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Synthesis of a Möbius carbon nanobelt

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Technologies for the creation of topological carbon nanostructures have greatly advanced synthetic organic chemistry and materials science. Although simple molecular nanocarbons with a belt topology have been constructed, analogous carbon nanobelts with a twist—more specifically, Möbius carbon nanobelts (MCNBs)—have not yet been synthesized owing to their high intrinsic strain. Here we report the synthesis, isolation and characterization of a MCNB. Calculations of strain energies suggest that large MCNBs are synthetically accessible. Designing a macrocyclic precursor with an odd number of repeat units led to a successful synthetic route via Z-selective Wittig reactions and nickel-mediated intramolecular homocoupling reactions, which yielded (25,25)MCNB over 14 steps. NMR spectroscopy and theoretical calculations reveal that the twist moiety of the Möbius band moves quickly around the MCNB molecule in solution. The topological chirality that originates from the Möbius structure was confirmed experimentally using chiral HPLC separation and circular dichroism spectroscopy.

Organic chemists have striven to realize a wide variety of structural features on the molecular scale in nanocarbons. For example, nanocarbons with spherical, sheet-like, cylindrical or other exotic structures are usually obtained as mixtures on applying a high energy to the appropriate carbon sources^{1–4}. In this context, molecular nanocarbon science, with which such substructures are created in a precisely controlled fashion, has attracted substantial attention, given that this approach is fundamentally able to circumvent the problem of the formation of such nanocarbon mixtures^{5,6}.

The history of the development of molecular nanocarbon science can be classified in terms of topology. Cycloparaphenylene, which was first proposed in the 1930s, is a ring-shaped molecular nanocarbon that represents a partial structure of carbon nanotubes^{7–10}. Although cycloparaphenylenes were initially difficult to synthesize due to their high intrinsic strain energies, several synthetic methods, such as those reported since 2008 by Jasti, Itami and Yamago and their co-workers^{11–13}, have enabled the creation of molecular nanocarbons that exhibit non-trivial topologies, such as cages^{14–17}, catenanes and knots^{18,19}. The next breakthrough in this research field was the synthesis of a carbon nanobelt (CNB) achieved by our group in 2017²⁰. The fully fused, belt-shaped topology of CNBs creates two non-convertible faces, that is, the inner and outer faces. Since then, the synthetic chemistry of CNBs and related belt-shaped arenes has been intensively investigated worldwide in the context of the bottom-up construction of carbon nanotube substructures^{21,22} as well as in the creation of new functional molecular nanocarbon materials.

The CNB structural feature of irreducible inner and outer faces can be extended to aromatic molecules with the topology of a Möbius strip, which is the simplest example of a non-orientable surface (Fig. 1a). Möbius-type molecules are found in nature²³ and have been of interest in synthetic organic chemistry, as demonstrated by the successful preparation of a non-conjugated Möbius-type double-stranded molecule by Walba et al. in 1982 (Fig. 1b, left)²⁴. Aromatic single-stranded molecules with Möbius aromaticity were realized by Herges and co-workers in 2003²⁵, and Möbius aromaticity was

further investigated by Grażyński and co-workers²⁶ and Osuka and co-workers^{27,28}. Despite several examples of single-stranded Möbius molecules^{29–33}, double-stranded aromatic molecules with a Möbius topology still remain limited due to the difficulties associated with their synthesis. As shown in Fig. 1b, saturated linkers (–CH₂O–) or chalcogen atom linkers (–S–) are necessary to reduce the strain caused by the Möbius topology (Fig. 1b, centre and right)^{34,35}. Even though Möbius-type CNBs have been theoretically proposed since the 1990s^{36–38}, a synthetic methodology to introduce Möbius topology to fully fused and fully conjugated all-*sp*² carbon structures still remains to be developed in molecular nanocarbon science.

Results and discussion

Here we report the synthesis, isolation and optical analysis of a Möbius carbon nanobelt (MCNB), that is, a fully fused CNB with a twist. The key to the synthesis of such MCNBs is a modification of our previously reported synthetic strategy for CNBs^{19,39}. As shown in Fig. 1c, (*n,n*)CNBs (*n* = 6, 8 and 12, where (*n,n*) is the chiral index of the corresponding carbon nanotubes) were synthesized via a reductive homocoupling reaction using cyclic molecules that consisted of dibromoparaphenylene and *cis*-ethenylene precursors^{19,39}. The important feature of this method is that a CNB can be generated when the number of repeat units is even, whereas an MCNB can be obtained when the number is odd. This is a simple but powerful method for the synthesis of a complex Möbius topology from highly symmetric precursors.

