Solution-phase stabilization of a cyclocarbon by catenane formation

Authors: Yueze Gao[1]*, Prakhar Gupta[1], Igor Rončević[2], Coral Mycroft[1], Paul J. Gates[3], Anthony W. Parker[4] and Harry L. Anderson[1]*

Affiliations:

[1] Department of Chemistry, Oxford University, Chemistry Research Laboratory, Oxford, United Kingdom.

[2] Department of Chemistry, The University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom.

[3] School of Chemistry, University of Bristol, Cantock's Close, Clifton, Bristol, BS81TS, United Kingdom.

[4] Central Laser Facility, Research Complex at Harwell, STFC, Rutherford Appleton Laboratory, Harwell Campus, Didcot OX11 0QX, United Kingdom.

*Corresponding author. Email: yueze.gao@chem.ox.ac.uk; harry.anderson@chem.ox.ac.uk

Abstract: Cyclo[*N*]carbons, molecular rings consisting solely of *N* carbon atoms, have previously been studied in the gas phase and on surfaces at cryogenic temperatures, but they are generally considered too reactive to be studied under ambient laboratory conditions. Here we report the synthesis of a cyclo[48]carbon catenane, in which the C_{48} ring is protected by being threaded through three other macrocycles. This cyclo[48]carbon [4]catenane is stable enough for spectroscopic characterization in solution at room temperature. Its mass spectrum displays the expected molecular ions; its ^{13}C nuclear magnetic resonance (NMR) spectrum gives a single resonance for all 48 sp^1 carbon atoms at 72.9 ppm and its Raman spectrum shows an intense peak at 1890 cm^{-1}, similar to linear polyynes.

One-Sentence Summary: A cyclo[48]carbon catenane has been synthesized that is stable enough for spectroscopic characterization under ambient laboratory conditions.

Main Text: Diverse carbon clusters, including cyclo[*N*]carbons up to $N = 36$, have been characterized in the gas phase (*1-3*), but the only molecular carbon allotropes yet to have been studied under ambient conditions are the fullerenes. Recently, several cyclo[*N*]carbons ($N = 6$, 10, 12, 13, 14, 16, 18, 20, 26) have been synthesized on surfaces by atom manipulation and investigated using scanning probe microcopy at temperatures of 4–10 K (*4–10*). However, all reported attempts at synthesizing cyclocarbons in solution have been unsuccessful (*11–16*) and it is generally assumed that they are too reactive to survive in solution or in the solid state above liquid helium temperatures. Their high reactivity stems from the fact that the conversion of sp^1 carbon into cross-linked amorphous sp^2/sp^3 carbon is thermodynamically favorable, and many materials with a high mass fraction of sp^1 acetylenic carbon are explosive for the same reason (*17*). Here we show that cyclo[48]carbon can be stabilized by supramolecular encapsulation, by formation of a [4]catenane, in which the ring of carbon atoms is threaded through three covalent macrocycles **M**. The cyclo[48]carbon [4]catenane $\mathbf{C_{48}{\cdot}M_3}$ is stable enough for spectroscopic characterization in solution under ambient conditions. This work was inspired by the pioneering studies of Cram (*18*) and Warmuth (*19*), who demonstrated that the highly reactive species cyclobutadiene and *ortho*-benzyne, respectively, can be stabilized by supramolecular encapsulation. Although catenane formation does not completely encapsulate the cyclocarbon, we reasoned that the presence of the threaded macrocycles would hinder cyclocarbon molecules from reacting together to form a crosslinked material and increase the lifetime in solution.

