 0.8$). Compound 18 was obtained as a slightly yellow resin (0.183 g, 0.117 mmol, 91%). ¹H NMR (300 MHz, CD₂Cl₂, 25°C, TMS): $\delta = 7.74$ (s, 2H), 7.69 (d, ${}^{3}J(H,H) = 8.4$ Hz, 2H), 7.60–7.53 (m, 14H), 7.25 (d, ${}^{3}J(H,H) = 8.2$ Hz, 4H), 7.22 (d, ${}^{3}J(H,H) = 8.2$ Hz, 2H), 6.98 (d, ${}^{3}J(H,H) = 8.1$ Hz, 2H), 6.94 (s, 1H), 6.93 (s, 1H), 3.94 (t, ${}^{3}J(H,H) =$ 6.4 Hz, 4H), 3.35 (s, 1H), 1.80-1.72 (m, 4H), 1.54-1.41 (m, 4H), 1.37 (s, 9H), 1.37–1.24 (m, 48H), 1.15 (s, 42H), 0.87 ppm (q, ³J(H,H)=6.5 Hz, 6H); ¹³C NMR (100 MHz, CD₂Cl₂, 25°C, TMS): $\delta = 154.16$, 153.39, $151.02,\ 142.00,\ 141.27,\ 140.41,\ 140.38,\ 140.05,\ 138.23,\ 137.25,\ 137.15,$ 132.39, 131.95, 130.71, 130.57, 128.33, 126.76, 126.69, 126.27, 125.99, 122.44, 121.04, 117.69, 116.73, 114.48, 112.44, 106.98, 94.90, 91.42, 86.03, 82.19, 80.01, 69.64, 69.62, 34.56, 32.01, 31.15, 29.77, 29.74, 29.64, 29.44, 29.41, 29.38, 29.31, 29.24, 26.02, 25.97, 22.77, 18.51, 13.96, 11.43 ppm; MS (MALDI-TOF) $C_{110}H_{146}O_2Si_2$ (1555.09): m/z: 1806.3 [M^++DCTB], 1555.1 [*M*⁺]; GPC (PS calibration): $M_{\rm w} = 1800 \text{ g mol}^{-1}$.

Synthesis of 19: Compound 6 (17.8 mg, 8.5 µmol), CuI (2 mg, 10.5 µmol), PPh₃ (4 mg, 15 µmol) and PdCl₂(PPh₃)₂ (4 mg, 5.7 µmol) were dissolved in piperidine (2 mL) under Ar and 18 (0.120 g, 77.1 µmol) in dry THF (4 mL) was added by syringe. The reaction mixture was heated to 70 °C and stirred for 3 d. The reaction was diluted with water (20 mL) and Et₂O (50 mL), the separated aqueous phase was extracted three times with Et₂O (20 mL each). Subsequently, the combined organic layers were washed with diluted H₂SO₄ (10%), water, and brine. The crude product was obtained after drying over Na2SO4 and removing the solvent in vacuo. Column chromatography (PE/CH2Cl2=4:1 to 3:1; TLC in 2:1, $R_{\rm f}$ =0.55) gave **19** (53.6 mg, 5.0 µmol, 59%) as a yellow solid slightly contaminated with the fivefold coupling product (<5%).¹H NMR (400 MHz, CD₂Cl₂, 25 °C, TMS): $\delta = 7.74$ (s, 12 H), 7.69 (d, ${}^{3}J(H,H) =$ 8.4 Hz, 12 H), 7.62-7.47 (m, 84 H), 7.35 (s, 6 H), 7.30-7.21 (m, 36 H), 7.06 $(d, {}^{3}J(H,H) = 7.8 \text{ Hz}, 12 \text{ H}), 7.02-6.97 \text{ (m, 18H)}, 6.97-6.91 \text{ (m, 24H)}, 3.99$ $(dt, {}^{3}J(H,H) = 5.3 Hz, 24 H), 2.92-2.81 (m, 12 H), 2.45-2.34 (m, 12 H),$ 1.88-1.74 (m, 24H), 1.57-1.43 (m, 24H), 1.38 (s, 54H), 1.35-1.18 (m, 306 H), 1.14 (s, 252 H), 0.90 (t, ${}^{3}J(H,H) = 7.5$ Hz, 18 H), 0.84 ppm (t, ${}^{3}J$ - $(H,H) = 5.6 \text{ Hz}, 36 \text{ H}); {}^{13}\text{C NMR} (125 \text{ MHz}, \text{ CD}_2\text{Cl}_2, 25 \,^{\circ}\text{C}, \text{ TMS}): \delta =$ 153.53, 153.52, 151.01, 143.91, 142.18, 142.00, 141.26, 140.52, 140.37, 139.90, 139.61, 139.23, 138.74, 138.23, 137.26, 137.17, 132.39, 132.23, 131.93, 131.47, 130.68, 130.56, 129.51, 128.33, 127.50, 127.49, 126.75, 126.68, 126.27, 125.99, 122.44, 121.29, 121.21, 116.75, 116.28, 114.15, 113.54, 106.98, 94.75, 93.83, 91.39, 89.23, 86.46, 69.60, 69.41, 34.56, 32.01, 31.99, 31.14, 29.79, 29.74, 29.70, 29.66, 29.50, 29.44, 29.42, 29.38, 27.28, 26.14, 26.07, 25.79, 22.77, 18.51, 15.41, 15.06, 13.98, 13.97, 11.40 ppm; MS (MALDI-TOF) $C_{762}H_{966}O_{12}Si_{12}$ (monoisotopic: 10646.23, distr. max.: 10655.25): m/z: 10879.9 [M⁺+dithranol], 10655.1 [M⁺], 10431.8 [M⁺ $-C_{16}H_{31}$], 10206.7 [$M^+-2C_{16}H_{31}$], 9226.1 [$M^+_{(5:1)}$], 8966.7; GPC (PS calibration): $M_{\rm w} = 10600 \text{ g mol}^{-1}$.

