A Giant Molecular Spoked Wheel

Robert May, Stefan-S. Jester,* and Sigurd Höger*

Kekulé-Institut für Organische Chemie und Biochemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Strasse 1, 53121 Bonn, Germany
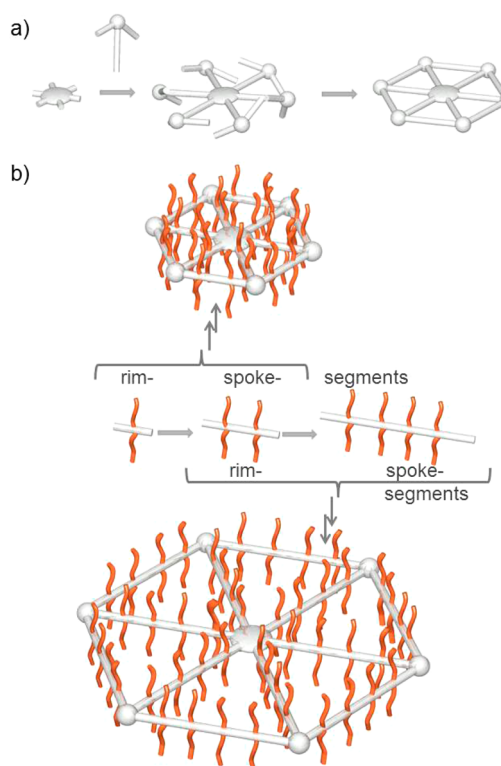
S *Supporting Information*

ABSTRACT: The modular synthesis of a defined, rigid molecular spoked wheel structure with the sum formula $C_{1878}H_{2682}$ and a diameter of about 12 nm is described. The attached 96 dodecyl side chains provide the solubility of the 25 260 Da compound in common organic solvents. At the octanoic acid/highly oriented pyrolytic graphite interface, the molecules self-assemble to form an ordered 2D lattice, which is investigated by scanning tunneling microscopy, displaying their structure with submolecular resolution.

Within the past few years, interest in nanoscale arylene- and arylene-ethynylene-based shape-persistent molecules has continuously increased.[1] Modern synthetic coupling methods and advanced protective group strategies allow the synthesis of defined structures with increasing dimensions. Appropriate processability makes these molecules interesting for (single molecule) optical or electro-optical applications or as building blocks for future nanotechnologies.[2] In one-dimensional molecules, the number of solubilizing side groups grows linearly with the molecule length, which compensates for the aggregation tendency due to the (also linearly) increasing contact area between the individual molecules,[3] and three-dimensional structures often show an inherently good solubility.[4] However, two-dimensional (2D) structures with a filled interior, such as polycyclic aromatic hydrocarbons, suffer from the fact that the number of solubilizing side chains which only decorate the periphery increases linearly with the molecule diameter, whereas the contact area between the rigid molecule parts grows quadratically.[5] Thus, beyond a certain size, disc-like molecules are hardly soluble. Shape-persistent macrocycles, on the other hand, are due to their hollow interior much more soluble, but they lose their rigidity above a certain diameter as a result of the limited persistence length of the phenylene or phenylene-ethynylene backbone.[6] One way toward phenylene-ethynylene structures with an increased structural rigidity relies on their covalent mounting around an intraannular spoke/hub system.[7] Here, the spokes are also able to carry solubilizing side groups and thus guarantee the processability of the compounds. Following the macroscopic example, the building blocks of the molecular spoked wheel (MSW) are referred to as *hub* (*n*-fold core), *spokes* (stiffening rods), and *rim* (macrocyclic ring, Scheme 1). The combination of structural rigidity and a straightforward synthetic approach is perfectly given in phenylene-ethynylene-butadiynylene structures.