Synthesis. The cyclocarbon catenane $\mathbf{C_{48}{\cdot}M_3}$ was prepared from a masked precursor, $\boldsymbol{m}$-$\mathbf{C_{48}{\cdot}M_3}$ (Fig. 1), which was synthesized by oxidative palladium-catalyzed Glaser coupling cyclo-oligomerization of a [2]rotaxane, prepared by active metal template-directed synthesis (*16,20-26.*), as detailed in the Supplementary Materials. The cobalt carbonyl phosphine masking groups stabilize $\boldsymbol{m}$-$\mathbf{C_{48}{\cdot}M_3}$ and act as temporary stoppers during its synthesis. The macrocycle **M** includes two nitrogen sites for binding copper during the active metal template-directed synthesis. We chose a macrocycle based on 2,2'-bipyridine, rather than phenanthroline, to make it less susceptible to oxidation (*27*) and aggregation. The macrocycle features *ortho*-methyl substituents to generate a more cylindrical cavity. The masked cyclo[48]carbon [4]catenane $\boldsymbol{m}$-$\mathbf{C_{48}{\cdot}M_3}$ was treated with *meta*-chloroperbenzoic acid (mCPBA) (*20*), followed by purification by gel-permeation chromatography, to give unmasked $\mathbf{C_{48}{\cdot}M_3}$ as an orange-red solution. A range of conditions was screened to optimize this unmasking reaction and purification protocol (Table S1), and the best results were obtained using mCPBA in combination with 2,2'-bipyridine (2,2'-bipy) at 0 °C with a short reaction time (3 minutes), followed by quenching excess mCPBA with phenanthroline (*27*). Phenanthroline and 2,2'-bipy were added because they react with mCPBA faster than the macrocycle **M**, thus protecting it from *N*-oxide formation. $\mathbf{C_{48}{\cdot}M_3}$ is not stable in the solid state, and evaporation of the solvent must be avoided during its synthesis. Solutions of $\mathbf{C_{48}{\cdot}M_3}$ in deuterated solvents, for analysis by NMR spectroscopy, were prepared by unmasking $\boldsymbol{m}$-$\mathbf{C_{48}{\cdot}M_3}$ in CD_2Cl_2, followed by gel-permeation chromatography, eluting with $CDCl_3$.

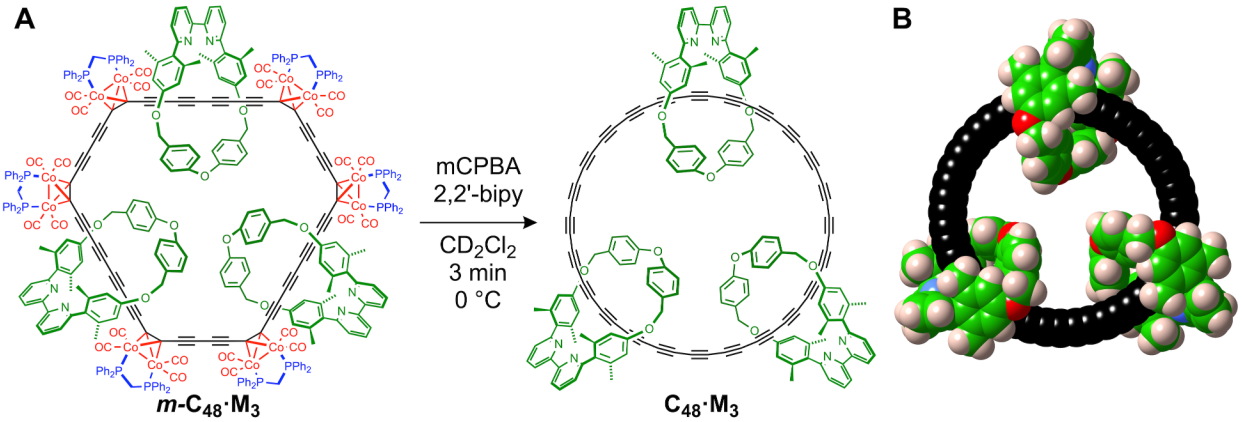


Fig. 1. Unmasking of the cyclo[48]carbon [4]catenane. (**A**) Synthesis of $\mathbf{C_{48}{\cdot}M_3}$ and (**B**) a projection of its calculated geometry to show the van der Waals surface. The optimized geometry of $\mathbf{C_{48}{\cdot}M_3}$ was calculated by the PM6 method, see Supplementary Materials.

Spectroscopic characterization. The first clear evidence for the formation of $\mathbf{C_{48}{\cdot}M_3}$ was provided by mass spectrometry. The mass spectrum of $\mathbf{C_{48}{\cdot}M_3}$ (Fig. 2) shows peaks for $[\mathbf{C_{48}{\cdot}M_3} + 3H]^{3+}$ at m/z = 783.596 (base peak), $[\mathbf{C_{48}{\cdot}M_3} + 2H]^{2+}$ at m/z = 1174.896, and $[\mathbf{C_{48}{\cdot}M_2} + 2H]^{2+}$ at m/z = 879.763, all of which fit extremely well to the predicted isotope distributions (Fig. 2). The peak attributed to the [3]catenane appears to arise from a trace byproduct generated by cleavage of the macrocycle during unmasking. (This interpretation is supported by ^{1}H NMR analysis and model reactions on a [2]rotaxane which show traces of macrocycle cleavage accompanying unmasking; see Supplementary Material, Section 3.2).