Synthesis of 2: TBAF solution in THF (5 mL, 1.0 m) was added slowly to **19** (0.113 g, 10.6μ mol) under Ar and the starting material was dissolved with the aid of an ultrasonic bath (5 min). The reaction mixture was stirred for 16 h before additional TBAF solution (5 mL, 1.0 m) was added. Again, the reaction flask was treated in an ultrasonic bath, then stirred overnight and diluted with Et₂O and water. The aqueous phase was ex-

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tracted with Et₂O, the combined organic layers were washed with water and brine and dried over Na2SO4. After removing of the solvent, the crude product was purified by radial chromatography (PE/CH₂Cl₂=2:1, $R_{\rm f}$ =0.51). Again, after removing of the solvent, the product was dissolved in CHCl₃ (3 mL), precipitated with MeOH (15 mL) and dried in vacuo to give 2 as a faintly yellow solid (70.6 mg, 8.04 µmol, 76%). M.p. > 250 °C (decomp); ¹H NMR (500 MHz, $C_2D_2Cl_4$, 25 °C, TMS): $\delta =$ 7.79 (s, 12 H), 7.72 (d, ${}^{3}J(H,H) = 8.3$ Hz, 12 H), 7.63 (d, ${}^{3}J(H,H) = 8.5$ Hz, 24 H), 7.58 (d, ${}^{3}J(H,H) = 8.3$ Hz, 24 H), 7.56–7.48 (m, 36 H), 7.40 (s, 6 H), 7.32-7.24 (m, 36H), 7.12-7.03 (m, 12H), 7.03-6.92 (m, 42H), 4.08-3.96 (m, 24H), 3.20 (s, 12H), 2.97-2.82 (m, 12H), 2.51-2.35 (m, 12H), 1.89-1.77 (m, 24H), 1.56-1.46 (m, 24H), 1.41 (s, 54H), 1.37-1.17 (m, 306H), 0.96–0.90 (m, 18H), 0.88 ppm (dt, ${}^{3}J(H,H) = 7.0$ Hz, 36H); ${}^{13}C$ NMR (125 MHz, $C_2D_2Cl_4$, 25 °C, TMS): $\delta = 153.60$, 153.46, 150.92, 143.34, $142.34,\ 141.77,\ 141.28,\ 140.87,\ 140.15,\ 139.71,\ 139.10,\ 137.81,\ 137.04,$ 136.98, 132.68, 132.39, 131.86, 131.45, 131.12, 130.97, 130.59, 129.47, 128.94, 128.38, 127.36, 126.83, 126.63, 126.41, 126.03, 121.09, 120.90, 120.88, 120.82, 117.11, 116.36, 114.32, 113.59, 95.46, 94.24, 89.40, 86.49, 83.86, 78.33, 69.84, 69.53, 34.63, 32.04, 31.49, 29.87, 29.84, 29.81, 29.75, 29.74, 29.72, 29.70, 29.56, 29.50, 29.45, 27.34, 26.17, 26.15, 25.87, 22.85, 15.56, 15.23, 14.37 ppm; MS (MALDI-TOF) $C_{654}H_{726}O_{12}$ (monoisotopic: 8770.62, distr. max.: 8779.65): m/z: 9030.2 [M++DCTB)], 8779.5 [M+], 8600.3, 7663.2 $[M_{(5)}^+]$, 7405.3; GPC (PS calibration): $M_w = 10000 \text{ g mol}^{-1}$. Under non-optimized reaction conditions (concerning the preceeding six-