Our recently developed convergent modular synthesis relies on a covalent template approach. Preformed spoke/rim

Scheme 1. Schematic Representation of the Synthesis and Construction Principle of Molecular Spoked Wheels[a]

[a](a) The central hub is decorated by spoke/rim segments, and a six-fold coupling reaction forms the rigid rim. (b) A stepwise coupling strategy leads to a homologous series of oligomers (with quadratic growth factor). Since the modular synthesis requires two rigid oligomers that differ in their length by a factor of 2, the spoke segments of the smaller MSW act as the rim segments of the larger MSW.

segments are connected to a central hub unit, and the subsequent intramolecular coupling (after deprotection) forms the rigid rim (Scheme 1a).[8]

The structure and size of the hub, spoke, and rim segments are such that linear oligo(phenylene-ethynylene-butadiynylene) building blocks (oPEBs) can be used for the rim segments and, with doubled length, also for the spoke segments (i.e., the building blocks for the rim and rod segments belong to the same polymer homologue series with a quadratic growth factor,
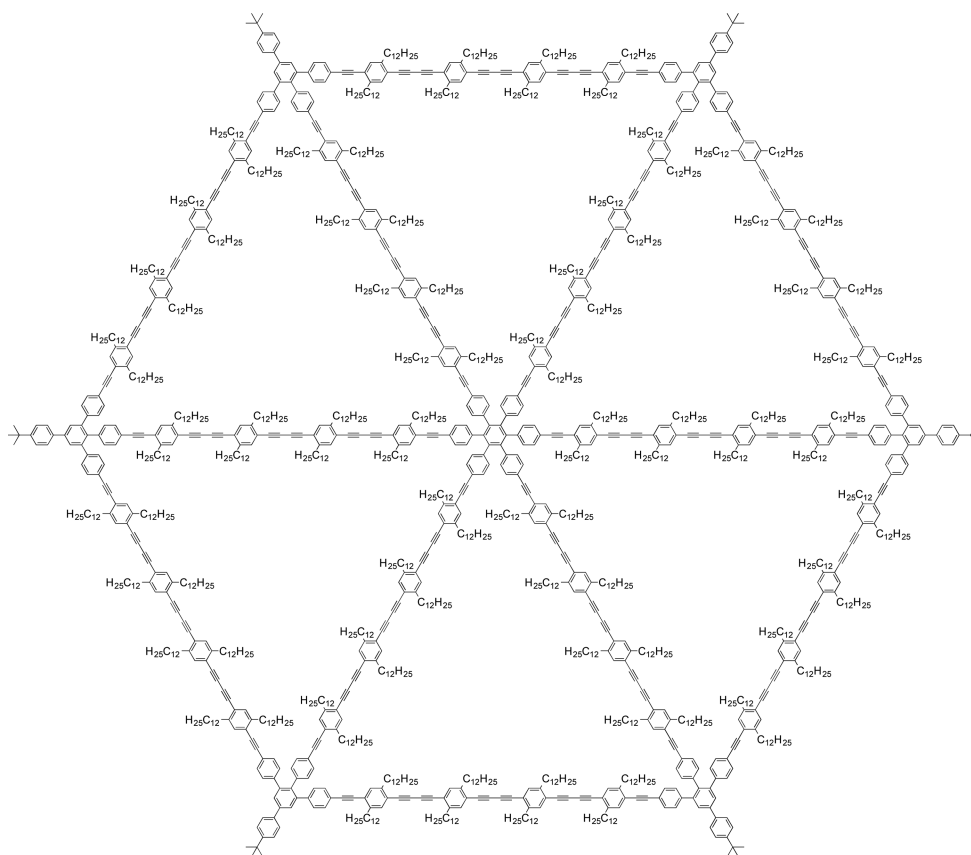
Figure 1. Chemical structure of **1** (sum formula $C_{1878}H_{2682}$) with a corner−corner diameter, $d_{tbu-tbu}$, of 11.9 nm and a rim−rim diameter, d_{C-C}, of 8.8 nm.

Scheme 1b).[9] During the final rim coupling step, the length of the rim segments is doubled so that rim and spoke segments have the same size, and this results in a spoked molecular hexagon (spoked wheel). Using this approach, we described recently a MSW with a backbone diameter of about 8 nm.[8] In principle, the synthesis of larger MSWs should be feasible if higher oligomers of the oPEBs are used as rim and rod segments, thus giving access to processable, molecularly defined, size-expanded rigid 2D structures.

Here we describe that **1**, a molecular spoked wheel with a corner-to-corner distance of about 12 nm (Figure 1), can indeed be obtained by the synthesis shown in Scheme 2 that follows the strategy discussed above.