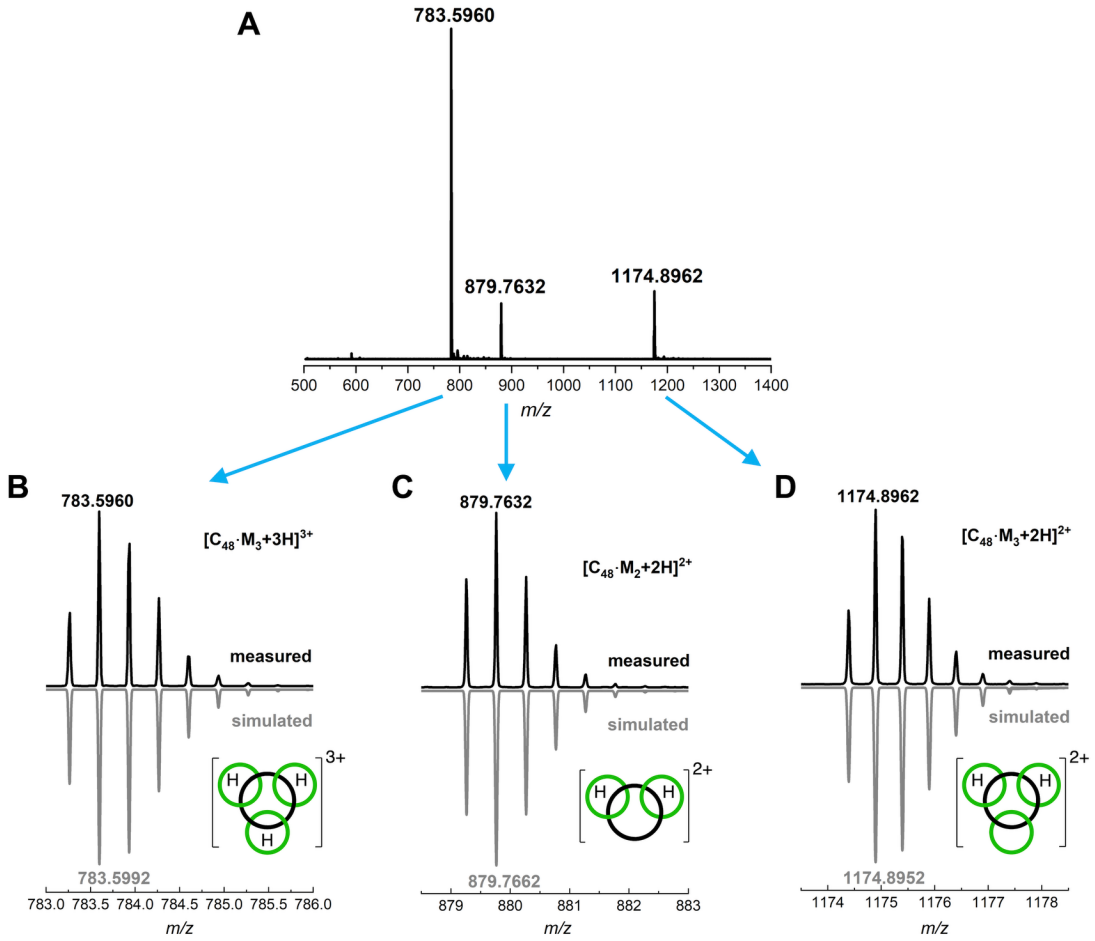


Fig. 2. Mass spectrum of C_{48}·M_3. (**A**) The whole high resolution nano-electrospray Q-Tof mass spectrum, run in 3:1 toluene:formic acid, and expansions of the signals from (**B**) [**C_{48}·M_3** + 3H]$^{3+}$ at *m/z* = 783.596, (**C**) [**C_{48}·M_2** + 2H]$^{2+}$ at *m/z* = 879.763, and (**D**) [**C_{48}·M_3** + 2H]$^{2+}$ at *m/z* = 1174.896.

