

Shape-persistent rings and wheels*

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Abstract: Shape-persistent macrocycles based on the arylene-ethynylene backbone are synthetically challenging targets that can be obtained in good to high yields either by statistical or by template-supported oxidative Glaser coupling of the corresponding bisacetylenes. The macrocycles can be adsorbed on highly oriented pyrolytic graphite (HOPG) to form well-ordered monolayers as visualized by scanning tunneling microscopy (STM). Moreover, bithiophene-containing macrocycles are able to bind fullerenes at the electron-rich sites of the rings. One-dimensional tubular structures based on shape-persistent macrocycles can also be obtained by oxidative acetylene coupling. These contain intraannularly bound conjugated polymers and represent bichromophoric systems that allow an accumulation of excitation energy on the conjugated core. In the field of defined 2D objects we describe molecular spoked wheels with a lateral expansion of more than 5 nm. These compounds are highly rigid. In order to provide sufficient solubility, they contain peripheral substituents and additional substituents orthogonal to the plane of the molecules.

Keywords: light-harvesting materials; macrocycles; supramolecular chemistry; surface functionalization; 2D oligomers.

INTRODUCTION

Shape-persistent macrocycles with an interior in the nanometer scale have attracted considerable attention during the past several years [1]. By analogy to rigid oligomers and polymers, where the end-to-end distance is equal to the effective contour length of the molecule [2], shape-persistent macrocycles can be described as cyclic objects with an average diameter $\langle d \rangle$ equal to their effective contour length l divided by π (Fig. 1) [1b].

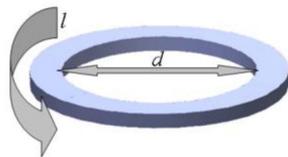
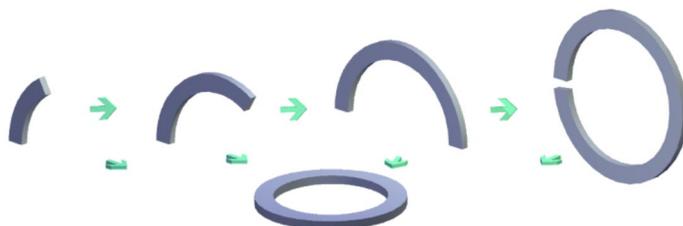


Fig. 1 For shape-persistent macrocycles, the following relationship applies: $\langle d \rangle = l/\pi$.

Some of the most prominent structural motifs for shape-persistent macrocycles are phenylene-ethynylene and phenylene-butadiynylene units. Bond formation can be performed by

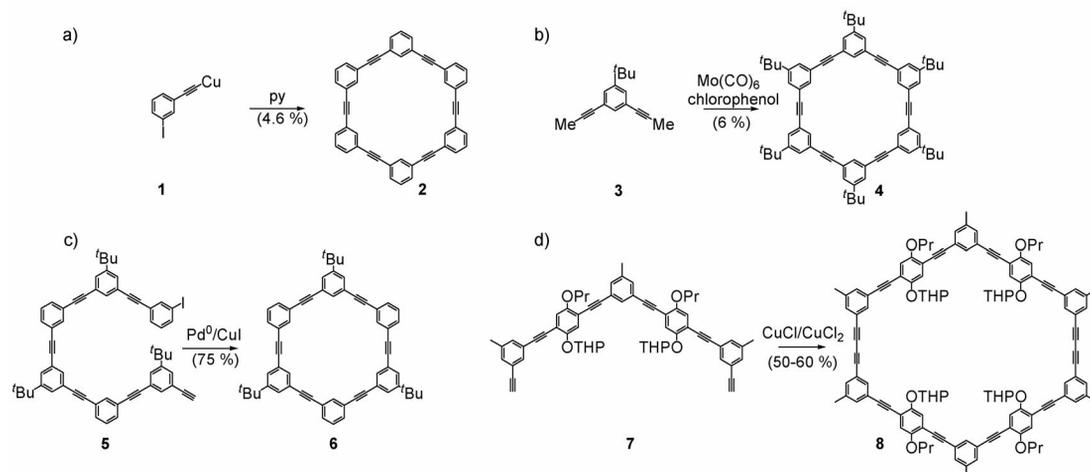
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Sonogashira–Hagihara coupling, alkyne metathesis, or Glaser coupling. The size of the building blocks used in the cyclization step can vary considerably. Either small building blocks form the cyclization precursor and cyclize in a statistical one-pot reaction, or a larger cyclization precursor is formed in a (multi-step) reaction and cyclized separately. In general, ring formation works better when larger subunits are reacted. Ideally, the cyclization is performed intramolecularly (Scheme 1) [3].