Strain energy calculation. The target size of the MCNB was determined using density functional theory (DFT) calculations. We found that MCNBs have a higher strain energy than CNBs of the same size (for details, see Supplementary Fig. 1), and that the strain of the MCNBs is mainly induced during the final bond-formation step. Figure 2a,b shows the hypothetical homodesmotic reactions using (*n,n*)MCNBs, (*n,n*)CNBs and their corresponding precursors (pre(*n,n*)MCNBs and pre(*n,n*)CNBs), based on which the strain induced in the final bond-formation step (ΔH_{FBF} (kcal mol^{–1})) was estimated. *Cis*-stilbene and phenanthrene were used as reference

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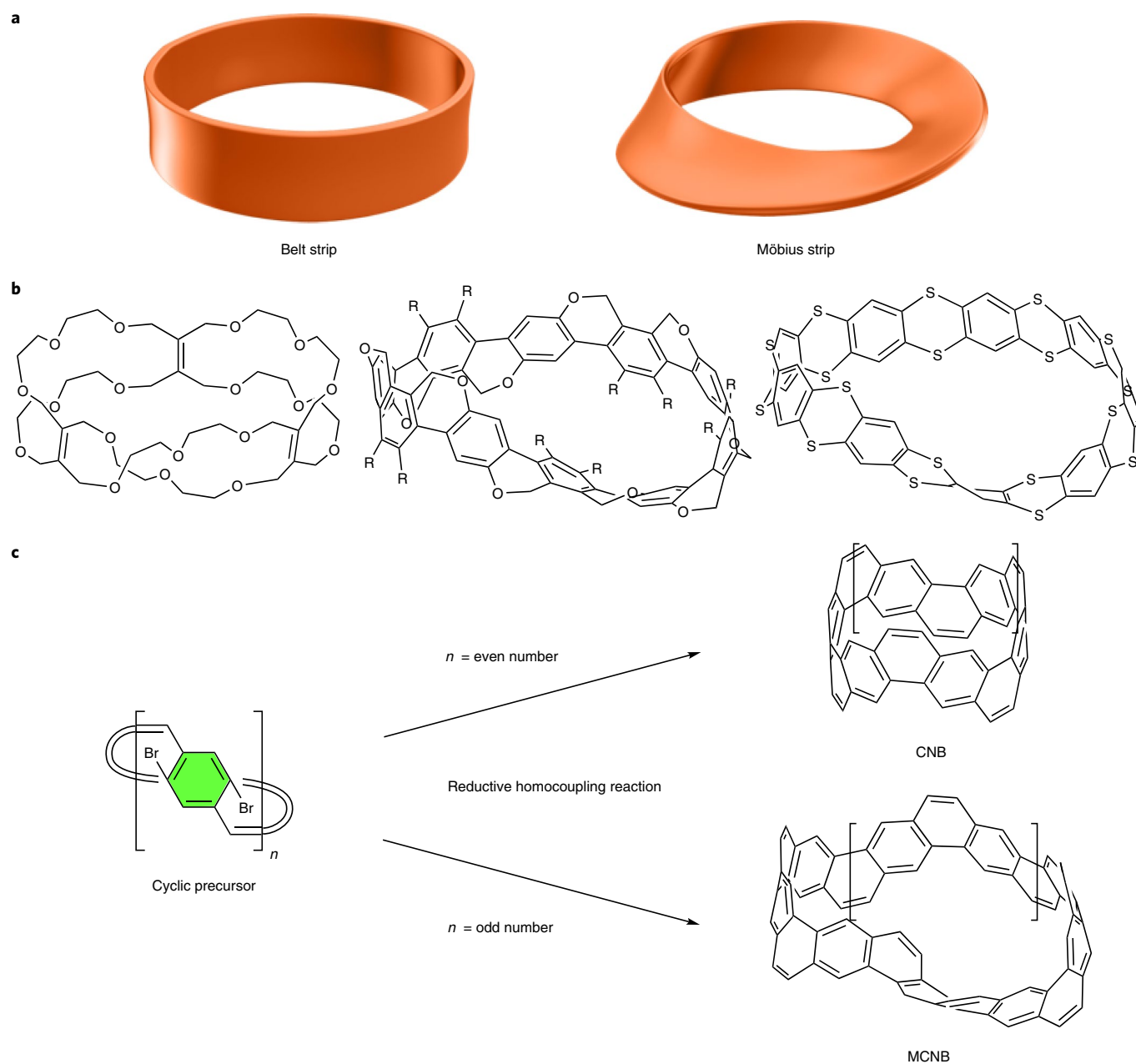


