VIP Two-Dimensional Oligomers

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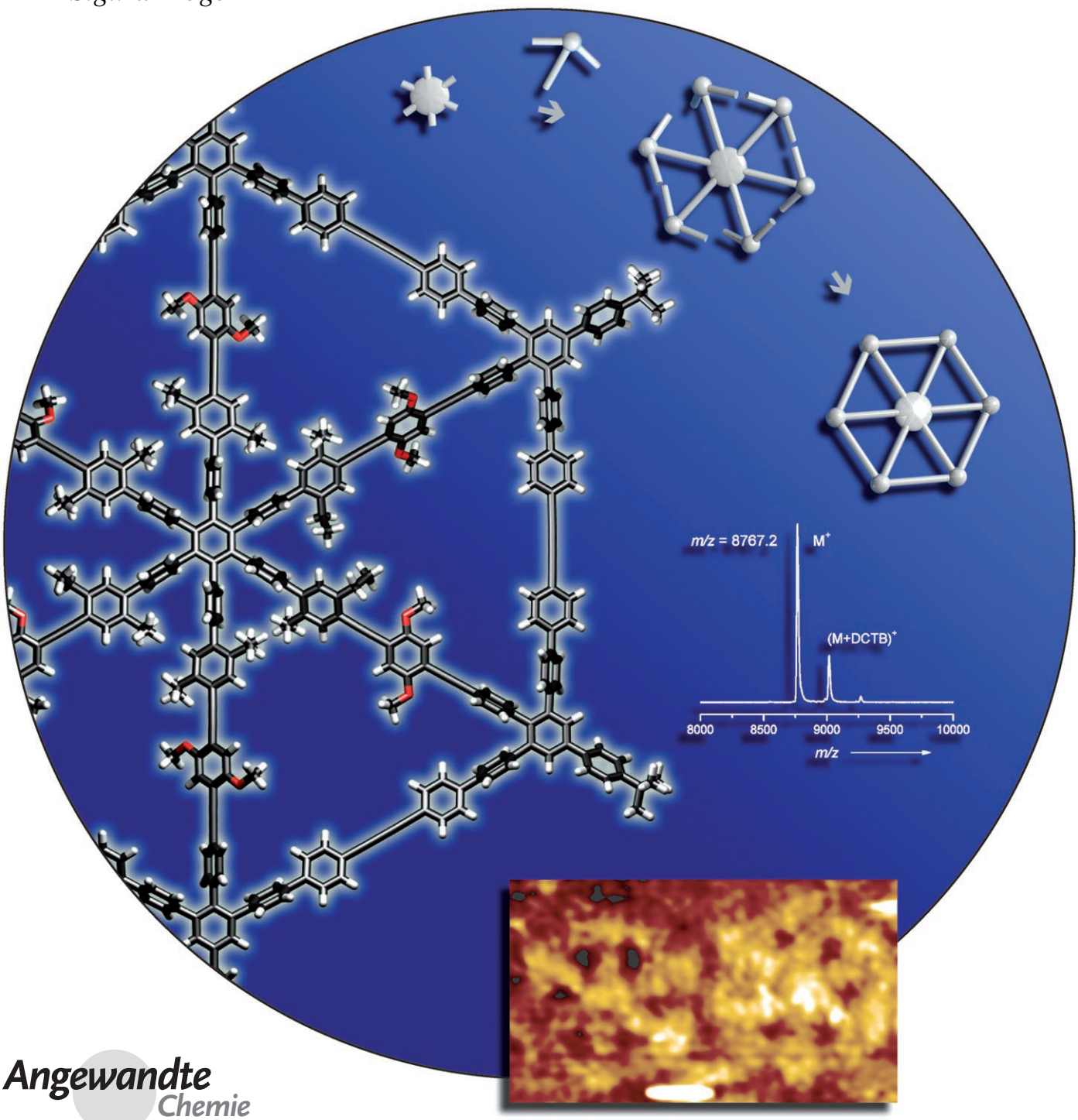
Molecularly Defined Shape-Persistent 2D Oligomers: The Covalent-Template Approach to Molecular Spoked Wheels**

Dennis Mössinger, Jens Hornung, Shengbin Lei, Steven De Feyter, and Sigurd Höger**