The corner piece **2** is easily obtained from the corresponding pyrylium salt and bromophenyl acetic acid.[10] oPEBs **3** and **4**, the spoke and rim segments, are synthesized according to our recently described protocol that relies on a repetitive statistical protection/homocoupling/deprotection sequence (see Supporting Information, SI) in which each of the steps doubles the rod length.[9a] The 3-cyanopropyl dimethyl silyl (CPDMS) and the more robust 3-cyanopropyl diisopropyl silyl (CPD*i*PS) protective groups ensure column chromatographic separation of the di- from the mono- and unprotected compounds due to different polarities and otherwise (mostly) behave like their commonly used trimethyl silyl and triisopropyl silyl analogues.[11] The coupling of (mono-CPD*i*PS-protected) rod **3** to the iodo positions of **2** is performed under standard Sonogashira−Hagihara conditions using PdCl$_2$(PPh$_3$)$_2$, CuI, and PPh$_3$ in piperidine/THF at rt to obtain the rim−corner−rim module **5** in 89% yield. Under the applied reaction

conditions, a high iodobromo selectivity can be observed, and no preferred oxidative addition with the intramolecular bromo position occurs.[12] By coupling **5** with the (mono-CPDMS) protected **4** via a copper-free method applying (allylPdCl)$_2$ as catalyst, ZnCl$_2$ as cocatalyst, and P(*t*Bu)$_3$ as ligand,[13] Glaser homocoupling is mostly avoided, and **6** is obtained in yields of 49−56%. **6** is selectively deprotected with K$_2$CO$_3$ in THF/MeOH to obtain **7** in a yield of 90%. The sixfold coupling of **7** to the hub **8** using Pd$_2$dba$_3$, CuI, and dppf in piperidine at 80 °C overnight leads to a crude product mixture from which **9** can be isolated using recycling gel permeation chromatography (recGPC) in a yield of 22%. The latter is deprotected using TBAF in THF to give the MSW precursor **10** in 98% yield. Subsequent cyclization under pseudo-high-dilution conditions is performed by adding it via a syringe pump into a solution of PdCl$_2$(PPh$_3$)$_2$, CuI, and I$_2$ in HN*i*Pr$_2$/THF at 50 °C over 72 h. **1** is obtained from the crude product mixture in a yield of 43% by recGPC as a bright yellow solid.

GPC analysis of **1** shows a discrete peak at 24.8×10^3 g/mol (polystyrene (PS) calibration). Although its actual molecular weight is nearly the same as that for **10** (GPC peak at 26.4×10^3 g/mol, PS calibration), in the course of the cyclization, the hydrodynamic volume has significantly decreased (suggesting a lower molecular weight) as a result of the planarization of the molecule. Nevertheless, in both cases, the overestimation factors f_i (which specify the degree of overestimation of the molecular weight) of the compounds i ($i = $ **1**, **10**) by a PS-calibrated GPC system are close to 1 ($f_1 = 0.98$ and $f_{10} = 1.04$). A similar observation has been made for other spoked wheel compounds described before.[7b,8] In addition, this behavior

