

Synthesis and STM Imaging of Symmetric and Dissymmetric Ethynyl-Bridged Dimers of Boron–Subphthalocyanine Bowl-Shaped Nanowheels

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Dedicated to Professor Jean-Pierre Launay

Recent progress in the manipulation of atoms or molecules by using STM^[1] has stimulated the design and synthesis of a variety of compounds that mimic macroscopic machineries. These molecules are commonly called “technomimetic”,^[2] because they are designed to transpose macroscopic-machinery functions at the scale of a single molecule, including the mechanical motions that they undergo. Recently, several examples that may be considered as mechanical molecular devices have been reported, such as molecular gears,^[3] motors,^[4] wheels,^[5] nanovehicles,^[6] including wheelbarrows^[7] and nanodragster.^[8] These individually addressable and controllable mechanical devices are providing the basis for future design of bottom-up nanomachines. Although controlled advanced functions at the molecular level is still a tremendous challenge, a lot of effort is spent on building and mastering the different pieces required to realize such integrated molecular devices.^[9]

In this context, the wheel—one of the simplest mechanical working units—is an interesting system to study and control at the atomic scale. We recently succeeded to prove the rotation of a triptycene wheel linked to an axle by working at low temperatures.^[5a] Unfortunately the preparation of extended nanovehicles equipped with the successful triptycene wheel^[6c] did not yield movable molecules, because triptycene tends to strongly physisorb by parallelization of the two phenyl rings close to the surface. In the nanovehicles developed by Tour’s group,^[6a] [60]-fullerene, *p*-carborane, and, more recently, an organometallic ruthenium complex^[5c] were used as nanowheels, but all three families have draw-

backs. [60]-fullerene derivatives have very low solubility and a high photoactive nature, making them incompatible with photochemical processes. Carboranes cannot be modified dissymmetrically to incorporate a tag, which would help investigate the wheel rolling versus sliding motions. Finally, the organometallic ruthenium complex would be very difficult to deposit cleanly due to decomposition before sublimation.

To improve the mechanical abilities and efficiencies of a molecular nanovehicle, new nanowheels have been designed, integrating the strong rigidity of their backbone combined with a low interaction with the surface. With this aim in view and in our search for the best candidate, we explored subphthalocyanine fragments,^[10] which have an interesting bowl-shaped structure due to the presence of the tetrahedral boron template at the center (Figure 1). The boron center gives rise to the distortion of the 12-membered-ring macrocycle due to its pyramidal structure,^[11] which shifts the boron atom above the plane defined by the three coordinated nitrogen centers.

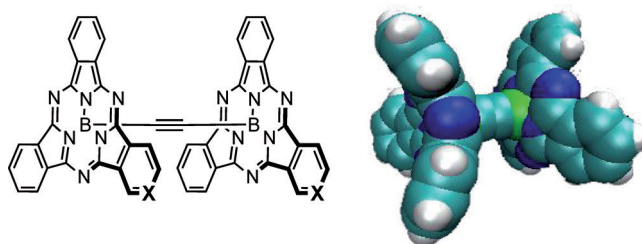


Figure 1. Chemical structure and molecular modelling of the dimers of nanowheels without (X=CH (**2a**)) or with the nitrogen tag (X=N (**2b**)).

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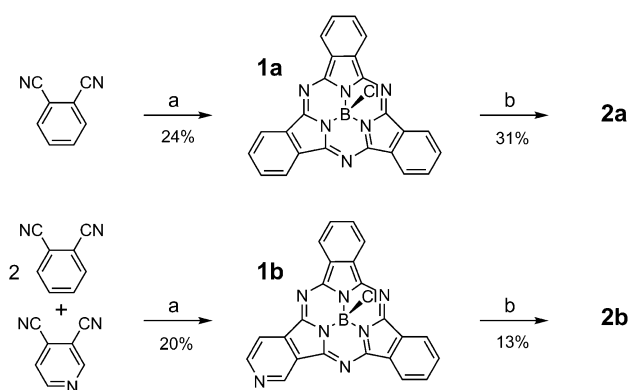
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Contrary to triptycene wheels, the non-planarity of these compounds should help to avoid a strong interaction of the aromatics with the surface, because it is impossible for them to be parallel. Therefore, combining a strong rigidity and a low affinity for the surface should facilitate a rolling motion of the wheel.