The ^{1}H and ^{13}C NMR spectra of **C_{48}·M_3** (recorded in $CDCl_3$ at –35 °C) are compared with those of a reference [2]rotaxane **Si_2C_{16}·M** in Fig. 3. This reference rotaxane contains the same macrocycle **M** as the catenane, and the ^{1}H NMR spectra of both compounds are very similar (except for signals from the tri-*iso*-propylsilyl group at 1.05 ppm, not shown in Fig. 3). The ^{13}C NMR spectra of the two compounds are also similar, except that **Si_2C_{16}·M** has 8 well resolved signals due to sp^{1} carbon atoms at 89.8, 86.4 and 63.0–61.9 ppm whereas **C_{48}·M_3** gives a single intense peak at 72.9 ppm for all 48 sp^{1} carbons. The simple ^{1}H and ^{13}C NMR spectra of **C_{48}·M_3** demonstrate that it has a symmetrical structure and that the threaded macrocycles move rapidly round the cyclocarbon ring, making all 48 sp^{1} carbon environments equivalent on the NMR timescale. This type of dynamic behavior often arises in catenanes when there is no strong interaction between the macrocycles (*20,28*). The ^{13}C chemical shift of the cyclic C_{48} unit in the [4]catenane (72.9 ppm) is higher than that for the carbons at the center of a linear C_{48} polyyne [4]rotaxane (63.7 ppm) by 9.2 ppm (*20,29*). This increase in chemical shift is consistent with previous experimental and computational studies that report a downfield shift in the ^{13}C NMR spectra of strained polyynes (*30–32*).

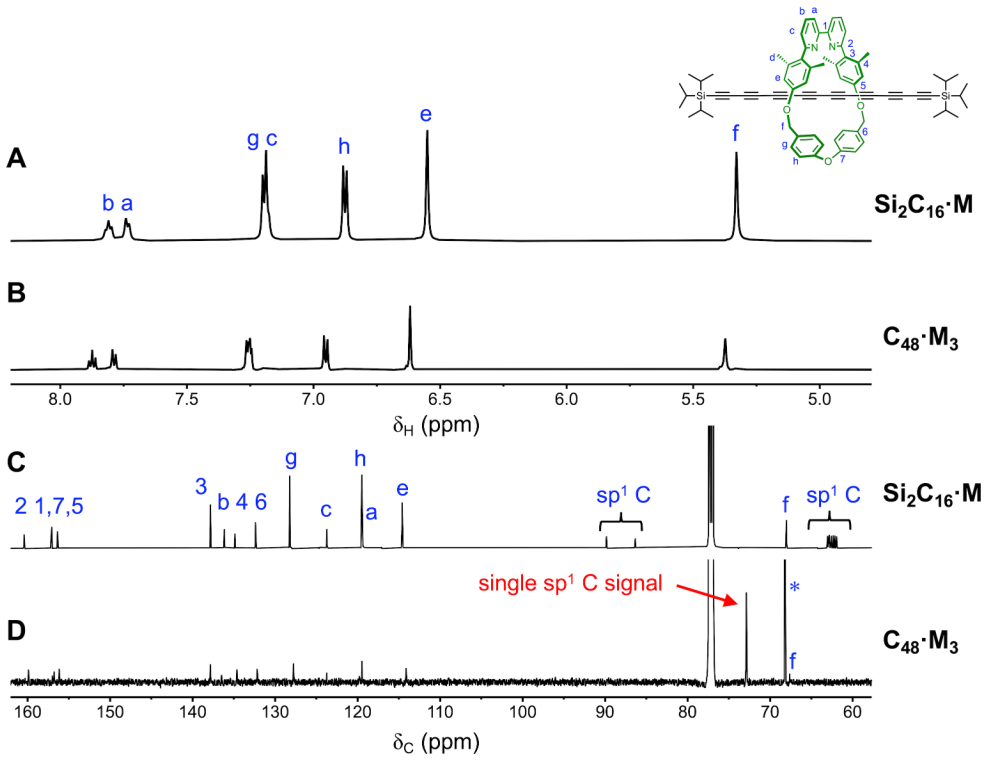


Fig. 3. ^{1}H and ^{13}C NMR spectra. **A**,**B**, ^{1}H NMR spectra (600 MHz, $CDCl_3$, diffusion-edited, –35 °C) and **C**,**D** ^{13}C NMR spectra (150 MHz, –35 °C) of the reference [2]rotaxane (**A** and **C**) and the [4]catenane **C_{48}·M_3** (**B** and **D**). (* indicates a signal arising from a trace of tetrahydrofuran.)