Fig. 1 | Representative Möbius-strip molecules. **a**, The models of belt- and Möbius-type strips. **b**, Previously reported belt-shaped double-stranded molecules with Möbius topology: a non-conjugated Möbius-type double-stranded molecule²⁴ (left), a Möbius-type cycloparaphenylene with saturated linkers ($-\text{CH}_2\text{O}-$) (ref. ³⁴) (centre) and a Möbius-type sulfur-embedded belt³⁵ (right). **c**, CNB, MCNB and their respective synthetic strategies.

molecules. For belts of a similar size, the ΔH_{FBF} of the MCNB was much higher than that of the CNB (for example, (6,6)CNB, $\Delta H_{\text{FBF}} = 40.2 \text{ kcal mol}^{-1}$; (7,7)MCNB, $\Delta H_{\text{FBF}} = 121.1 \text{ kcal mol}^{-1}$). As (6,6)CNB was successfully synthesized using a nickel-mediated homocoupling reaction, the strain energy allowed by this synthetic method was estimated to be approximately 40 kcal mol^{-1} . Based on these considerations, the synthetic pathway and the symmetry of the product, (15,15)MCNB ($\Delta H_{\text{FBF}} = 51.1 \text{ kcal mol}^{-1}$) and (25,25)MCNB ($\Delta H_{\text{FBF}} = 29.6 \text{ kcal mol}^{-1}$) were selected as the targets. The strain energies of the molecules were overall 85.7 and $49.4 \text{ kcal mol}^{-1}$, respectively, which indicates that the strain decreases with increasing size of the MCNB (for details, see Supplementary Fig. 1).

Synthesis. Our synthetic route to the MCNBs is shown in Figs. 3 and 4. To improve the solubility of the intermediates and products,

n -butoxy groups were introduced to the starting material **2**. Thus, (25,25)MCNB with 20 butoxy groups (**1**) was targeted and synthesized from simple precursors **2** and **5** over 14 steps. First, the unsymmetric functionalization of phenanthrene **2** was investigated to ensure a *Z*-selective Wittig reaction sequence. During the screening of the Lewis-acid-catalysed formylation of **2**, we found that monoformylated **3** was obtained selectively using TiCl_4 and MeOCHCl_2 in a high yield (75%), and that a subsequent chloromethylation with ZrCl_4 and MeOCH_2Cl smoothly afforded the bifunctional phenanthrene **4a** with formyl and chloromethyl groups in an 84% yield. The formyl and chloromethyl groups of **4a** were then converted into acetal and phosphonium groups, respectively, to yield **4b**. The sequential Wittig reaction of **5** with **4a** followed by **4b** produced the key intermediate **7c** (Fig. 3a). Starting from **7c** as the monomer, its dimer (**8c**), trimer (**9c**) and pentamer (**10c**) were synthesized via Wittig