fold coupling reaction) we found the following properties for the deprotected incomplete coupling products.

Data for 1:5 coupling product: ¹H NMR (400 MHz, CD₂Cl₂, 25 °C, TMS): δ = 7.75 (s, 10H), 7.69 (d, ³*J*(H,H) = 8.4 Hz, 10H), 7.65 (s, 1H), 7.62–7.48 (m, 70H), 7.35 (s, 5H), 7.26 (d, ³*J*(H,H) = 8.3 Hz, 20H), 7.23 (d, ³*J*-(H,H) = 8.1 Hz, 10H), 7.08–7.03 (m, 12H), 7.01–6.96 (m, 15H), 6.96–6.87 (m, 23 H), 4.02–3.95 (m, 20H), 3.17, 3.16 (2 s, 10H), 2.90–2.81 (m, 10H), 2.72–2.63 (m, 2H), 2.45–2.27 (m, 12H), 1.86–1.74 (m, 20H), 1.55–1.44 (m, 20H), 1.38 (s, 45H), 1.36–1.10 (m, 255H), 0.93–0.81 ppm (m, 45H); MS (MALDI-TOF) C₅₆₂H₆₂₁IO₁₀ (monoisotopic: 7656.71, distr. max.: 7663.74): *m/z*: 7914.9 [*M*⁺+DCTB], 7664.5 [*M*⁺], 7483.9; GPC (PS calibration): *M*_w=9300 gmol⁻¹.

Data for 1:4 coupling product: ¹H NMR (400 MHz, CD₂Cl₂, 25 °C, TMS): δ = 7.75 (s, 8H), 7.69 (d, ³*J*(H,H) = 8.4 Hz, 8H), 7.64 (s, 2H), 7.59 (d, ³*J*(H,H) = 8.4 Hz, 8H), 7.50 (d, ³*J*(H,H) = 8.4 Hz, 8H), 7.50 (d, ³*J*(H,H) = 8.5 Hz, 16H), 7.34 (s, 4H), 7.26 (d, ³*J*(H,H) = 8.4 Hz, 8H), 7.50 (d, ³*J*(H,H) = 8.5 Hz, 16H), 7.34 (s, 4H), 7.26 (d, ³*J*(H,H) = 8.4 Hz, 16H), 7.23 (d, ³*J*(H,H) = 8.2 Hz, 8H), 7.07–7.01 (m, 12H), 7.00–6.96 (m, 14H), 6.95–6.85 (m, 20H), 4.01–3.95 (m, 16H), 3.18, 3.17, 3.16 (3 s, 8H), 2.85 (q, ³*J*(H,H) = 7.0 Hz, 8H), 2.67 (q, ³*J*(H,H) = 7.3 Hz, 4H), 2.42–2.27 (m, 12H), 1.85–1.74 (m, 16H), 1.56–1.43 (m, 16H), 1.38 (s, 36H), 1.37–1.17 (m, 204H), 0.91–0.80 ppm (m, 36H); MS (MALDI-TOF) C₄₇₀H₅₁₆I₂O₈ (monisotopic: 6541.81, distr. max.: 6547.83): *m/z*: 6798.5 [*M*⁺+DCTB], 6548.5 [*M*⁺], 6368.2 [*M*⁺-C₁₅H₃₀]; GPC (PS calibration): *M*_w =8700 gmol⁻¹.