Dilute solutions of **C_{48}·M_3** in organic solvents decompose slowly at room temperature. In dichloromethane, **C_{48}·M_3** has a half-life of 92 hours (3 µM concentration, 20 °C), as shown by the decay of the UV-vis absorption bands in Fig. 4A. Surprisingly, the rate of decomposition of **C_{48}·M_3** is not strongly dependent on concentration: when monitored by ^{1}H NMR spectroscopy at 300 µM concentration (20 °C, $CDCl_3$) the rate of decomposition is similar to that when monitored by UV-vis at 3 µM concentration, see fig. S10. The catenane is much less stable in the solid state and removal of the solvent by evaporation results in immediate decomposition to give insoluble material. We also tested unmasking of the corresponding cyclo[48]carbon cobaltcarbonyl phosphine complex with no threaded macrocycles, ***m*-C48** (for synthesis, see Scheme S5). Treatment of a dilute (1 µM) solution of ***m*-C48** in dichloromethane with mCPBA gives a lemon yellow solution with a similar UV-vis absorption spectrum to that of **C_{48}·M_3**, indicating the formation of unmasked cyclo[48]carbon. This naked cyclocarbon decomposed with a half-life of about 1 hour at 20 °C at 0.9 µM concentration (fig. S12a), and much more rapidly at higher concentrations (fig. S12e), preventing purification or characterization by mass spectrometry or NMR spectroscopy. The identification of this non-catenane cyclo[48]carbon must be regarded as tentative, because, so far, we have only characterized it by UV-vis spectroscopy, yet the match with the absorption spectra of **C_{48}·M_3** strongly suggests that this species is **C_{48}** (fig. S14). The absorption bands of this putative cyclo[48]carbon are shifted to shorter wavelengths than those of **C_{48}·M_3**, by about 7 nm, as generally observed when comparing polyyne polyrotaxanes with the naked polyyne dumbbells (*20,24*) (see also fig. S15 for comparison of the UV-vis spectra of **Si_2C_{16}** and **Si_2C_{16}·M**). We have not yet purified **C_{48}**, and the presence of byproducts from the unmasking reaction probably affect its stability, but it appears that decomposition of **C_{48}** is much more concentration-dependent than that of **C_{48}·M_3**.

Solutions of **C_{48}** in dichloromethane decompose with a half-life of less than a minute at a precursor concentration of 15 µM (see fig. S12e).

