

# Synthesis and Structure of [9]Cycloparaphenylene Catenane: An All-Benzene Catenane Consisting of Small Rings

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enes ([9]CPPs) has been synthesized. Density functional theory calculations suggested that [n]CPPs (n = 5, 6) are highly strained upon the formation of catenanes compared with the corresponding uncatenated CPPs, whereas [n]CPP catenanes ( $n \ge 7$ ) are not strained. The synthesis of ([9]CPP)([9]CPP)catenane was accomplished via the following route: (i) a spirosilylation, (ii) a nickel(0)-mediated macrocyclization, (iii) a desilylation, and (iv) reductive aromatization reactions. An X-ray diffraction analysis revealed a catenated structure of ([9]CPP)([9]CPP)catenane.

nnovative methods for the synthesis of mechanically Linterlocked molecules (MIMs) have unlocked previously inaccessible areas of science and technology.<sup>1</sup> Representative MIMs such as catenanes and molecular knots exhibit distinct topologies due to their three-dimensionally interlocked structures.<sup>1,2</sup> Since the first synthesis of a catenane by Wasserman in 1960,<sup>3</sup> synthetic methods for MIMs have been extensively investigated. Prior to the 1980s, methods based on covalent templates and statistical threading have been predominantly used for the synthesis of catenanes and rotaxanes.<sup>4</sup> Sauvage and coworkers subsequently developed a method that is based on the use of a 1,10-phenanthroline-Cu complex, which improved the product yield and later enabled the first synthesis of a molecular trefoil knot.<sup>5</sup> In addition to this coordinative template method, several types of reversible interactions, for example, electrostatic and  $\pi - \pi$  stacking interactions as well as hydrogen and halogen bonding, have been widely used to date.<sup>6</sup> However, all of these methods require polar or coordinative functional groups and thus impose severe limitations on the synthesis of nonpolar MIMs. Except for one example of a cycloalkane-based catenane, reports on the synthesis of heteroatom-free MIMs that consist solely of carbon and hydrogen atoms have remained elusive until very recently.

Cycloparaphenylene (CPP) is a challenging building block for the construction of topological structures.<sup>8</sup> CPPs have received much attention during the past decade due to their highly symmetric structure and radial  $\pi$ -conjugation mode. Since the first synthesis of [n]CPPs (n = 9, 12, 18; n = number of paraphenylene units) by Bertozzi, Jasti, and coworkers in 2008,<sup>8h</sup> several CPP derivatives have been synthesized using strain-releasing strategies. Whereas the generation of CPP catenanes and knots (Figure 1a) has been actively sought after in the field of synthetic chemistry, their synthesis and isolation





**Figure 1.** (a) Previously reported mechanically interlocked cycloparaphenylenes (m = 0, 1). (b) Synthetic strategy for mechanically interlocked cycloparaphenylenes.

remain elusive. In 2016, Räder, Müllen, and coworkers reported a detailed mass analysis of a mixture of CPPs, which suggested the potential presence of CPP catenanes and trefoil knots, although results of further spectral or structural investigations were not reported at that time given that individual components proved difficult to isolate.<sup>9</sup> Moreover,

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**Figure 2.** Strain energies of catenated and uncatenated [n]CPPs as a function of the ring size (n) calculated at the B3LYP/6-31G(d) level of theory on hypothetical homodesmotic reactions.

because of the synthetic limitations, all previously reported  $\pi$ conjugated catenanes contain phenanthroline moieties.<sup>10</sup> Thus efficient synthetic routes to heteroatom-free catenanes and knots are in high demand.

Very recently, we have established a new strategy to synthesize heteroatom-free MIMs.<sup>11</sup> Because spirobi-(dibenzosilole) is quantitatively converted into two biphenyls upon treatment with fluorides in alcohol,<sup>12</sup> the spirosilane unit can be used as a removable template for the construction of interlocked structures. We have used this "traceless" synthetic methodology to synthesize and isolate the ([12]CPP)([12]-CPP)catenane and ([12]CPP)([9]CPP)catenane as well as a [24]CPP trefoil knot (Figure 1a,b).<sup>11a</sup> The synthesis and isolation of these CPP MIMs enabled us to reveal their characteristic physical properties such as the vortex-like dynamic motion of the CPP trefoil knot and the rapid energy transfer between the two rings in ([12]CPP)([9]CPP)-catenane.