Synthesis of 1: Under Ar, CuCl (96 mg, 0.97 mmol) and CuCl₂ (13 mg, 97 $\mu mol)$ were suspended in dry pyridine (5 mL) and heated to 50 °C. Compound 2 (17 mg, 1.94 µmol) in pyridine (10 mL) was added over 4 d (pseudo high-dilution conditions). The syringe was rinsed with pyridine (5 mL), which was added slowly (12 h) to the stirred reaction mixture at 50°C. After stirring for another 12 h and cooling to RT, the reaction was diluted by adding CHCl₃ (200 mL) and water (50 mL). Subsequently, the organic layer was separated and washed with aqueous NH₃ (25%), water, HOAc (10%), water, NaOH (10%), and brine. After drying over Na₂SO₄ and evaporation of the solvent the crude product was filtered through a short silica gel column using CHCl₃ as eluent ($R_{\rm f}$ =0.90). The solvent was evaporated nearly to dryness and the crude cyclization product was precipitated by the addition of MeOH. GPC analysis of the precipitate (12.3 mg, 72%) indicated the presence of a small amount of the dimer. The yellowish powder was dissolved in a small amount of THF and purified by preparative GPC. The dry product fraction was dissolved in CHCl₃ (1 mL) and precipitated by the addition of MeOH (15 mL) twice. Drying in vacuo gave of the pure 1 as slightly yellow solid (10.0 mg, 1.14 µmol, 59%). M.p. > 250 °C (decomp); ¹H NMR (500 MHz, $C_2D_2Cl_4$, 120 °C, TMS): $\delta = 7.84$ (s, 12 H), 7.76 (d, ${}^{3}J(H,H) = 8.4$ Hz, 12 H),

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7.68–7.62 (m, 48H), 7.57 (d, ${}^{3}J(H,H)=8.5$ Hz, 12H), 7.54 (d, ${}^{3}J(H,H)=8.3$ Hz, 24H), 7.41 (s, 6H), 7.32 (d, ${}^{3}J(H,H)=8.2$ Hz, 24H), 7.26 (d, ${}^{3}J(H,H)=8.3$ Hz, 12H), 7.13 (d, ${}^{3}J(H,H)=8.0$ Hz, 12H), 7.04 (s, 6H), 7.01–6.93 (m, 36H), 4.08 (dt, ${}^{3}J(H,H)=6.5$ Hz, 24H), 2.98–2.88 (m, 12H), 2.50–2.40 (m, 12H), 1.91–1.81 (m, 24H), 1.60–1.50 (m, 24H), 1.47 (s, 54H), 1.45–1.26 (m, 306H), 1.00–0.90 ppm (m, 54H); MS (MALDI-TOF) C₆₅₄H₇₁₄O₁₂ (monoisotopic: 8759.53, distr. max.: 8767.56): *m/z*: 17507.5 [2M⁺], 13135.9 [3M²⁺], 9268.3 [M⁺+2DCTB], 9018.0 [M⁺+DCTB], 8767.2 [M⁺], 4414.4, 4383.9 [M²⁺]; GPC (PS calibration): $M_w = 96000$ gmol⁻¹.

Acknowledgements

This work was supported by the Belgian Federal Science policy through IAP 6/27, the Fund for Scientific Research-Flanders (FWO), the Belgian National Fund for Scientific Research (F.R.S.-FNRS), the Deutsche Forschungsgemeinschaft and the Sonderforschungsbereich 624. M.S. is Chargé de Recherches of the F.R.S.-FNRS. The authors thank the Institute Laue–Langevin for providing beamtime at the instrument D11.

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> Received: September 19, 2008 Published online: February 3, 2009