Two-dimensional rigid structures have received increasing attention in materials science, both in basic research and industrial application. For example, polymer–clay nanocomposites have been investigated thoroughly with regard to their stiffness, strength, thermal stability, and gas and liquid permeability.[1] Uniformly disk-shaped synthetic clay platelets (e.g. Laponite RD, $d \approx 25$ nm) have also been analyzed recently in order to understand fundamental physical and chemical aspects of polymer–clay composite materials.[2,3]

Alternatively, rigid two-dimensional (2D) organic oligomers and polymers with similar lateral expansions could be employed as model compounds or even used for the formulation of new composites. While linear shape-persistent organic oligomers are well investigated as models for the corresponding polymers and also have their own field of applications (e.g. in photooptics), rigid two-dimensional oligomers are relatively unexplored.[4–8] However, this approach has numerous potential benefits as these structures are molecularly defined and 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 (Figure 1).[9] Although some defined rigid 2D structures have already been described, an approach towards objects in a size range of the inorganic counterparts can be rarely found.[10] Here we describe the first example of new molecular objects that fulfill the aforementioned criteria. Scanning tunneling microscopic (STM) investigations can be used to visualize the molecules and confirm their proposed size and shape.

Our synthetic approach to large two-dimensional oligo(arylene ethynylene)s is outlined in Scheme 1. Target structure **C** consists of hub, spoke, and rim subunits based

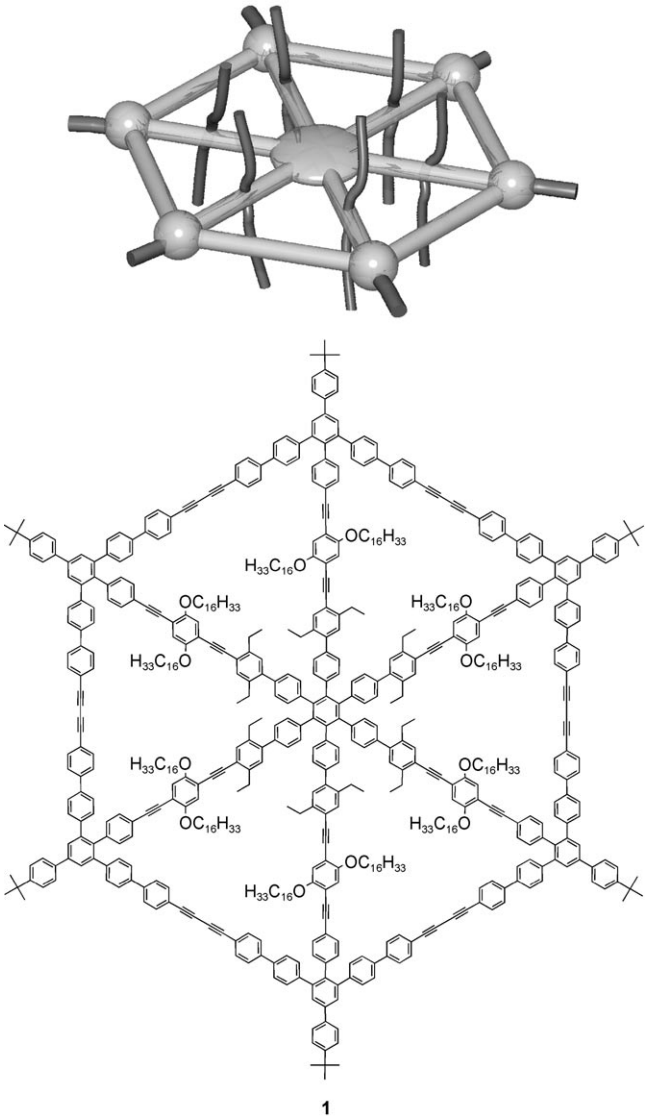
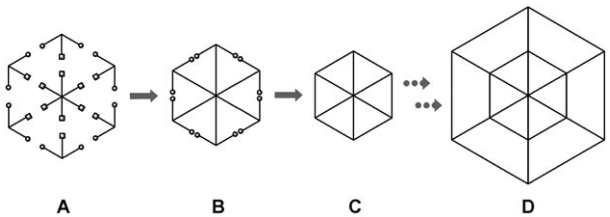


Figure 1. Schematic illustration of rigid 2D oligomers with side groups above and below the molecular plane and at the periphery (top). Structure of the first-generation 2D oligomer **1** (bottom).