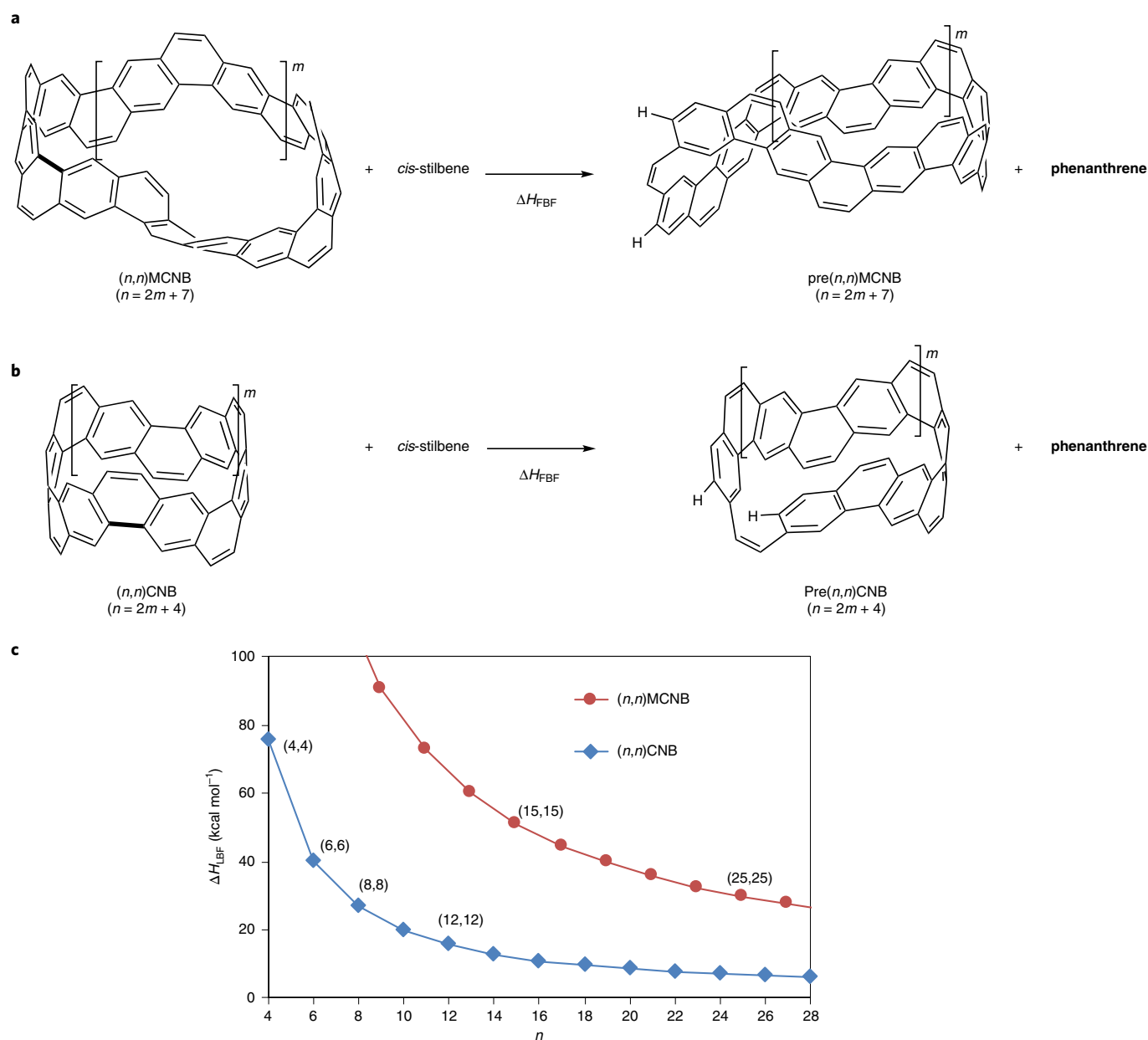


Fig. 2 | Theoretical analysis of the intrinsic strain of MCNBs. a,b, Hypothetical homodesmotic reactions to estimate the strain increase during the final C–C-bond-formation steps for (n,n) MCNB (**a**) and (n,n) CNB (**b**). For pre(M)CNBs, the bromine atoms are replaced with hydrogen atoms for clarity. **c**, Plot of the heat of formation for the equations in **a** and **b** as a function of the size of the CNBs and MCNBs. For all the calculations, the B3LYP level of theory and 6-31G(d) basis sets were used.

reactions (Fig. 3b). In these reactions, the formyl and phosphonium groups reacted selectively, as the chloromethyl and dimethylacetal groups were inert under the reaction conditions. The macrocyclization was performed with **10d**, which was derived from **10c** and bore formyl and phosphonium groups to yield **11** in a 67% yield. The reductive coupling of **11** with Ni(cod)₂ (cod, 1,8-cyclooctadiene) and 4,4'-methoxycarbonyl-2,2'-bipyridyl gave (BuO)₂₀(25,25)MCNB (**1**) in a 20% yield (Fig. 4a). In contrast, only a trace mass peak corresponding to (BuO)₁₂(15,15)MCNB for the macrocycle **12** was observed under similar conditions (Fig. 4b; see Supplementary Fig. 2 for details). According to DFT calculations, the failure to generate the (15,15)MCNB structure might be due to the huge strain required for the formation of the final bond ($\Delta H_{\text{FBF}} = 51.1 \text{ kcal mol}^{-1}$).

The thus obtained Möbius belt **1** was characterized using high-resolution mass spectrometry and NMR spectroscopy. The

high-resolution mass spectrum showed an isotope pattern with its highest peak at 3,944.9449, which is in good agreement with the simulated pattern and mass number ($m/z = 3,944.9423$) expected for C₂₈₀H₂₆₀O₂₀ (for details, see Supplementary Fig. 3). The DFT-optimized structure of **1** shows a C₂-symmetry with a long (~38 Å) and a short (~30 Å) axis (Fig. 5a). The broadened aromatic signals in the ¹H NMR spectrum observed at 25 °C converged at 140 °C into seven singlet signals, which can be assigned to a–h (shown in Fig. 5b) as supported by DFT calculations (see Supplementary Fig. 7 for details). These results indicate that the twist moiety of the Möbius belt moves quickly around the belt at a high temperature, as predicted for Möbius cyclacenes⁴⁰. As shown in Fig. 5c, the molecular motion was simulated using a density functional tight binding with molecular dynamics (DFTB-MD) calculation (for details, see Materials and methods in the Supplementary Information).