Herein, we report the design and the synthesis of two new prototypes of nanowheels and their corresponding dimers as

models of two-wheel-terminated axles. For this family of molecules, theoretical calculations predicted a high rigidity and low physisorption properties on a gold surface. The first nanowheel is symmetric, whereas the second one integrates a tag on one of the three iminoisoindole subunits (an additional nitrogen on the periphery of the molecule); this allows monitoring of the rolling motion of the wheel by low-temperature ultrahigh-vacuum STM imaging.^[3d,12] Calculated STM images demonstrated the advantage of a dissymmetric wheel; this was also confirmed experimentally.

Subphthalocyanine consists of three iminoisoindole fragments and was first obtained in 1972 by Meller and Ossko^[13] who used the boron center as a template to preassemble three 1,2-dicyanobenzene building blocks and to avoid the assembly of four subunits that yields phthalocyanine.^[14] As shown on Scheme 1, the synthesis of the symmetric sub-



Scheme 1. Chemical synthesis of the nanowheels and formation of the wheel dimers. a) BCl_3 , *o*-xylene/hexane 1:1, 140 °C, Ar, 20 min; b) ethynylmagnesium bromide, THF, microwave heating (200 W), 100 °C (under pressure), Ar, 15 min.

phthalocyanine **1a** was achieved by following the methodology described by Torres et al.^[15a] Reaction of 1,2-dicyanobenzene with boron trichloride in a two-phase system composed of a 1:1 mixture of *o*-xylene and hexane yielded, after toluene extraction and column chromatography, boron subphthalocyanine chloride (**1a**) in 24% isolated yield as a purple solid. This low yield is due to difficulties of purification, directly related to the low solubility of the molecule. We were not able to obtain a pure sample of **1a** with only successive washings with toluene, methanol, and hexane as described in the published procedure.^[15b] Subsequently, column chromatography was undertaken to obtain pure **1a**, but induced an important loss of material by irreversible adsorption on silica. Interestingly, the choice of the reaction solvent is a key issue, because the reaction in pure *o*-xylene gave only 3% of subphthalocyanine in the same conditions.

The dissymmetric wheel **1b** was synthesized by following a statistical reaction. Two equivalents of 1,2-dicyanobenzene were reacted in the presence of boron trichloride with one equivalent of 3,4-dicyanopyridine. After purification by column chromatography, the tagged, pure, nanowheel **1b** was obtained as a purple solid in 20% yield. In this case the

low yield is mainly due to the statistical conditions of the reaction, which limit the yield to 44%. Surprisingly, **1b** is more soluble than **1a** in common solvents, such as CH_2Cl_2 or CHCl_3 . Wheel **1b** was also fully characterized by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and UV/Vis absorption spectroscopy, the result of the latter is similar to spectra reported in the literature for other subphthalocyanines.^[15] The integration of the ^1H NMR signals is particularly informative for **1b**, which displays the expected 3:4:4 ratio for a nitrogen-tagged fragment combined with two iminoisoindole fragments.