Scheme 1. Two different rigid building blocks (**A**) undergo sixfold coupling to form star-shaped molecule **B**, which is cyclized to give the rigid 2D oligomer **C**. A repetitive synthesis using **C** as a hub should enable further radial growth to form higher generations, for example, **D** as a representative of the second generation.

[*] Dr. S. Lei, Prof. Dr. S. De Feyter
Department of Chemistry
Laboratory of Photochemistry and Spectroscopy, and
INPAC—Institute for Nanoscale Physics and Chemistry
Katholieke Universiteit Leuven
Celestijnenlaan 200-F, 3001 Leuven (Belgium)
Fax: (+32) 16-327-990
E-mail: steven.defeyter@chem.kuleuven.be
Homepage: http://www.chem.kuleuven.be/research/mds/mds_en.html
Dipl.-Chem. D. Mössinger, Prof. Dr. S. Höger
Kekulé-Institut für Organische Chemie
Biochemie der Universität Bonn
Gerhard-Domagk-Strasse 1, 53121 Bonn (Germany)
Fax: (+49) 228-73-5662
E-mail: hoeger@uni-bonn.de
Homepage: http://www.chemie.uni-bonn.de/oc/ak_ho/
Dipl.-Chem. J. Hornung[+]
Institut für Technische Chemie und Polymerchemie
Universität Karlsruhe
Engesserstrasse 18, 76131 Karlsruhe (Germany)
[+] Present address: ETH Zürich
Laboratorium für Organische Chemie
HCI G 306
Wolfgang-Pauli-Strasse 10, 8093 Zurich (Switzerland)

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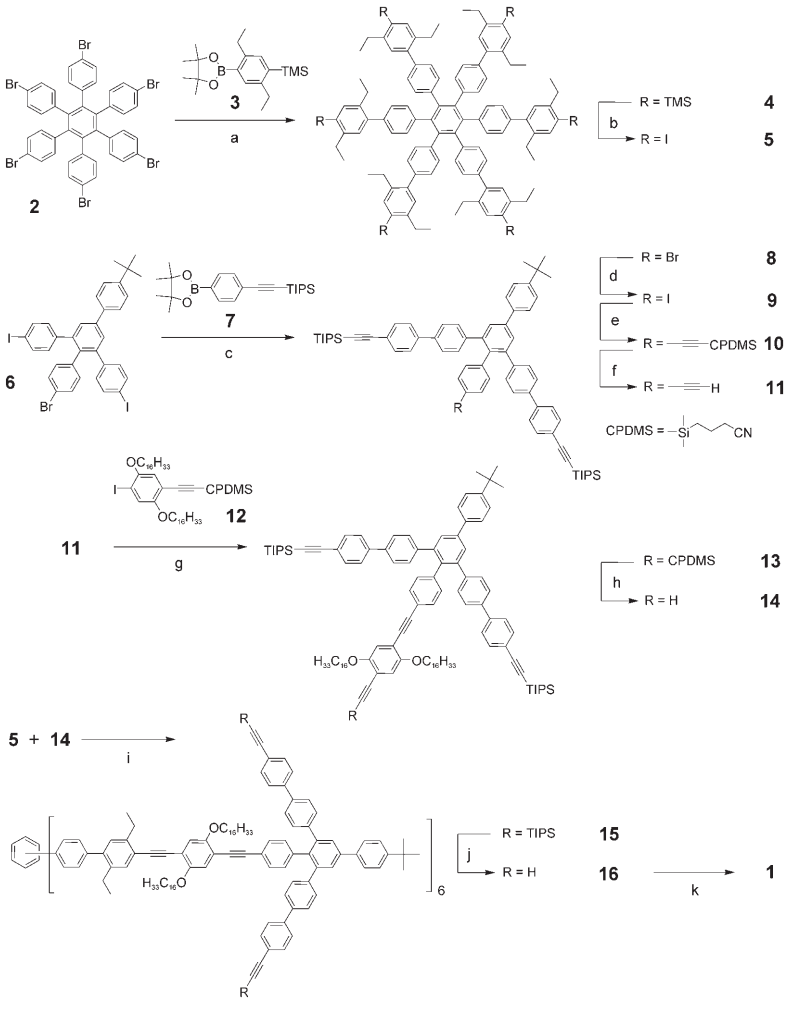
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