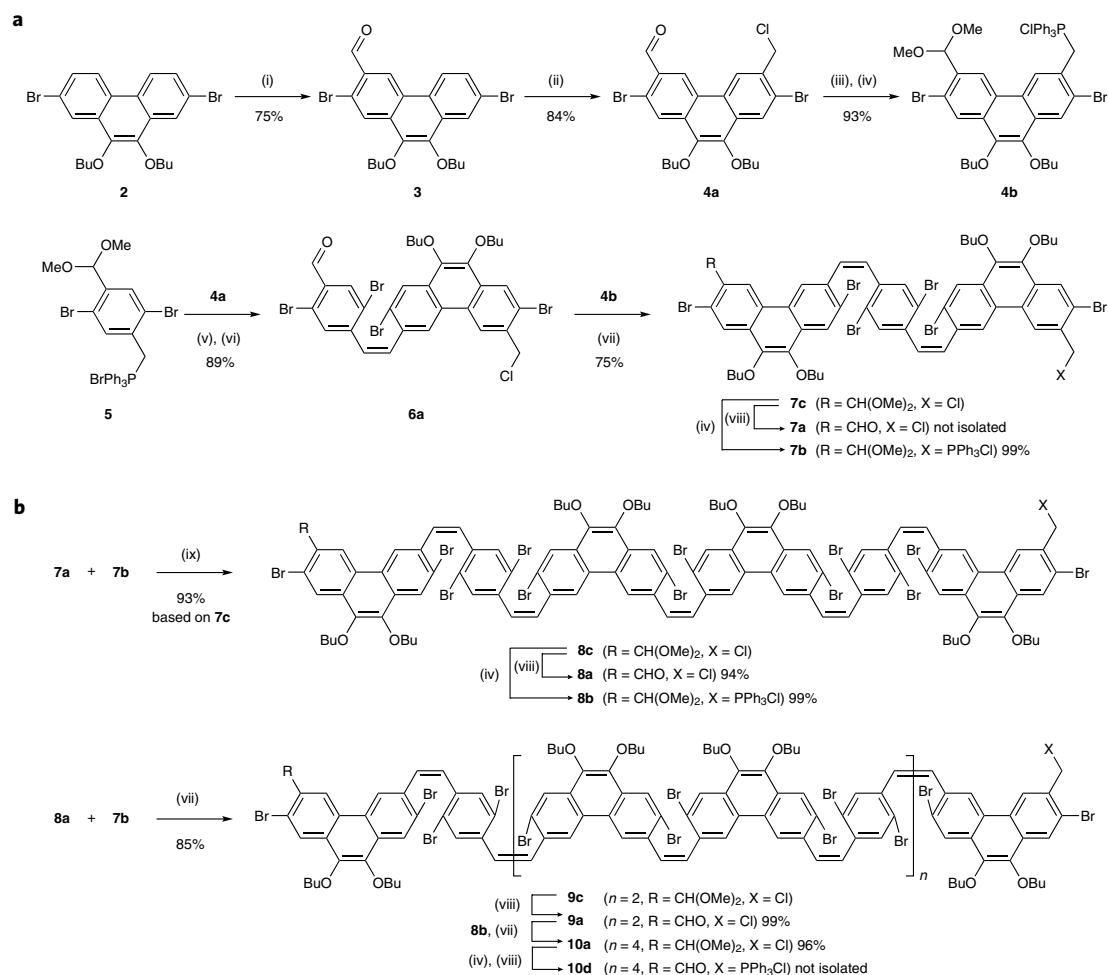


Fig. 3 | Synthesis of the precursors of a MCNB. a, Synthesis of a repeating units **7a–7c**. **b**, Preparation of precursor **10d** by sequential Wittig reactions. Reagents and conditions: (i) TiCl_4 , MeOCHCl_2 , dichloromethane, -45°C ; (ii) ZrCl_4 , MeOCH_2Cl , 1,2-dichloroethane, room temperature (r.t.); (iii) TsOH , $\text{CH}(\text{OMe})_2$, THF/methanol, r.t.; (iv) PPh_3 , $\text{CH}(\text{OMe})_2$, $80\text{--}90^\circ\text{C}$; (v) DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), dichloromethane, -10°C ; (vi) $\text{HCl}(\text{aq})$, THF, 40°C ; (vii) TMG (1,1,3,3-tetramethylguanidine), THF, r.t.; (viii) TFA (trifluoroacetic acid), chloroform, r.t.; (ix) LiHMDS (Li hexamethyldisilazide, molecular sieve 4A (MS4A), chloroform/THF, -78°C to -60°C . Ts, *p*-toluenesulfonyl.