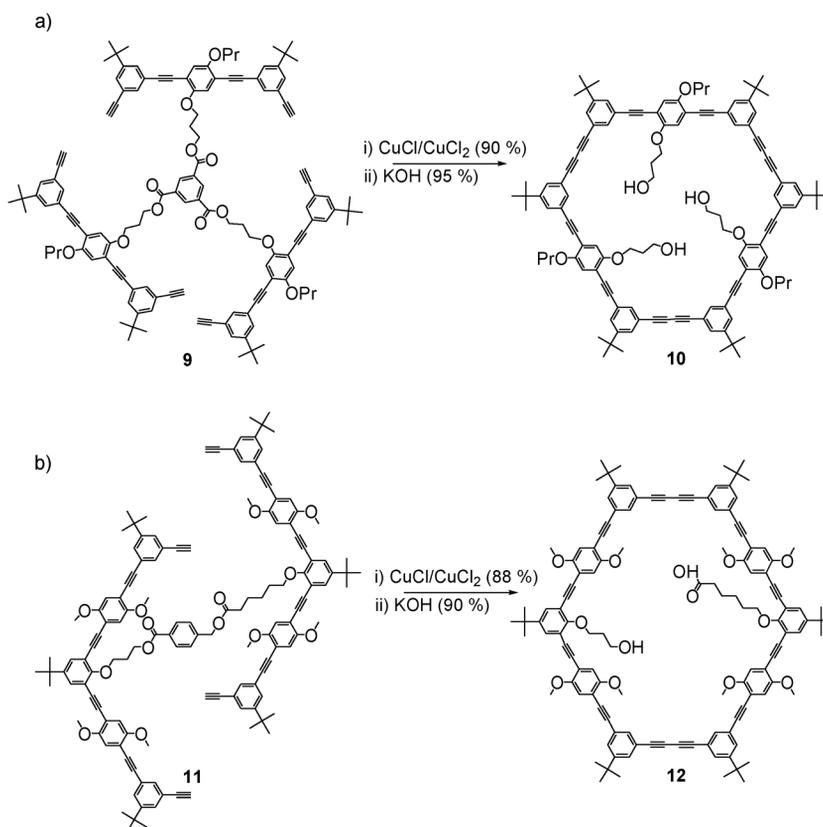
Scheme 1 Shape-persistent macrocycles can be prepared from building blocks of different size.

For example, Staab synthesized the cyclohexamer of *m*-phenylacetylene in 4.6 % yield by sixfold Stephens–Castro coupling [4]. A similar yield was obtained by Bunz when alkyne metathesis was used as the cyclization reaction [5]. However, Moore prepared this structural motif in 75 % yield by the intramolecular cyclization of the corresponding α -iodo- ω -ethynyl precursor under high-dilution conditions [6]. Regrettably, the synthesis of the cyclization precursor requires a time-consuming multistep synthesis. In our studies, we often use the intermolecular Glaser coupling of two acetylene-terminated “half-rings” under pseudo high-dilution conditions (i.e., slow addition of a pyridine solution of the bisacetylenes to a suspension of the copper catalyst/oxidant mixture in the same solvent) [7]. Isolated yields are in the range of about 50 % (Scheme 2) [8].



Scheme 2 Synthesis of shape-persistent phenylene-ethynylene macrocycles from building blocks of different size.

