

CARBON NANOMATERIALS

Carbon nanobelts do the twist

Using a bottom-up synthetic method, an all sp^2 -hybridized carbon nanobelt with a Möbius topology is prepared. The macrocyclization step is a Wittig reaction between an aldehyde and phosphorous ylide at opposite edges of a strip that induces a twist.

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Carbon nanomaterials are promising candidates for an array of optoelectronic applications, but traditional synthetic methods result in heterogeneous mixtures of structures, which are often not desirable. Alternatively, synthetic organic chemistry enables

fragments of carbon nanomaterials to be prepared with unprecedented atomic precision, providing a way to access and tune carbon nanomaterials. In particular, synthetic methods to prepare carbon nanobelt (CNB) structures that map onto various chirality carbon nanotubes (CNTs)

have undergone a renaissance in the past few years¹. Using a variety of methods and strategies, all sp^2 -hybridized CNBs have been prepared that map onto armchair, zigzag and chiral nanotubes. With these strategies rapidly evolving, the range of possible topologies of carbon nanomaterials are also

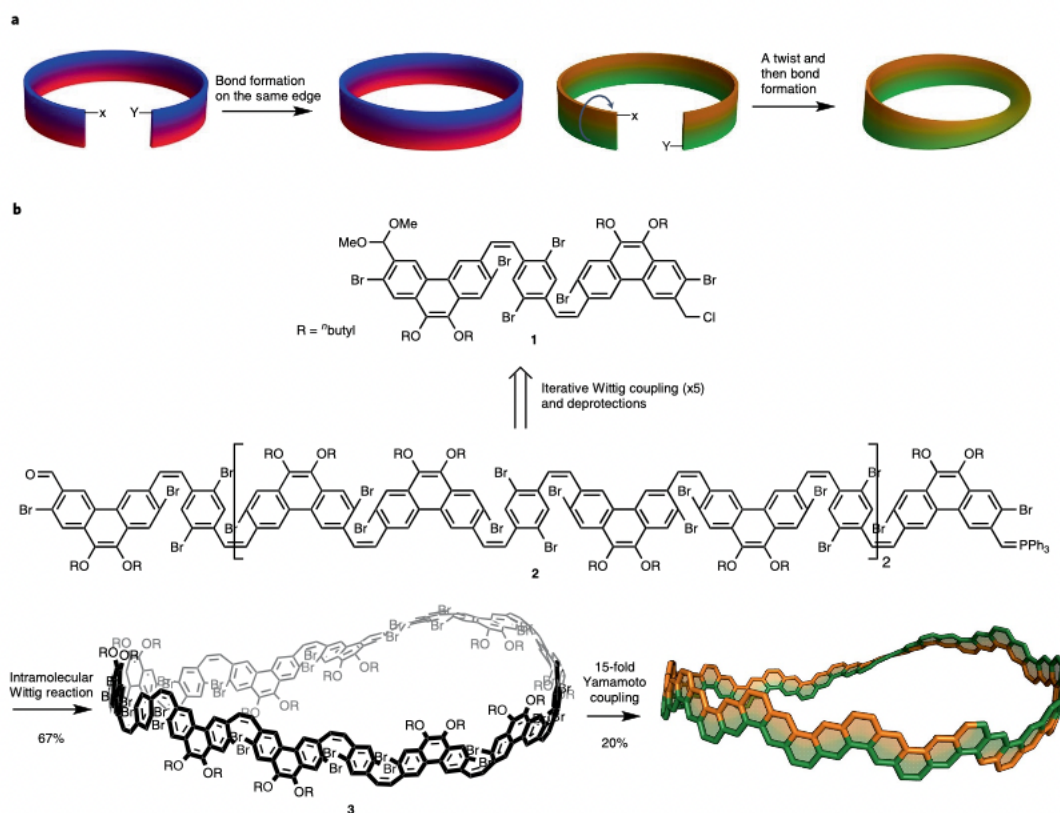


Fig. 1 | Synthetic strategy to prepare a MCNB. **a**, Two different topologies can be created by closing a strip. **b**, Iterative Wittig reactions and Yamamoto couplings are used to synthesize a (25,25) MCNB.

increasing and our imagination is truly the only limit.

Now reporting in *Nature Synthesis*, Itami and co-workers report a synthetic method to prepare an all sp^2 -hybridized CNB that has a Möbius topology — a Möbius carbon nanobelt (MCNB)². Although Möbius objects have appeared in works of art and in mathematics for centuries, the MCNB is the first example of this topology being introduced into a CNB using a rational bottom-up synthetic approach.