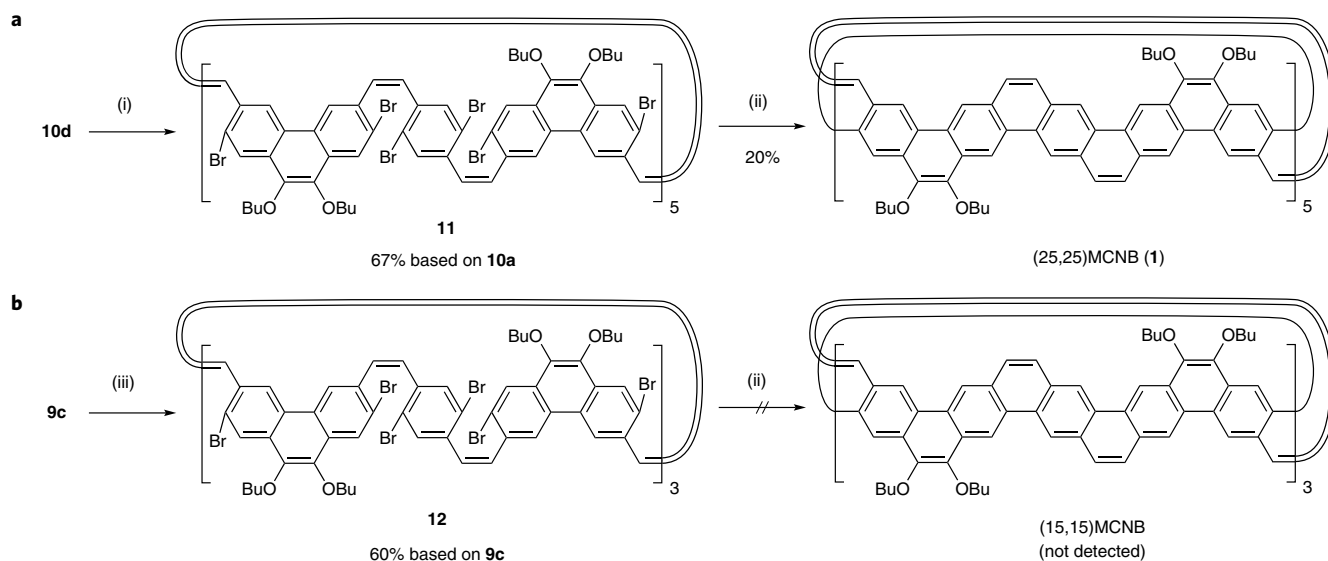


Fig. 4 | Synthesis of a MCNB. a, Macrocyclization of **10d** and Ni-mediated homocoupling to afford $(\text{BuO})_{20}(25,25)\text{MCNB}$ (**1**). **b**, Unsuccessful attempt to synthesize $(15,15)\text{MCNB}$ from cyclic precursor **12**. Reagents and conditions: (i) Pr_2NEt , MS4A, chloroform, 0°C ; (ii) $\text{Ni}(\text{cod})_2$, 4,4'-methoxycarbonyl-2,2'-bipyridyl, NMP (*N*-methylpyrrolidone), 70°C . (iii) PPh_3 , $\text{CH}(\text{OMe})_2$, 90°C ; TFA , chloroform, r.t.; TMG , THF, r.t.