In order to increase the product yields, we explored the use of covalent templates [9]. By intramolecularization of the coupling reaction—and still working under pseudo high-dilution conditions—high product yields can be obtained even when smaller building blocks are used (Scheme 3). Moreover, nonsymmetric macrocycles can also be obtained in high yield—a synthetic challenge that cannot be



Scheme 3 Covalent template approach toward shape-persistent phenylene-ethynylene macrocycles.

mastered with Staab's statistical approach but relies instead on Moore's stepwise precursor synthesis [10].

Despite all methodological progress that has been made during the last few years, the synthesis of new shape-persistent macrocycles is often still a challenge on its own. Nevertheless, more and more the synthesis is only one part of a complex scientific question. The function of the molecules or their aggregates plays an increasingly important role. The supramolecular chemistry of shape-persistent macrocycles is, therefore, an area of growing interest. In this report, we will concentrate briefly on three topics that have attracted our attention during the past few years.

SURFACE PATTERNING WITH MACROCYCLES

Self-assembly of organic molecules on a solid support as the basis of the creation of complex nanoscale structures and molecule-based devices is currently a highly active research area. It provides an attractive route to pattern nanostructures by the *bottom-up* approach. The pattern periodicities are determined by the size of the organized objects that can be colloidal, macromolecular, molecular, and supramolecular [11]. Modern analytical tools, e.g., scanning tunnelling microscopy (STM), made a breakthrough in the investigation of molecules on (semi)conducting surfaces and allow not only the investigation of single-molecule adsorbates but also multicomponent assemblies [12].

Shape-persistent macrocycles are attractive objects for the preparation of self-assembled monolayers (SAMs). They can be decorated with flexible alkyl chains at the outside, and their interior as well as the molecular backbone can be functionalized independently. Therefore, functionalized shape-per-

sistent macrocycles allow not only the creation of *nanopatterned surfaces* but also the formation of *functionalized nanopatterned surfaces* by choosing the proper functionalization. Recently, it has been shown by us and others that shape-persistent arylene-ethynylene macrocycles can form ordered monolayers at highly oriented pyrolytic graphite (HOPG) surfaces [13]. Even functionalized macrocycles could be deposited on HOPG. Sometimes, the ordered domains have only limited size expansion. Although in previous work we investigated in detail the synthesis of macrocycles with intraannular carboxylic acid groups, we were not able to pattern large areas with these compounds in a regular way. Even more disappointing were all attempts to observe co-deposits with an additional guest molecule containing appropriate (basic) binding sites. However, one major lesson that we learned from those investigations was that the macrocycles planarize at the HOPG surface in order to increase the interaction of the aromatic backbone with the graphite [13b,g].

Based on this observation, we turned our attention also toward rings based on corner units with a bond angle different from 120° . Bithiophenes turned out to be interesting candidates for that purpose. Indeed, the bithiophene-containing ring **13** adsorbed from solution at HOPG to form extended well-ordered monolayers that could be visualized with submolecular resolution by means of STM. Moreover, **13** could form co-deposits with C_{60} [14a]. At first, we assumed that the fullerene would adsorb inside the ring cavity and stay in contact with the uncovered HOPG. However, close inspection of the co-adsorbate showed that each macrocycle binds two fullerene guest molecules. This indicates that each of the electron-rich bithiophene units of the macrocycle binds a fullerene (Fig. 2).