The synthesis of **2a** and **2b**—the wheel dimers bridged by an acetylene moiety—was achieved in a single step by reaction of wheel **1a** or **1b** with 1.7 equivalents of ethynylmagnesium bromide in THF with microwave heating at 100 °C (i.e., under pressure) for 15 min. After chromatography, the two-wheel-equipped axle was obtained as a dark purple solid with a satisfying 31% yield, starting from **1a** and a lower 13% yield in the case of **1b**. Surprisingly, both carbon atoms of ethynylmagnesium bromide reacted in a one-pot fashion, allowing the formation of **2a** and **2b** in a single step. The highest yields were obtained with a 1:1.7 boron chloride/ethynyl magnesium bromide ratio instead of the stoichiometric 1:0.5 ratio. This excess of the organomagnesium derivative may act as a base to deprotonate the acidic proton of the alkyne to allow the $\text{SubPc-B-C}\equiv\text{CH}$ intermediate to react with a second subphthalocyanine. Furthermore, reactions with conventional heating (2 h in THF at a refluxing temperature) did not yield the desired compound.

Both the wheel dimers bridged by an acetylene moiety, **2a** and **2b**, were fully characterized. ^1H NMR spectra of **2a** and **2b** are very similar to those of the wheels due to the negligible interaction between the two wheels. The spectrum of **2b** shows the expected 2:1 integration for the phenyl versus pyridyl protons. The presence of the disubstituted ethyne bridge was confirmed by mass spectrometry and elemental analysis. It must be noted that **1b** is chiral due to the non-inversion of the bowl-shaped structure. Thus, we obtained a racemic mixture of two enantiomers of **1b** and consequently **2b** was obtained as a mixture of three stereoisomers: (*R,R*), (*S,S*), and the *meso*-(*R,S*)-isomer. The chirality of the molecules is not a drawback when working with single molecules on surfaces.

Elastic Scattering Quantum Chemistry (ESQC) STM image calculations^[16] were performed to probe the efficiency of the tag design in **2b** on a Au(111) surface. A modified version of the ASED semi-empirical molecular orbital method^[17] was used to optimize the molecular conformation and the physisorption distance to the surface. The calculated image (Figure 2) was found to display a large difference between a wheel with the tag pointing up and a wheel with the tag pointing down. The former one appears with a smaller lobe compared with the latter. Experimental STM images at low temperature in ultrahigh vacuum (LT-UHV-STM) were recorded to prove the theoretically predicted efficiency of the nitrogen tag.

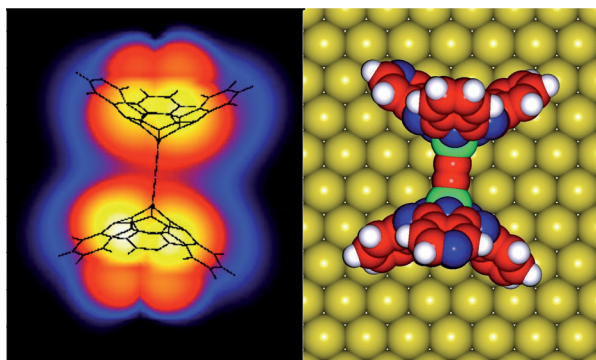


Figure 2. ESQC constant-current STM image (left) calculated by using the optimized conformation of wheel dimer **2b** (right) adsorbed onto a Au(111) surface (2 nm × 2.5 nm in size, voltage bias 0.12 V, set up current 20 pA). The top wheel has the nitrogen tag in contact with the surface, while the wheel in the bottom has the tag pointing up (nitrogen atoms are shown in blue).

STM images of **2b** recorded at low temperature in ultra-high vacuum are presented in Figure 3. Two covalently linked wheels are clearly distinguishable. Compared with the already-published images of single wheels **1a** adsorbed onto Au(111), which appeared as three-spoke entities,^[18] Figure 3 demonstrates that the wheels in **2b** are not parallel to the surface. In Figure 3a the heights of the wheels are the same, whereas in Figure 3c different heights are measured. This asymmetry confirms the calculations and corresponds to different positions of the nitrogen tags. In Figure 3a both tags are pointing down, the nitrogen atoms are adsorbed onto the Au(111) surface, whereas in Figure 3c one of the tags is pointing up. This is not surprising because the most