on rigid building blocks. The sixfold rotational symmetry permits a feasible synthesis requiring only two different modules for the formation of **B** and an intramolecular coupling to give **C**. Our concept allows functionalization above and below the plane (hub and spokes) as well as at the periphery (corners and edges of the rim). Radial expansion with similar modules should make "higher generations" accessible (**D**). If we apply dendrimer terminology to describe our concept, the spoked wheel **C** represents a first-generation rigid 2D oligomer. Spiderweb **D**, yet not realized, would represent a second-generation structure.[11]

This approach is not limited to specific bond-forming reactions, and alternatives including bond formation under thermodynamic control can also be envisaged. In our first approach we focused on Pd-catalyzed C–C coupling reactions for the formation of **B** and oxidative acetylene coupling for the cyclization giving **C**.[12,13] We have chosen butadiyne formation as the cyclization reaction because previously our group demonstrated that template-supported (intramolecular) acetylene dimerization gives nearly quantitative yields of the corresponding macrocyclic coupling products.[14–16]

Scheme 2 displays the synthesis of the novel 2D oligomer **1**. Sixfold Suzuki reaction of hexa(4-bromophenyl)benzene (**2**)[18] with the aryl boron pinacolate **3**[19] and subsequent iododesilylation using iodine monochloride gave the "hub" component **5**. Although **5** is barely soluble in chloroform, the twelve ethyl side groups made it possible to purify **5**, a prerequisite for the success of the following reaction sequence. Component **6**, accessible from the corresponding pyrylium salt,[20] was coupled with two equivalents of the boronate **7** to yield **8**.[21] Prior to the subsequent Hagihara–Sonogashira coupling with (3-cyanopropyl)dimethylsilyl(CPDMS)-acetylene, **8** was transformed into the more reactive iodo compound **9** by halogen–metal exchange and treating the intermediate with diiodoethane. The CPDMS group is a polar analogue of the trimethylsilyl group and simplifies the chromatographic separation of coupling products, starting material, and dehalogenated side products.[14h,22] Base-catalyzed deprotection of **10**, coupling with **12**, and removal of the CPDMS groups gave **14**. Here again, thanks to the CPDMS group, purification of **13** by column chromatography was straightforward even on a hundred-milligram scale. Furthermore, the consecutive polarity change of the products in the reaction sequence guaranteed that **14** was not contaminated even with traces of side product, an absolute requirement for the next crucial coupling steps. The coupling of **5** with nine equivalents of **14** at 70 °C for 3 d gave high yields of the sixfold coupling product **15** along with less than 5% of the fivefold coupling product.[23] Since intermediate **15** and the incomplete coupling products have the same R_f values on TLC, the reaction progress can be determined only by ^{1}H NMR spectroscopy or mass spectrometry. Column chromatographic purification at this point of the synthesis was not possible. However, after deprotection the corresponding desilylated five- (and four-fold) coupling products have greater R_f values so that **16** could be purified by radial chromatography.

The intramolecular dimerization of acetylene units was performed under pseudo-high-dilution conditions by adding a dilute solution of **16** in pyridine over four days to a slurry of $CuCl/CuCl_2$ in the same solvent. The reaction mixture was stirred for an additional 16 h before the crude reaction product was analyzed by gel permeation chromatography (GPC). When the reaction was performed at room temperature, the reaction mixture contained about 65% of **1** along with 20% of a low-molecular-weight impurity ($M_w \approx 2000\ g\,mol^{-1}$) of unknown origin and structure and 15%