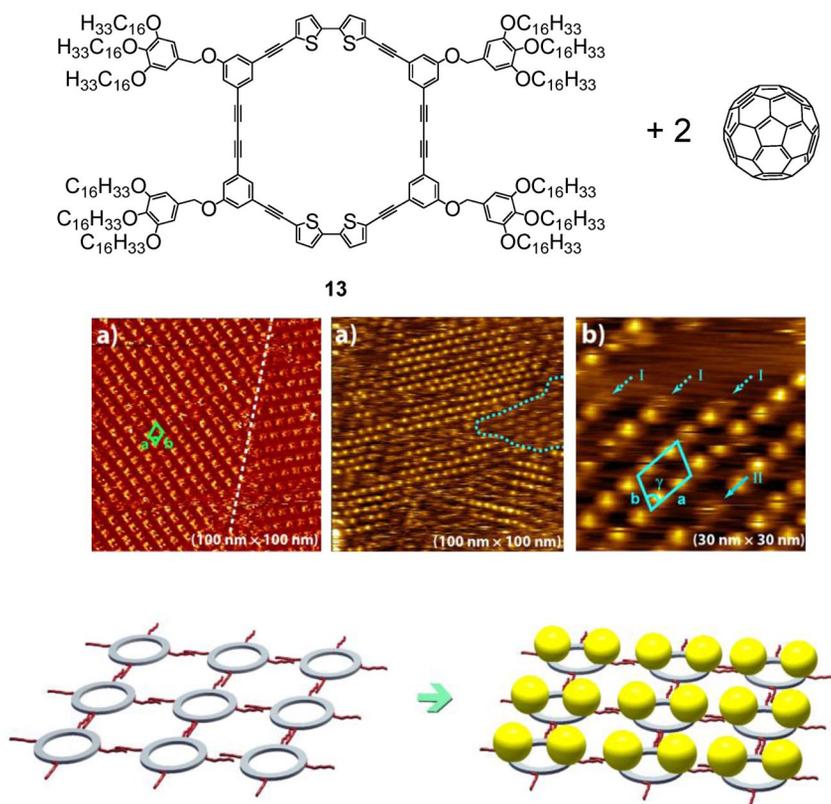


Fig. 2 Structure of **13** (top); STM images of **13** (scan size $100 \times 100 \text{ nm}^2$, middle left), STM images of **13** \times C_{60} (scan size $100 \times 100 \text{ nm}^2$, middle center), STM images of **13** \times C_{60} (scan size $30 \times 30 \text{ nm}^2$, middle right); schematic presentation of a macrocycle template and a macrocycle template with guests (bottom) (in part reprinted from ref. [14a], with permission; copyright © (2006) American Chemical Society).

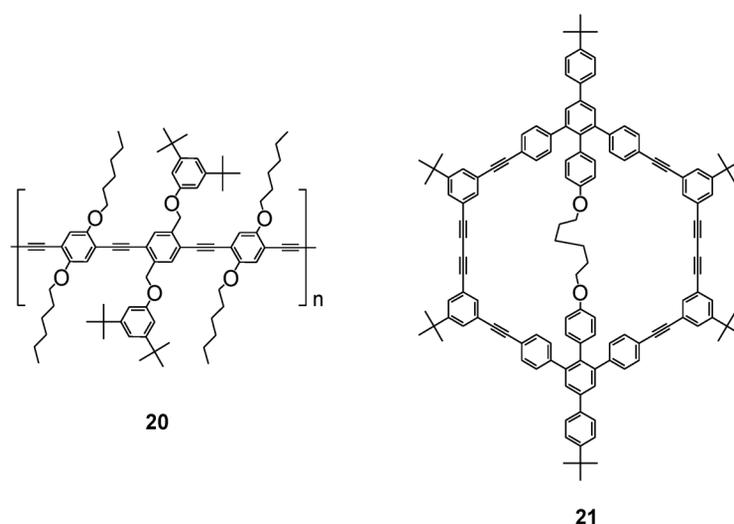


Fig. 3 Model compounds “polymer only” (20) and “ring only” (21).

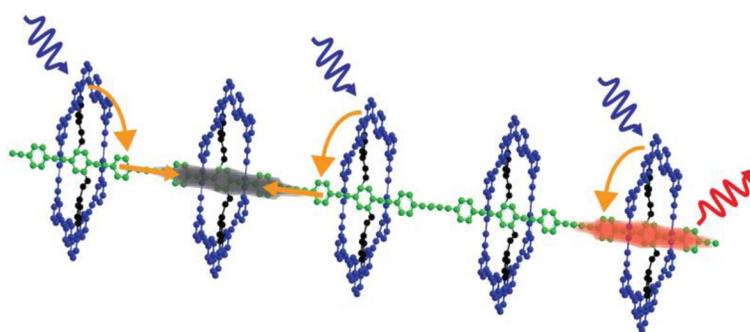


Fig. 4 Schematic of the light-harvesting properties of the macrocycle-encapsulated conjugated polymers **19**. Excitation energy from the rings is accumulated at the polymer where it can emit light or self-annihilate (in part reprinted from ref. [17], with permission).