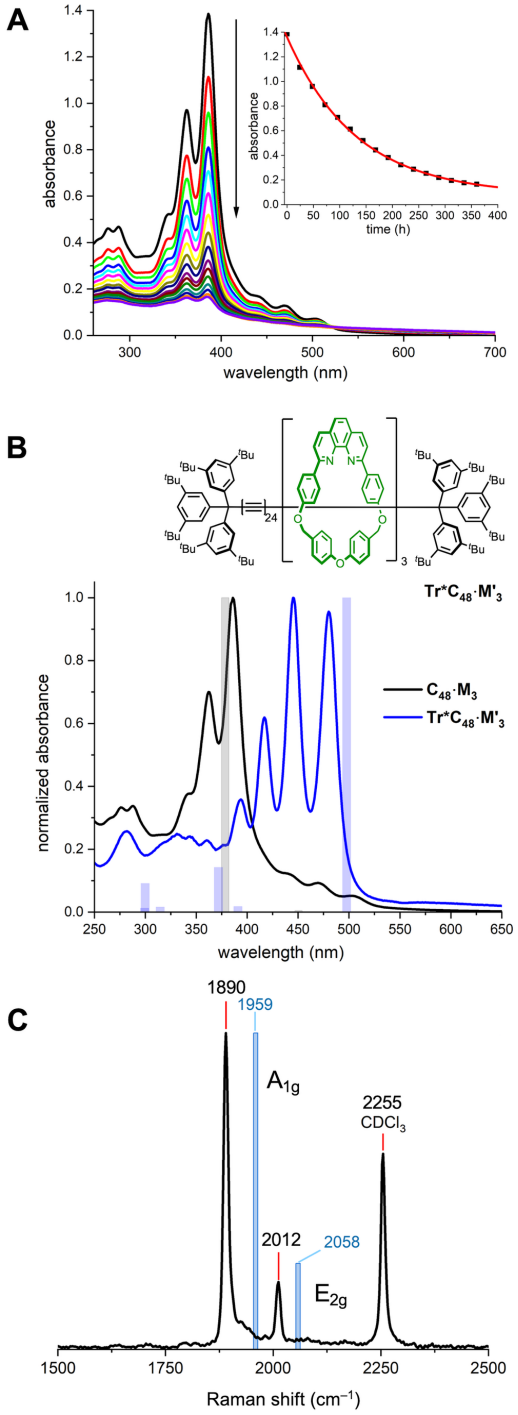


Fig. 4. Optical spectra of C_{48}·M_3. (**A**) UV-vis spectra in CH_2Cl_2 recorded over 360 hours, showing the rate of decomposition at 20 °C in the dark (1 cm path length; 3 µM). The insert shows a fit of the absorbance at 386 nm to a first-order decay with a half-life of 92 hours. (**B**) Comparison of UV-vis spectra of cyclo[48]carbon catenane **C_{48}·M_3** (black) and linear C_{48} polyyne [4]rotaxane (**Tr*C_{48}·M'$_3$**, blue); vertical bars show vertical transitions from TD-DFT calculations. (**C**) Raman spectrum obtained using an excitation wavelength of 514 nm; vertical blue bars denote calculated peaks.

The UV-visible absorption spectrum of the **C_{48}·M_3** [4]catenane is compared with that of a linear end-capped C_{48} polyyne [4]rotaxane **Tr*C_{48}·M'$_3$** (*20*) in Fig. 4B. The linear polyyne exhibits a progression of intense absorption bands in the visible region (400–500 nm) with the 0-0 transition at 480 nm, whereas the spectrum of the cyclocarbon catenane is most intense in the UV (350–400 nm) with a dominant 0-0 transition at 386 nm. The suppression of long-wavelength absorption bands is a general feature of cyclic π-systems, when compared with their linear analogues, due to the difference in selection rules (*33–35*). Time-dependent DFT (TD-DFT) calculations on cyclo[48]carbon and the linear polyyne $C_{48}H_2$ (in vacuum) closely resemble the observed spectra of **C_{48}·M_3** and **Tr*C_{48}·M'$_3$** (see vertical bars in Fig. 4A and fig. S16).

The resonance Raman spectrum of **C_{48}·M_3** exhibits an intense peak at 1890 cm^{-1} (recorded in $CDCl_3$ with excitation at 514 nm, Fig. 4C), similar to the transitions observed in the Raman spectra of linear polyynes (*36–39)*. **C_{48}·M_3** also exhibits a weaker peak at 2012 cm^{-1}. Both peaks are reproduced by computational simulations, supporting assignment of the 1890 and 2012 cm^{-1} to the symmetric (A_{1g}) C-C stretching vibration and the doubly degenerate asymmetric (E_{2g}) C-C stretch, respectively (see blue bars in Fig. 4C and Supplementary Materials, Section 8 for details). The experimental Raman spectrum of **C_{48}·M_3** is also similar to the predicted Raman spectra of cyclocarbons such as C_{30} (*40*).

Conclusion and outlook. We have synthesized a cyclocarbon that is sufficiently stable in solution under ambient conditions to permit characterization using standard spectroscopic techniques, whereas previously cyclocarbons have only been characterized in the gas phase or on surfaces at temperatures of 4–10 K. The factors that enabled us to achieve this objective are: (a) the use of threaded macrocycles to provide supramolecular encapsulation conferring enhanced stability by hindering access to the cyclocarbon, (b) the selection of a large cyclocarbon, C_{48}, with a low level of strain (*41*), and (c) the development of mild reaction conditions for unmasking the masked cyclocarbon intermediate. The cyclo[48]carbon [4]catenane is moderately stable in solution at 20 °C, with a half-life of 92 hours. It is much more stable than the naked cyclo[48]carbon, with a half-life of about 1 hour at 20 °C and 0.9 μM concentration, and it decomposes rapidly at higher concentrations. Even unprotected cyclo[48]carbon is much more stable than reactive intermediates such as *ortho*-benzyne, which only persists for a few nanoseconds under typical solution-phase conditions (*42,43*). The stabilization of C_{48} by catenane formation is analogous to the stabilization of *ortho*-benzyne by encapsulation in a hemicarcerand (*19*); however a view of the van der Waals surface of **C_{48}·M_3** (Fig. 1B) shows that only part of the cyclocarbon is encapsulated by the threaded macrocycles. These results may inspire the design of other host molecules that are even more effective in stabilizing cyclocarbons through supramolecular encapsulation.

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Experimental work: YG, PG

Theoretical analysis and computational simulations: IR

Mass spectrometry: PJG

Raman spectroscopy: AWP, YG

NMR spectroscopy: CM, YG

Writing: All authors.

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Supplementary Materials

Materials and Methods

Supplementary Text

Figs. S1 to S66

References (*46–51*)