Scheme 2. Convergent Synthesis of 1[a]
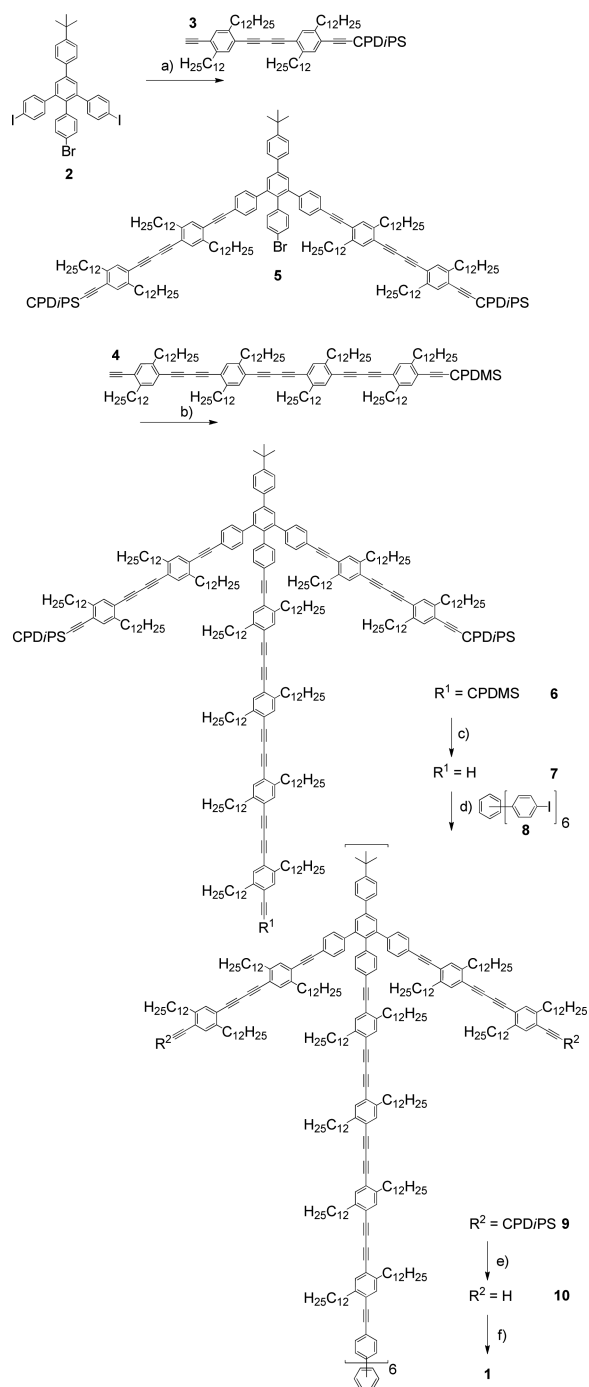
[a]Conditions: (a) PdCl$_2$(PPh$_3$)$_2$, CuI, PPh$_3$, piperidine, THF, rt, 89%; (b) (C$_3$H$_5$PdCl)$_2$, ZnCl$_2$, P(tBu)$_3$, HNiPr$_2$, 80 °C, 49−56%; (c) K$_2$CO$_3$, THF/MeOH, rt, 90%; (d) Pd$_2$(dba)$_3$, CuI, dppf, piperidine, 80 °C, 22%; (e) TBAF, THF, rt, 98%; (f) PdCl$_2$(PPh$_3$)$_2$, CuI, I$_2$, HNiPr$_2$, THF, 50 °C, 43%.

differs significantly from arylene-butadiynylene oligomers which have overestimation factors of around 3.[9] It therefore seems rather general that in 2D phenylene-ethynylene structures the higher persistence length of their constituents as compared to those of PS (which gives rise to larger overestimation factors) is compensated by their expansion in the second dimension.

The ^{1}H NMR spectrum of **1** correlates well with the molecular structure, although all signals are rather broad, even

at elevated temperatures. Also, the MALDI-MS analysis of **1** shows a rather broad signal at m/z with a maximum at 25 350 Da (25 260 Da is expected). This is a result of analytes with a different degree of side chain loss that occurs during the ionization process and different degrees of matrix inclusion, as it is also observed for shape-persistent macrocyclic structures.[14] It must be concluded that conventional spectrometric and spectroscopic analytics commonly used for organic molecules have their limits due to the enormously extended size of the rigid title compound.