MOLECULAR SPOKED WHEELS

Large 2D shape-persistent, carbon-rich molecules of defined size, shape, and constitution exhibit interesting properties such as 2D crystallinity on surfaces [18], liquid crystallinity [19], and interesting optical properties [20]. Moreover, shape-persistent organic structures are expected to show reinforcement effects in polymer-based nanocomposite materials [21].

Defined molecular organic structures with a diameter of one up to several nanometers are described in the recent literature; for example, Haley’s oligo(dodecadehydro-benzo[18]annulene)s [22] and Müllen’s C_{222} -graphenes [23]. A summary on 2D oligomers and polymers has been published by Schlüter [24]. Recently, we introduced all-covalent molecular spoked wheels into the field of large defined organic compounds in the 5 nm range [25]. A major difference to the majority of 2D molecules described before is that we have not only substituents at the periphery of the compound but also perpendicular to the plane of the compound (Fig. 5).

Although shape-persistent macrocycles tend to pack in flat (2D) arrangements on surfaces, single-crystal structures [19b,26], and molecular dynamics (MD) simulations [13b,g] reveal considerable deviations from the perfectly planar macroconformation. By contrast, molecular spoked wheels have

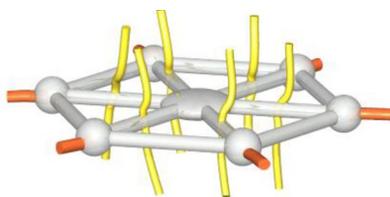
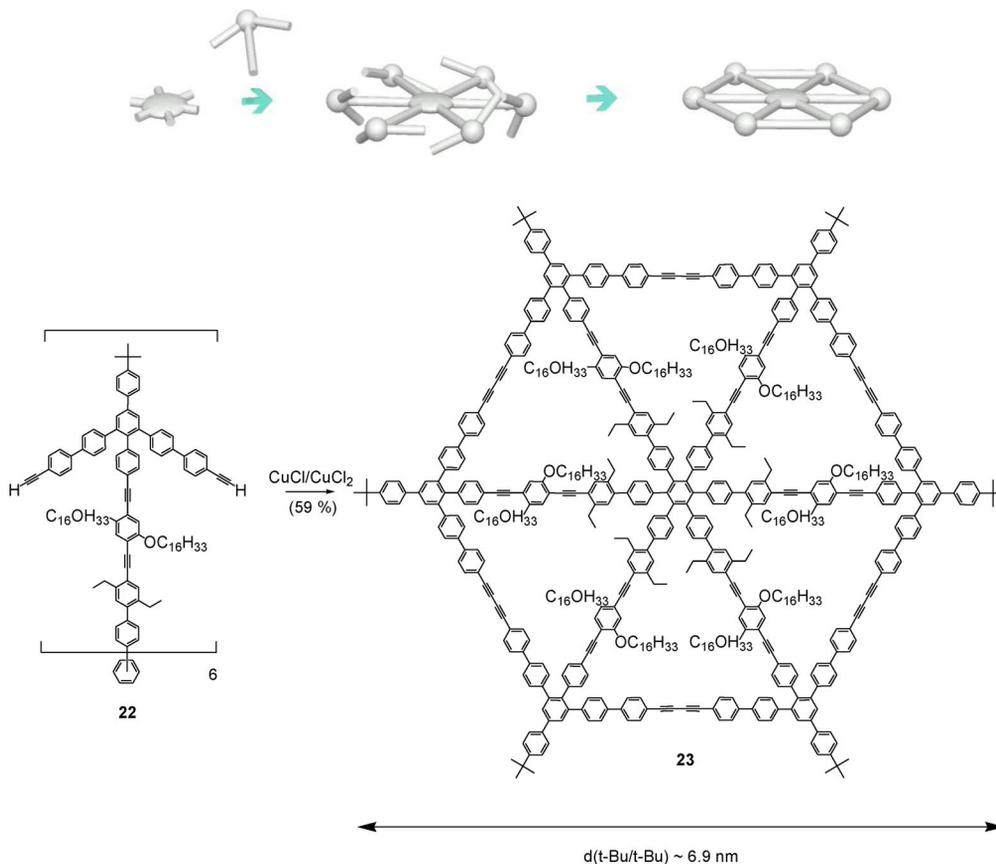


Fig. 5 Schematic presentation of the wheel structure with substituents at the periphery and orthogonal to the wheel plane.

been designed as reinforced macrocycles and combine favorable properties both from large disc-shaped polycyclic aromatic hydrocarbons (shape-persistence, strict planarity, high symmetry) and conventional macrocycles (solubility, easy characterization, introduction of functional groups in the molecular plane).