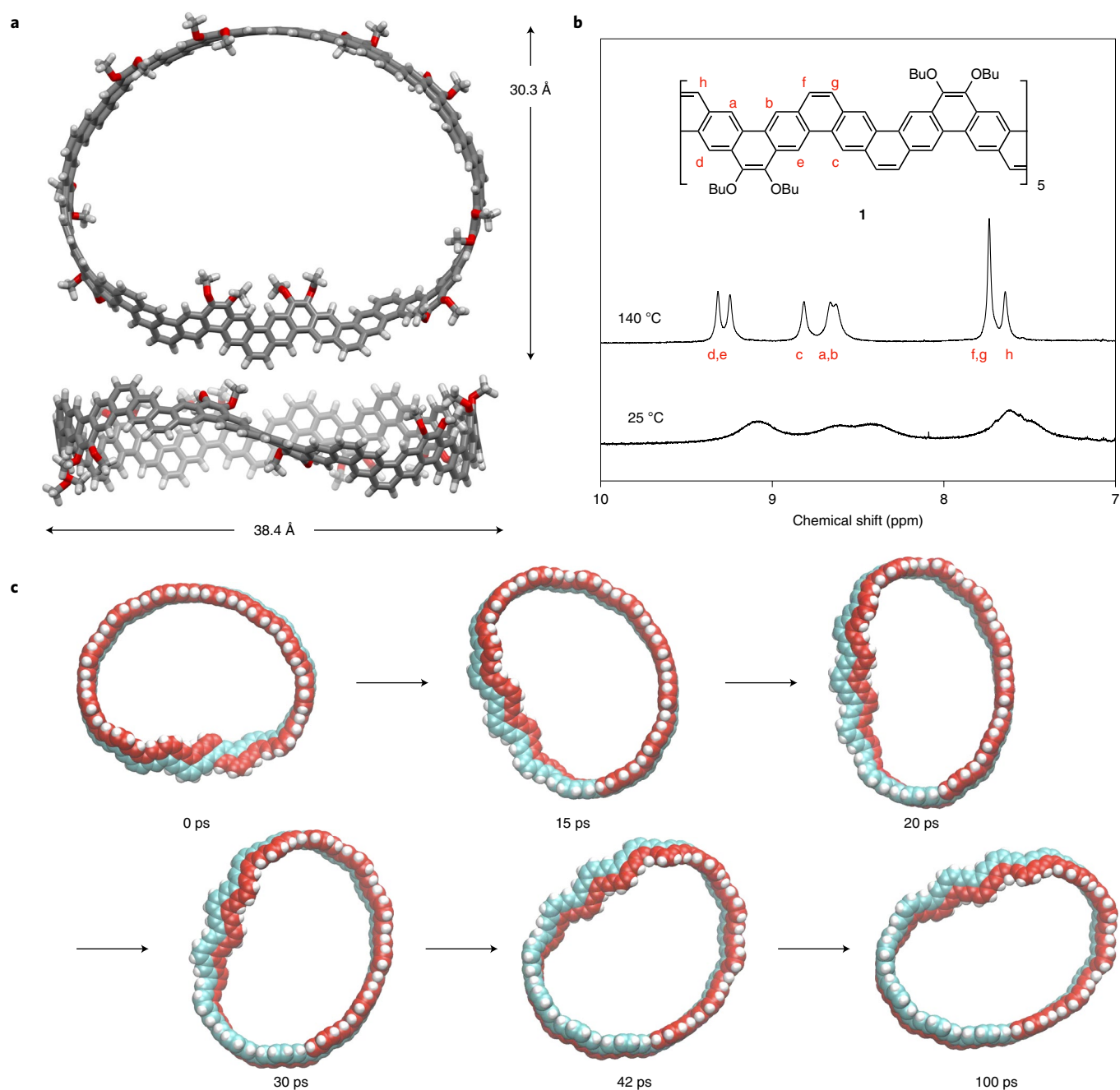


Fig. 5 | Structure and dynamics of MCNB 1. **a**, The structure of **1** was optimized at the B3LYP/6-31G(d) level of theory, whereby the butoxy groups were replaced by methoxy groups. **b**, Aromatic region of the ^1H NMR spectra of **1** in 1,1,2,2-tetrachloroethane- d_2 at 25 °C and at 140 °C. **c**, Snapshots of the DFTB-MD simulation of (25,25)MCNB (carbon, red or blue; hydrogen, white). For the details, see Supplementary Video 1).

Photophysical properties. The photophysical properties of Möbius CNB **1** were also investigated. As shown in Fig. 6a, absorption maxima at 389 and 409 nm as well as a small absorption peak at 477 nm were observed, and greenish-blue fluorescence with maxima at 480, 513 and 551 nm were observed on excitation at 380 nm. Based on the fluorescence quantum yield (10%) and half-life (14.1 ns), the radiative and non-radiative decay rate constants (k_r and k_{nr}) were estimated to be 7.1×10^6 and $6.4 \times 10^7 \text{ s}^{-1}$, respectively. Time-dependent DFT calculations of **1** suggested that, unlike in the D_{3h} -symmetric (6,6)CNB, the $S_0 \rightarrow S_1$ transition (assignable to the small band at 477 nm) is symmetry allowed ($f=0.6239$), which reflects the lowered symmetry caused by the Möbius topology (Supplementary Fig. 4). The topological chirality of **1** was also examined experimentally.

Chiral separation of **1** was successfully achieved using chiral HPLC, and the circular dichroism (CD) spectrum of each fraction was collected (Fig. 6b and Supplementary Figs. 5 and 6). Based on the CD spectra simulated using time-dependent DFT calculations (for details, see Supplementary Fig. 6), the first and second fractions were tentatively assigned to *M* and *P* chirality, respectively.