However, a final structure proof came from scanning tunneling microscopy (STM) that was applied to image a self-assembled monolayer of **1** at the solution/solid interface of octanoic acid (OA) and highly oriented pyrolytic graphite (HOPG; Figure 2a,b and SI), providing submolecular resolution even at ambient conditions. The molecules form on the substrate a hexagonal 2D pattern. Each of the molecules represents the shape of the MSW structure. The hub, spokes, and rim appear brightly (as expected for unsaturated hydro-
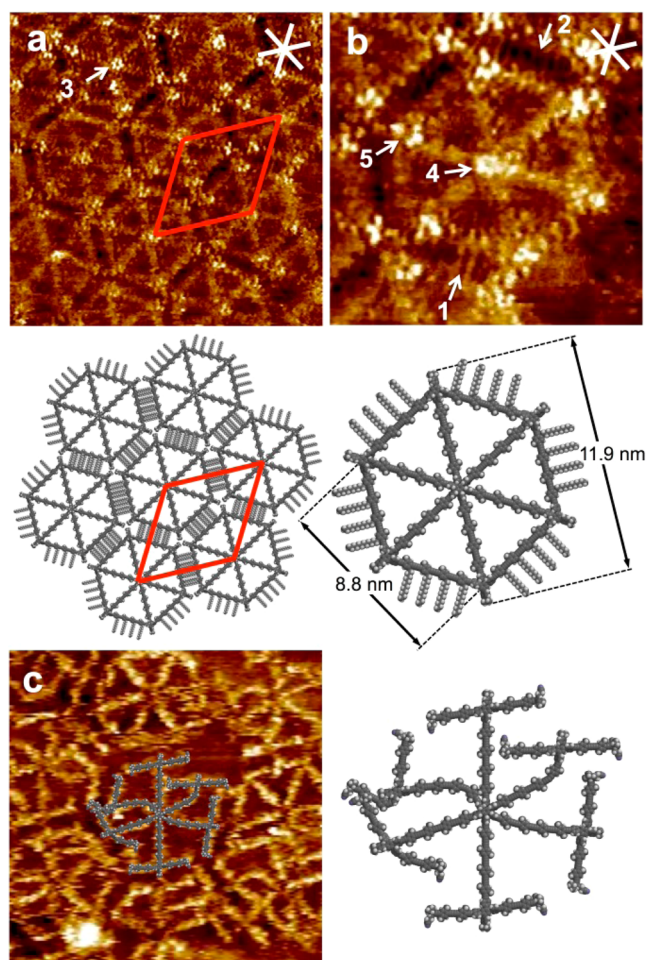

Figure 2. STM images and (supra-)molecular models of **1** (a,b) and **9** (c) at the OA/HOPG interface. (a) Overview STM image of **1** that forms a hexagonal pattern to which a unit cell of $a = b = (10.8 \pm 0.2)$ nm, $\gamma = (60 \pm 2)°$ is indexed (33.0 × 33.0 nm^2; $V_S = -0.6$ V, $I_t = 17$ pA, $c = 3 \times 10^{-7}$ M). (b) High-resolution STM image of one molecule of **1** (15.3 × 15.3 nm^2; $V_S = -0.6$ V, $I_t = 17$ pA, $c = 3 \times 10^{-7}$ M). (c) STM image of **9** (30 × 30 nm^2 (internal scanner calibration); $V_S = -0.8$ V, $I_t = 5$ pA, $c = 3 \times 10^{-7}$ M). The white asterisks indicate the directions of the HOPG main axes. Throughout all models, the alkyl chains are partly omitted for clarity.

carbons), whereas the six triangular pores, each formed by two spokes and a rim segment, appear darker.[15] Adjacent rim segments of neighboring molecules are aligned in parallel with a distance that matches the space required for intermolecularly interdigitating dodecyl side chains that decorate the rim and can be seen in some regions of the high-resolution image of Figure 2b (arrows 1 and 2). Six phenylene units of the central hub (Figure 2a,b, e.g., arrows 3 and 4) as well as four of the five phenylene units of the quinquephenylenes that connect the spoke and rim segments (Figure 2b, e.g., arrow 5) appear as bright spots with appropriate symmetries. The molecules form bi/multilayers even at submonolayer concentration (see SI), reflecting their tendency to aggregate. Contrary to the rigid structure of **1**, in STM images of the CPD*i*PS-protected MSW precursor **9** (Figure 2), a considerable bending of the phenylene-ethynylene constituents is observed that is clearly a result of the restricted persistence length of the phenylene-ethynylenes,[6] as it is also found in molecular dynamics calculations. Both STM investigations together experimentally prove the rigidification of the compounds upon cyclization.[7b] The microscopic investigations of **9** and **1** are an additional analytical tool for the compound characterization, and they give direct insight into the conformation of the molecules (on a substrate) which is not accessible via conventional organic compound analytics.

In summary, we expanded our modular synthetic strategy toward molecular spoked wheel structures by using polymer homologue phenylene-ethynylene-butadiynylene oligomers as building blocks to synthesize a rigid disc-like defined structure with a diameter of about 12 nm. Since the higher elements of these oligomer series are readily available, processable homologues with sizes well above 10 nm should be accessible. In addition, the importance and informative value of microscopic techniques for the characterization of nanoscale compounds is highlighted.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional STM images, detailed synthesis, and characterization of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

stefan.jester@uni-bonn.de
hoeger@uni-bonn.de

Notes

The authors declare no competing financial interest.

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