Scheme 2. a) PEPPSI catalyst,[17] KOH, THF, 5 h reflux, 66%; b) ICl, $CHCl_3$, 0–20 °C, 24 h, 91%; c) $[Pd(PPh_3)_4]$, Cs_2CO_3, H_2O, THF, 3 d reflux, 26%; d) *n*BuLi, $C_2H_4I_2$, THF, −78 °C, 2 h, 20 °C, 94%; e) [(3-cyanopropyl)dimethylsilyl]acetylene (CPDMS-acetylene), $[PdCl_2(PPh_3)_2]$, CuI, PPh_3, THF, piperidine, 20 °C, 24 h, 62%; f) K_2CO_3, THF/MeOH (2:1), 3 h, 20 °C, 98%; g) $[PdCl_2(PPh_3)_2]$, CuI, PPh_3, THF, piperidine, 20 °C, 4 h, 65%; h) K_2CO_3, THF/MeOH (2:1), 16 h, 20 °C, 92%; i) $[PdCl_2(PPh_3)_2]$, CuI, PPh_3, THF, piperidine, 70 °C, 3 d; j) excess TBAF, 1 M in THF, 5% H_2O, 20 °C, 3 d, 46% (2 steps); k) CuCl, $CuCl_2$, pyridine, 50 °C, 4 d, 59%. TBAF = $[NBu_4]F$, TIPS = triisopropylsilyl, TMS = trimethylsilyl.

of impurities of slightly higher molecular weight, presumably dimers of **1** (Figure 2). However, as we have shown previously on other systems, using the same coupling conditions at slightly elevated temperatures (50 °C) has a strong influence on the product distribution and, in this case, suppressed the

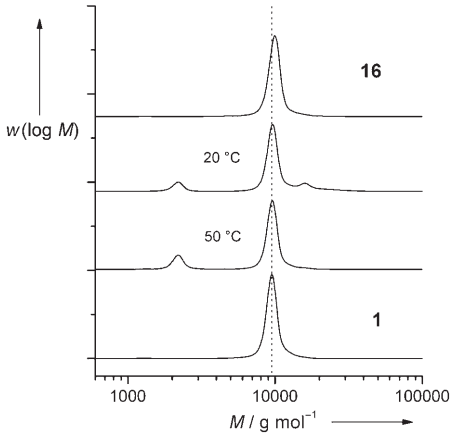


Figure 2. Molecular-weight distributions obtained by GPC analysis (THF, polystyrene calibration). From top to bottom: precursor molecule **16**, crude products of the oxidative cyclizations at 20 °C and 50 °C, and 2D oligomer **1** after GPC purification. Note that the hydrodynamic radius of **16** is larger than that of **1**. $w(\log M)$ = weight fraction.

formation of higher-molecular-weight side products nearly completely.[24,25] As also observed for other template-directed acetylene dimerizations, the hydrodynamic volume of **1** is smaller than that of **16**.[14]

Purification by preparative GPC gave pure **1** in 59% yield. Oligomer **1** is a slightly yellow solid which does not melt below 250 °C (decomp.). It is moderately soluble in THF ($\approx 1.5\ mg\,mL^{-1}$) and well soluble in chloroform ($\approx 7.5\ mg\,mL^{-1}$) and tetrachlororethane (TCE) ($>15\ mg\,mL^{-1}$), and exhibits a violet-blue fluorescence in solution.[26]

The cyclization is accompanied by an increase of rigidity and, therefore, the ^{1}H NMR spectrum of 2D oligomer **1** exhibits broadened signals at room temperature even in good solvents, most probably due to hindered rotation of the *p*-phenylene units.[27] The resolution in high-temperature measurements in TCE at 90 °C is comparable to that of precursor **16** at room temperature. The precursor's characteristic signal at $\delta = 3.2$ ppm for the terminal alkyne units is absent in the spectrum of **1**, which shows, together with the high symmetry of the spectrum, that the cyclization is complete (see the Supporting Information).