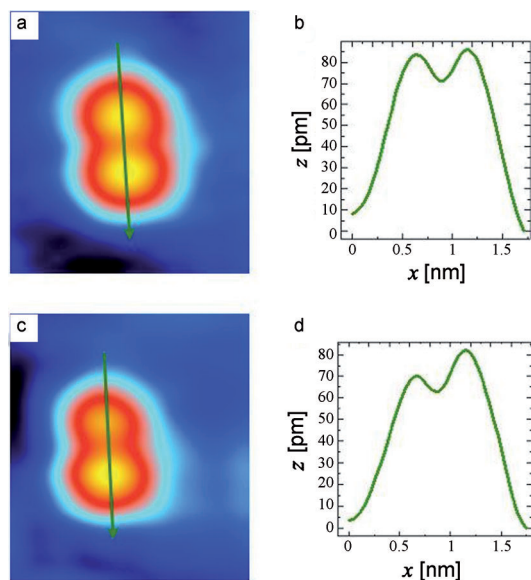


Figure 3. STM images of a dimer of a nanowheel molecule on Au(111) with a) both tags pointing up or c) only one tag pointing up (2.25 × 2.5 nm, $V=0.12$ V, $I=20$ pA). When the tag is pointing down, the wheel appears with a smaller lobe. The green arrows indicate the direction of the line scans shown in (b) and (d).

stable conformation is the one with the two nitrogen atoms in contact with the surface.

We expect this new family of nanowheels to contribute to the development of nanomachines, such as nanovehicles, which require wheels to move efficiently on a surface pushed by the STM tip with the aim to transport small molecules (nanocarrier machines) long distances. Previously, proof of the rolling motion of a wheel required a fine study of the variation of the time-dependent, tunneling, electric-current intensity passing from the STM tip to the surface through the molecule during the manipulation of the molecule. This involved both tricky STM experiments and time-consuming calculations to fit the experimental current with the mechanical behavior of the molecule under the influence of the STM tip. Herein, due to the efficiency of the tag, LT-UHV STM imaging has proven sufficient to identify the conformation of the wheels on the surface, and is thus expected to be sufficient to prove the rotation in future nanovehicles equipped with such subphthalocyanine wheels, the synthesis of which is currently underway.

Experimental Section

Wheel 1a (boron subphthalocyanine chloride): A solution of boron trichloride in hexane (1 M, 3.9 mL, 3.90 mmol, 1 equiv) was added to a solution of 1,2-dicyanobenzene (500 mg, 3.90 mmol, 1 equiv) in anhydrous *o*-xylene (4 mL). The medium was heated at 140 °C for 20 min and the subphthalocyanine was extracted with toluene. After evaporation of solvents, the crude material was purified by column chromatography (SiO₂, CH₂Cl₂). Compound **1a** was obtained as a purple solid in 24% yield. ¹H NMR (300 MHz, CDCl₃): $\delta=8.92$ (dd, 6H, $J=3.0$, $J=5.9$ Hz), 7.92 ppm (dd, 6H, $J=3.0$, $J=5.9$ Hz); ¹³C NMR (75 MHz, CDCl₃): $\delta=133.5$, 133.1, 115.9, 115.2 ppm; UV/Vis (CH₂Cl₂): $\lambda_{\max}(\epsilon)=302$ (32900), 511 (19900), 562 nm (72400 mol⁻¹ dm³ cm⁻¹); MS (DCI/NH₃): m/z : calcd for C₂₄H₁₂BClN₆; C 66.93, H 2.81, N 19.51; found: C 66.14, H 2.54, N 18.97.