Conclusion

In conclusion, we successfully synthesized a MCNB, that is, a topological molecular nanocarbon with a twist on armchair CNBs. The strategy of using a variant of the previously used CNB precursor, cyclo(dibromoparaphenylene-*Z*-ethenylene) with an odd number of units led to the discovery of a rational synthetic route to such

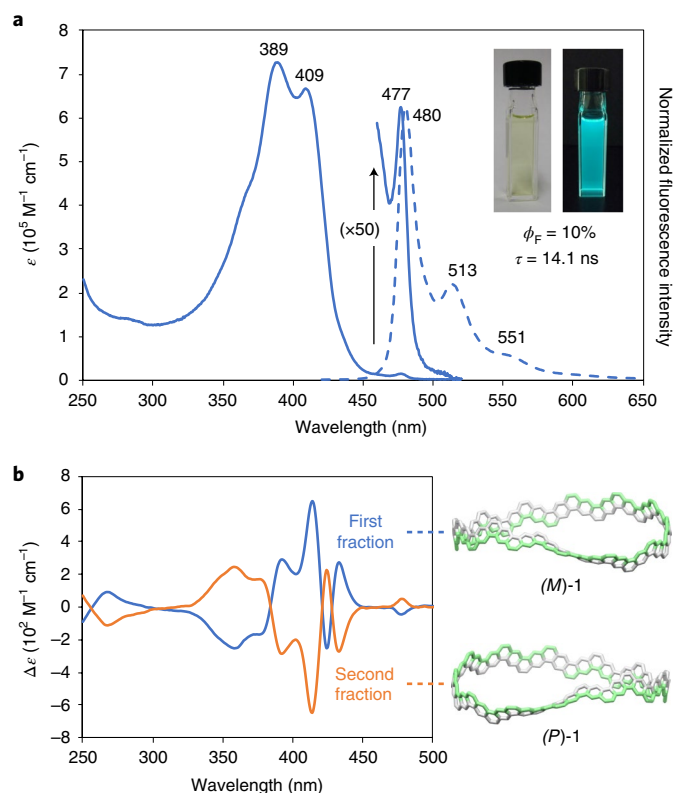


Fig. 6 | Photophysical properties of MCNB 1. **a**, Absorption (solid line) and fluorescence (dashed line) of a dichloromethane solution of **1**. Insets: photographs of a dichloromethane solution of **1** with (right) or without (left) ultraviolet light irradiation (254 nm). **b**, CD spectra of dichloromethane solutions of **1** separated using chiral column chromatography (CHIRALPAK-IE) with tentative structural assignments (*M* or *P*); butoxy groups are omitted for clarity. ϵ , absorption coefficient; τ , fluorescence lifetime; ϕ , fluorescence quantum yield.

MCNBs. DFT calculations of the intrinsic strain energies suggested that the synthesis of MCNBs with large sizes would be most promising, and therefore, (25,25)MCNB was selected as the target. The synthesis was carried out via *Z*-selective Wittig and intramolecular homocoupling reactions with nickel complexes to yield decabutoxylated (25,25)MCNB (**1**) over 14 steps. NMR spectroscopy and DFTB-MD calculations revealed that the Möbius twist structure moved quickly around the molecule in solution. Photophysical measurements revealed that the synthesized MCNB exhibited a greenish-blue fluorescence with a symmetry-allowed $S_0 \rightarrow S_1$ transition caused by the lowered symmetry. Experimentally, chiral HPLC separation and CD spectroscopy revealed that the chirality originates from the Möbius topology. The combination of strain calculations with a rational synthetic strategy can be expected to create a variety of topological molecular nanocarbons, which will promote the progress of materials science in this area.

Methods

For the synthesis of (BuO)₂₀(25,25)MCNB (**1**), to a 50 ml flask filled with argon gas were added Ni(cod)₂ (130 mg, 0.473 mmol, 30 equiv.), 4,4'-methoxycarbonyl-2,2'-bipyridyl (129 mg, 0.473 mmol, 30 equiv.) and NMP (9.6 ml). After the mixture was stirred at 70 °C for 1 h, the NMP (6.2 ml) solution of **11** (100 mg, 0.0157 mmol) was added and the resulting mixture was stirred at 70 °C for 20 min. The mixture was cooled to 0 °C and aqueous NH₄Cl (12 ml) was added. The organic layer was extracted with chloroform, washed with brine, dried over Na₂SO₄ and then evaporated in vacuo. The crude product was purified by column chromatography (chloroform) and preparative thin-layer chromatography (hexane:chloroform:ethanol, 15:85:0.5) to afford (BuO)₂₀(25,25)MCNB (**1**) (12.7 mg, 20%).

Data availability

Source data are provided with this paper. The experimental data and the characterization data for all of the compounds prepared in the course of these studies are provided in the Supplementary Information.

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Author contributions

K.I. and Y.S. conceived the project and prepared the manuscript with feedback from the other authors. T.W., K.Y., M.K. and K.W. performed the synthetic experiments and photophysical measurements. Y.S., K.W., J.P. and Y.H. performed the computational study.

Competing interests

The authors declare no competing interests.

Additional information

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