Herein we report the synthesis, structure, and photophysical properties of ([9]CPP)([9]CPP)catenane (1). The synthesis of small CPPs has been widely investigated as (i) the photophysical properties of relatively small CPPs ([5]-[11]CPPs) differ dramatically from each other depending on their ring size<sup>13</sup> and (ii) the synthesis of smaller CPPs is highly challenging due to their high intrinsic strain.<sup>14</sup> Therefore, CPP catenanes that consist exclusively of small CPPs are of high interest with respect to both their photophysical properties and the synthetic difficulties associated with their generation. Prior to the experimental efforts, we theoretically investigated the relationship between the strain energy and the ring size of CPP catenanes.

Initially, we calculated the strain energies of CPP catenanes to examine the effect of an interlocked system on the intrinsic strain. Density functional theory (DFT) calculations at the B3LYP/6-31G(d) level of theory were used for all of the structures. The strain energies<sup>14</sup> of the catenanes consisting of two [*n*]CPPs are plotted in Figure 2. The strain increases for *n* = 6 and is very high for *n* = 5. This is due to a repulsion from the benzene ring that resides within the CPP ring, suggesting that the ring size of [5]CPP is too small for the formation of catenane structures. Because the strain does not significantly change for *n* > 6, the effect of the strain on the formation of the catenane can be considered negligible when the size is larger than that of [6]CPP. This result represents an important guideline for the molecular design of CPP catenanes.

We attempted the synthesis of [9]CPP catenane 1 (Figure 3a). The C-shaped unit 2 has already been reported as a precursor for ([9]CPP)([12]CPP)catenane.<sup>11a</sup> Compound 2 was subjected to our previously developed spirosilylation conditions.<sup>11a</sup> The dilithiation of 2 followed by the addition of SiHCl<sub>3</sub>(tmeda)<sup>15</sup> afforded spirosilane 3 in 49% yield.



**Figure 3.** (a) Synthesis of ([9]CPP)([9]CPP) catenane 1. Reaction conditions: (i) *n*-BuLi; then TMEDA, SiHCl<sub>3</sub>, THF/Et<sub>2</sub>O. (ii) Ni(cod)<sub>2</sub>, 2,2'bipyridyl, DMF. (iii) *n*-Bu<sub>4</sub>NF, dioxane/*n*-BuOH. (iv) Sodium naphthalenide, THF; then I<sub>2</sub>. Abbreviations: cod = 1,5-cyclooctadiene, DMF = *N*,*N*dimethylformamide, TMEDA = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine. (b) Plausible intermediates **4a**,**b** for the generation of 1 and [9]CPP from 3 with the relative total energies ( $\Delta E$ ) calculated by using the B3LYP/6-31G(d) level of theory. (c) ORTEP drawing of 1 with thermal ellipsoids at 50% probability. One of disordered [9]CPPs, solvent molecules, and hydrogen atoms are omitted for clarity.

Spirosilane 3 was also obtained as a side product during the synthesis of ([9]CPP)([12]CPP)catenane. A homocoupling reaction of 3 using  $Ni(cod)_2$  and 2,2'-bipyridyl furnished pseudocatenane 4a. Without complete purification, a desilylation reaction using TBAF and a reductive aromatization reaction with sodium naphthalenide were carried out sequentially. Thus [9]CPP catenane was obtained in 1.6% yield relative to 3 and [9]CPP was obtained as a side product in 16% yield; other side products might be the polymeric insoluble compounds obtained from the homocoupling step. The formation ratio of catenane to CPP is 1:10, which is much lower than that of [12]CPP catenane and [12]CPP (~1:1). This might be due to the fact that the formation ratio of the pseudocatenane 4a is decreased relative to 4b on account of the strain of 4a. DFT calculations indicated that 4a is 6.4 kcal $mol^{-1}$  higher in energy than 4b, which may imply the difficulty of the macrocyclization step for the formation of 4a (Figure 3b). The molecular structure of 1 was confirmed unequivocally by X-ray crystallography (Figure 3c). A single crystal of 1 was obtained from the vapor diffusion of hexane into a THF solution of 1 at room temperature. Compound 1 exhibits an interlocked catenane structure with disorder in one of the [9]CPP rings, and hexane molecules are incorporated in the voids of the crystal.