Wheel 1b: A solution of boron trichloride in hexane (1 M, 2.3 mL, 2.3 mmol, 3 equiv) was added to a solution of 1,2-dicyanobenzene (198 mg, 1.55 mmol, 2 equiv) and 3,4-pyridinedicarbonitrile (100 mg, 0.77 mmol, 1 equiv) in anhydrous *o*-xylene (3 mL). The medium was heated at 140 °C for 20 min and the subphthalocyanine was extracted with toluene. After evaporation of solvents, the crude material was purified by column chromatography (SiO₂, CH₂Cl₂). Compound **1b** was obtained as a purple solid in 20% yield. ¹H NMR (300 MHz, CDCl₃): $\delta=8.15$ –8.05 (m, 2H), 7.99–7.96 (m, 1H), 7.85–7.81 (m, 4H), 7.78–7.74 ppm (m, 4H); ¹³C NMR (125 MHz, CDCl₃): $\delta=152.1$, 147.6, 133.8, 132.4, 116.6, 115.9, 112.4, 110.2 ppm; UV/Vis (CH₂Cl₂): $\lambda_{\max}(\epsilon)=305$ (33300), 512 (22500), 572 nm (79000 mol⁻¹ dm³ cm⁻¹); MS (DCI/NH₃): m/z : calcd for C₂₃H₁₁BClN₇; C 64.0, H 2.57, N 22.71; found: C 64.8, H 2.69, N 22.86.

Wheel dimers 2a and 2b (1,2-di(B-subphthalocyanine) boron ethyne): A solution of ethynylmagnesium bromide in tetrahydrofuran (158 μ L, 0.079 mmol, 1.7 equiv) was added to a solution of wheel **1a** or **1b** (0.046 mmol, 1 equiv) in freshly distilled tetrahydrofuran (3 mL of). The medium was heated at 100 °C for 15 min (200 W microwave heating). After evaporation of the solvent, the crude material was purified by column chromatography (SiO₂, CH₂Cl₂). Compounds **2** were obtained as purple solids in 31% isolated yield for **2a** and in 13% isolated yield for **2b**.

2a: ¹H NMR (500 MHz, CDCl₃): $\delta=8.88$ (dd, 12H, $J=3.0$, $J=5.9$ Hz, H_a); 7.91 ppm (dd, 12H, $J=3.0$, $J=5.9$ Hz, H_b); ¹³C NMR (125 MHz, CDCl₃): $\delta=150.3$, 134.3, 129.5, 122.1 ppm; UV/Vis (CH₂Cl₂): $\lambda_{\max}(\epsilon)=$

271 sh (19400), 299 (30300), 510 (21000), 530 sh (29500), 555 sh (62900), 569 nm ($73800 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$); HR-MS (FAB): m/z : calcd for: 421.1373; found: 421.1342 [$M+H$ -SubPc] $^+$; elemental analysis (%) calcd for $C_{30}H_{24}B_2N_{12}$: C 73.74, H 2.97, N 20.64; found: C 74.71, H 2.64 N 20.36. **2b**: ^1H NMR (300 MHz, CDCl_3): δ = 8.87–8.86 (m, 4H); 8.06–7.98 (m, 6H); 7.63–7.62 (m, 2H); 7.56–7.48 (m, 4H), 7.25–7.21 (m, 4H); 7.09–7.06 ppm (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ = 158.9, 152.8, 136.4, 135.2, 119.4, 118.4, 116.9, 115.1 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 305 (32800), 512 (22100), 558 sh (65700), 572 nm ($77900 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$); HR-MS (FAB): m/z : calcd for: 422.1325; found: 422.1311 [$M+H$ -SubPc] $^+$; elemental analysis (%) calcd for $C_{48}H_{22}B_2N_{14}$: C 70.62, H 2.72, N 24.02; found: C 70.36, H 2.57 N 24.62.

Computational details: In the semiempirical version of ESQC used here^[16] the full-tip apex-molecule surface was described like a complete electronic-scattering defect described by its full valence electronic structure. The corresponding scattering matrix was calculated by taking into account a bulk lateral size equivalent to the body of the tip supporting the tip apex. The tip apex was supposed to be only composed of Au atoms with a 6s atomic orbital description per atom like the Au(111) surface, the bulk behind the surface and the tip body.

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