A Möbius topology can be envisioned by considering the ways a flat two-dimensional strip can be connected into a cylindrical object³. In a more common scenario, a flat strip can be wrapped around to form a cylinder by connecting the top edge of one side of the strip with the top edge of the other side (Fig. 1a, left). Adding a single twist to the strip such that the top edge meets the bottom edge creates a Möbius strip with a non-orientable surface (Fig. 1a, right). Möbius molecules pose a formidable synthetic challenge as a twist needs to be forced into the molecule before making the final bond that closes the cyclic structure. Not surprisingly, synthetic examples of Möbius molecules are very rare^{1–6}. Theoretical calculations of Möbius π -conjugated molecules also motivate their synthesis due to the potential to investigate basic concepts of aromaticity, which are critical to understanding optical and electronic properties of materials. Hückel aromaticity follows a $(4n + 2)$ π -electron rule whereas Möbius aromaticity follows a $4n$ π -electron rule. The change in the number of π -electrons is a result of the change in p -orbital phases as the molecule makes a twist, cancelling out when they meet back at the point of origin. Experimentally, this results in noticeably different optoelectronic properties of Möbius molecules compared with their Hückel counterparts¹.

The synthetic approach to the MCNB in this work is an adaptation of previous methods used to make armchair CNBs reported by the Itami group^{7,8}. Based on this earlier work⁷, the authors surmised that the upper-bound for the build-up of strain energy in the final bond-forming reaction (Yamamoto coupling) is ~ 40 kcal mol⁻¹. As a consequence of this consideration, the Itami

group targeted the (25,25) MCNB — this larger Möbius belt alleviates the demand of the synthesis in that the twisted belts are much more strained than the previously synthesized armchair belts. The other key feature in their synthetic strategy is to target a precursor that has two functional groups for macrocyclization that are positioned on opposite edges of the ultimate belt, therefore forcing the twist.

An appropriate precursor to the (25,25) MCNB is key Wittig precursor **2** (Fig. 1b); the aldehyde and phosphorus ylide are on opposite edges of the belt precursor, and a Wittig macrocyclization should lead to a macrocycle with a single twist. After macrocyclization, Itami and co-workers envisioned that a sequential Yamamoto reductive aryl–aryl coupling reaction would deliver the target MCNB. In a forward sense, Wittig precursor **2** was prepared by sequential Z-selective Wittig reactions using building block **1** — this key molecular building block can be converted to a phosphonium ylide via the chloride or an aldehyde by deprotection of the acetal, providing an iterative method to build up a linear structure. As planned, a series of Z-selective iterative Wittig couplings and functional group interconversions enables the preparation of linear precursor **2** in good yields. Once the linear molecule **2** is prepared, an intramolecular Wittig via a twist is executed to deliver the Möbius nanobelt precursor macrocycle **3** in an excellent 67% yield. A one-pot 15-fold intramolecular Yamamoto coupling affords the (25,25) MCNB in a remarkable 20% overall yield (on average, $\sim 90\%$ for each C–C bond-forming reaction).

Interestingly, a (15,15) MCNB belt could also be targeted using the same building blocks, but was unsuccessful in the Yamamoto coupling reaction, presumably owing to the higher strain energy. The (25,25) MCNB was characterized using mass spectrometry and ¹H NMR spectroscopy, which was corroborated by predicted spectra. Increasing the temperature while obtaining the ¹H NMR spectrum results in sharper peaks compared with the room-temperature spectrum, which is consistent with dynamic movement of the twist throughout the belt. The

intramolecular Wittig reaction can occur in two orientations and, as a result, the reaction should produce two enantiomers in equal amounts. This prediction was verified by separation of enantiomers and matching of the circular dichroism spectrum to the simulated spectrum of each, further confirming the structure.

This MCNB is a new topological nanocarbon. Notably, the CNB has Möbius topology but does not show obvious Möbius aromatic properties, which would require delocalization through the macrocycle. Although the goal here was to construct an aromatic belt with Möbius topology, further experiments exploring the electronic structure of the reduced or oxidized structure (which may be more globally aromatic) will provide interesting information on Möbius aromatic hydrocarbon belts. Overall, this synthetic approach represents an important advancement in the development of topologically diverse nanocarbons by a bottom-up synthetic organic chemistry. And like the recent explosion of CNBs, this breakthrough will inspire many more Möbius π -conjugated molecules with new properties. □

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Competing interests

The authors declare no competing interests.