This assumption is further supported by MALDI-TOF mass spectra of both **16** and **1** (Figure 3). Beside matrix adduct peaks there are distinct molecule peaks at *m*/*z* 8779.8 (**16**, calcd.: 8779.7) and *m*/*z* 8767.2 (**1**, calcd.: 8767.6), respectively. The difference of 12.6(± 0.5) *m*/*z* units fits perfectly with the loss of twelve acetylene protons during the cyclization. Minor peaks in the mass spectrum of 2D oligomer **1** originate from doubly charged molecules (*m*/*z* 4383.9), as well as dimers and trimers (see the Supporting Information).[28]

Oligomer **1** is indeed a molecular spoked wheel as confirmed by STM. With this technique the structure,

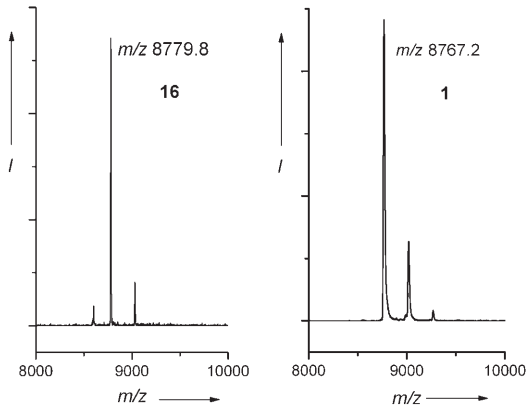


Figure 3. MALDI-TOF mass spectra of precursor molecule **16** (left) and cyclic 2D oligomer **1** (right); matrix material: 2-[2*E*-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) ($250.34\ g\,mol^{-1}$).

conformation, and self-assembling properties of organic molecules can be characterized on atomically flat conductive substrates with submolecular resolution, even under ambient conditions.[29,30] 2D oligomer **1** was adsorbed on the surface of highly oriented pyrolytic graphite (HOPG) after application of one microliter of a $0.1\ mg\,mL^{-1}$ solution of the compound in toluene. STM characterization was carried out under ambient conditions at room temperature. The images reveal some isolated bright disks or clusters on top of a featureless background (Figure 4). By comparison of the diameter and

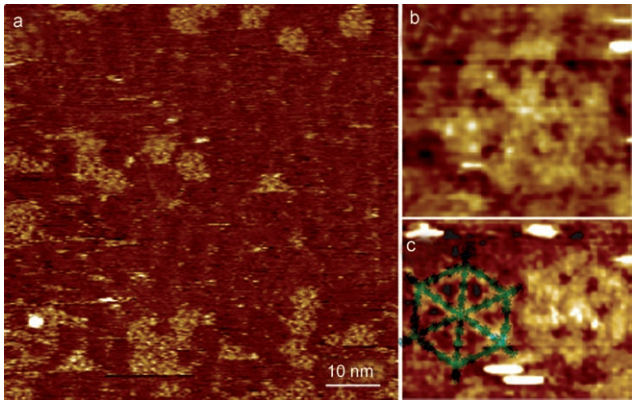


Figure 4. Large-scale (a) and high-resolution (b,c) STM images of 2D oligomer **1** immobilized on graphite. An optimized molecular model is superimposed on the left molecule of the STM image in (c). Tunneling conditions are $I_t = 16$ pA, $V_t = 1.04$ V for (a); $I_t = 15$ pA, $V_t = -1.04$ V for (b,c).

the internal structure of the disks (see below) with a molecular model, it can be safely concluded that the disks correspond to individual molecules. Sometimes only the upper part of such a disk is visible. This can be attributed to the lateral manipulation of individual molecules induced by the STM tip. The 2D oligomers could often be revealed with submolecular resolution. The hub, spoke, and rim subunits of the molecule can be clearly distinguished and appear bright due to the high tunneling probability of the phenylene ethynylene moieties. The sixfold symmetry and the 5.7-nm

measured distance between two opposite apexes are consistent with an optimized molecular model. The STM observation provides clear evidence of the rigidity and shape-persistence of these giant wheel-like molecules.

We have described the first representative of new shape-persistent two-dimensional oligomers. In a rational modular synthesis we obtained a molecularly defined, stable, highly symmetrical, and rigid disk-shaped compound measuring seven nanometers in diameter (opposite *t*-butyl groups). Peripheral *t*-butyl groups and alkyl chains attached to the planes of the molecule provide sufficient solubility such that the compound can be fully characterized. The immobilized oligomer was also visualized on HOPG by means of STM. Our synthetic concept permits functionalization at various positions in the plane of the molecules, so that the rim can be reserved for the construction of the next generation in a repetitive approach. Ongoing studies focus on this topic as well as detailed investigations of functionalized and mesomorphic derivatives of **1**.

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