The photophysical properties of 1 were measured and compared with those of [9]CPP to investigate the effect of the catenane structure on the electronic properties. UV-vis absorption spectra, fluorescence spectra, absolute fluorescence quantum yields ( $\Phi_{\rm F}$ ), and the fluorescence lifetime ( $\tau$ ) of 1 and [9]CPP are shown in Figure 4a. Both the absorption and fluorescence spectra of 1 are similar to those of [9]CPP, although the fluorescence spectrum is slightly bathochromically shifted, which is similar to the case of [12]CPP and its catenane. The absolute fluorescence quantum yield of 1 ( $\Phi_{\rm F}$  = 0.54) is slightly lower than that of [9]CPP ( $\Phi_{\rm F} = 0.73$ ). Timeresolved fluorescence measurements were conducted, which revealed fluorescence lifetimes of 11.3 ns. According to the equations  $\Phi_{\rm F} = k_{\rm r} \times \tau$  and  $k_{\rm r} + k_{\rm nr} = \tau^{-1}$ , the radiative  $(k_{\rm r})$  and nonradiative  $(k_{nr})$  decay rate constants from the singlet excited state were determined  $(k_r = 4.8 \times 10^7 \text{ s}^{-1}; k_{nr} = 4.1 \times 10^7 \text{ s}^{-1}).$ Compared with those of uncatenated [9]CPP ( $k_r = 6.9 \times 10^7$  $s^{-1}$ ;  $k_{nr} = 2.5 \times 10^7 s^{-1}$ ), both rate constants are affected by the catenane structure. The frontier molecular orbitals of 1 and [9]CPP with their respective orbital energy values are shown in Figure 4b. The HOMO and HOMO-1 are localized on each [9]CPP ring, whereas the LUMO and LUMO+1 are delocalized over the two rings.

In summary, we have synthesized and structurally characterized a catenane that consists of two [9]CPP rings. DFT calculations indicated that [n]CPPs (n = 5,6) are highly strained upon the formation of catenanes, whereas [n]CPPs (*n*  $\geq$  7) are not. The synthesis of ([9]CPP)([9]CPP)catenane (1) was accomplished via the following synthetic route: (i) a spirosilylation of C-shaped units (2), (ii) a macrocyclization via a nickel(0)-mediated homocoupling, (iii) a fluoridemediated desilylation, and (iv) sequential reductive aromatization reactions. The three-step yield of 1 relative to spirosilane 3 (1.6%) is lower than that of ([12]CPP)([12]CPP)catenane (16%) and similar to that of ([12]CPP)([9]CPP)catenane (1.5%). A single-crystal X-ray diffraction analysis of [9]CPP catenane revealed a catenated structure in which one of the two [9]CPP rings is disordered. The optical properties of 1 are similar to those of [9]CPP, albeit the emission of 1 is slightly



Figure 4. (a) UV–vis absorption (solid lines) and fluorescence (dotted lines) spectra as well as absolute fluorescence quantum yields ( $\Phi_F$ ) and fluorescence lifetime ( $\tau$ ) of 1 and [9]CPP in CH<sub>2</sub>Cl<sub>2</sub>. Excitation wavelength: 340 nm; emission wavelength for the lifetime measurement of 1: 510 nm. (b) Frontier molecular orbitals of 1 and [9]CPP were calculated at the B3LYP/6-31G(d) level of theory (isovalue: 0.02).

red-shifted relative to that of [9]CPP, which indicates weak  $\pi - \pi$  interactions for the catenated structure. Further investigations into the synthesis of heteroatom-free catenanes and knots are currently in progress in our laboratory.

# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.9b04599.

Experimental details and spectra of all new compounds (PDF)

Cartesian coordinates of optimized structures (XYZ)

## **Accession Codes**

CCDC 1974070 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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## Notes

The authors declare no competing financial interest.

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