We have been able to show that large, reinforced macrocycles of this kind are accessible in a so-called “covalent template approach”: In a convergent synthesis, six spoke/rim modules are coupled to a hexaiodo hub affording a star-shaped precursor molecule with 12 acetylene units (**22**). In an intramolecular reaction, adjacent acetylene units dimerize and form 6 defined butadiyne bridges. This means that the precursor contains its own template, which remains covalently bound inside the molecular spoked wheel (Scheme 5).



Scheme 5 Spoked wheel synthesis; schematically (top) and by Glaser coupling.

The molecular structure of **23** has been demonstrated by matrix-assisted laser desorption/ionization-mass spectrometry (MALDI-MS), ^1H NMR, and gel permeation chromatography (GPC). In addition, the spoked wheel could be adsorbed on HOPG and visualized by means of STM (Fig. 6). Molecular modeling and small-angle neutron scattering (SANS) studies indicate that the rigidity of the spoked wheel is considerably higher than that of the open precursor or of the ring-only compound which consists only of the rim without spokes [25].

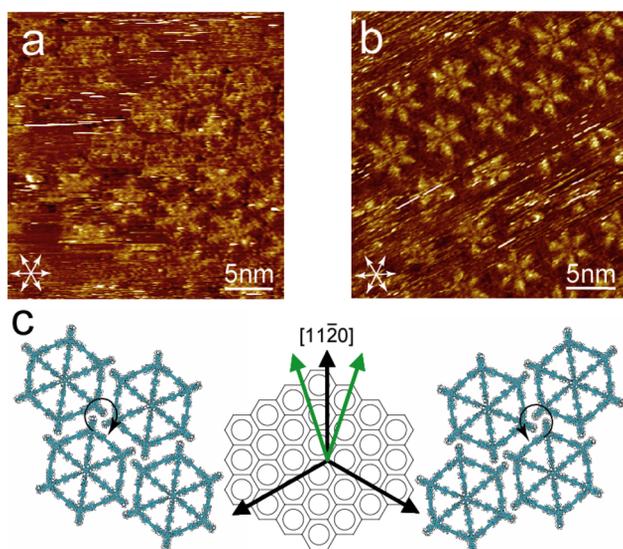


Fig. 6 Top: STM images of two ordered domains showing a different orientational chirality. The molecules in (a) are staggered clockwise while those in (b) are staggered counter-clockwise. The arrows in the lower left of the STM images indicate the major symmetry axes of the graphite lattice (e.g., the equivalent $\langle 1\ 1\ \bar{2}\ 0 \rangle$ directions). (c): Left and right: Corresponding molecular models. Middle: Cartoon of the basal plane of graphite indicating the equivalent $\langle 1\ 1\ \bar{2}\ 0 \rangle$ directions (black) and the unit cell vector directions of the molecular wheel 2D organization (reprinted from ref. [25], with permission).

CONCLUSION

We have shown that the synthesis of shape-persistent macrocycles by oxidative acetylene coupling offers pathways not only to macrocycles, but also toward more complex molecular structures. In particular, the intramolecular expression of this coupling reaction (covalent template approach) leads to high cyclization yields, which is a prerequisite for incorporating rigid macrocycles into advanced functional materials. Applications may include sensing (based on porous materials), energy conversion (based on light-harvesting systems), molecular electronics (based on templated surfaces), or materials reinforcement (based on 2D structures). These investigations contribute to the current efforts of our group and several other groups to transfer shape-persistent macrocycles from the field of molecular science into applications in materials science.

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