Porous Covalent Organic Nanotubes and Toroids: A Carbon Nanotube Analogue

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Abstract

Despite the noteworthy progress made in the nanotubular architectures with well-defined lengths and diameter, the synthesis of a purely covalent bonded organic nanotube, so far, proved to be elusive. Our work includes a hitherto unavailable structure, "Covalent Organic Nanotubes (CONTs)," to the repertoire. Strong covalent bonds between C, N, and O imparts high thermal and chemical stability of CONTs. This novel bottom-up approach provides an edge over the carbon nanotubes (CNTs) in functionalization, synthetic conditions, and porosity. CONT-1 exhibits a BET surface area of 321 m²g⁻¹. These flexible CONTs intertwine with each other. The computational studies establish the role of solvent as the critical driving force for this type of convolution. Upon ultrasonication, the intertwined CONT-1 coil to form the toroidal superstructure.

Background

Covalent bonds are well known for their strength and diversity.¹ They impart excellent thermal and mechanical resistance in extended solids such as diamond, silicon carbides, etc.² The covalent bonds' diversity allows the formation of a wide variety of organic, bioorganic molecules and polymers. The development of porous organic cages and porous covalent organic frameworks through dynamic covalent chemistry has extended the reticular chemistry of porous materials to **zero (0D), two (2D), and three (3D)** dimensions.³⁻⁵ However, controlling the periodic arrangement of covalent bonds in extended one-dimensional solid is still in infancy. Nanotubes are one of such covalent bonded structures where limited synthetic approaches have been employed.^{6,7} These one-dimensional hollow tubular nanostructures can exhibit many promising applications in electronic devices, energy storage, catalysis, membrane separation, and biosensors.⁸⁻¹⁰ Carbon nanotubes (CNTs) are the most explored members of this family, which are constructed by rolling up two-dimensional graphite sheets around the edges.¹¹⁻¹³ Undoubtedly, CNT exhibits extraordinary electronic and mechanical properties; however, the synthesis of CNTs demands harsh reaction conditions and high temperature.^{14,15} Furthermore, the incorporation of pre-designed functionalities is difficult due to their insolubility in common organic solvents. This necessitates an alternative approach where structural divergence would be encoded within the molecular building blocks, and atomic precision is achieved via microscopic reversibility. This would render the unidirectional growth of the nanotube. One strategy to achieve such architectural wonder could be using covalent connectivity to control bonding and spatial orientation. The high covalent bond strength would impart excellent thermal and mechanical resistance. The diversity alongside would allow the access of vast arrays of dimensions, similar to the allotropes of carbons.

Herein, we present a new design strategy and its execution to synthesize purely covalent bonded porous organic nanotubes. We could combine a set of carefully designed organic building blocks using dynamic covalent chemistry to create one-dimensional covalent organic nanotubes (CONTs). We have exploited the dihedral angle (~120°) of the tetratopic triptycene building blocks combined with linear ditopic ligand (180°) to construct one-dimensional CONTs. Our synthetic approach, being a one-pot synthesis, is

different from synthesizing any random polymer. Instead, we focused on creating a porous single-walled nanotube with an atomically precise periodic structure. The reversible Schiff base bond formation reaction imparts error correction to the system, which selectively allows the formation of the ordered porous covalent 1D tubular framework over the random polymeric structure. Unlike the conventionally reported nanotube structures, the one-pot reaction strategy that we have developed here for CONTs enables the opportunity for large-scale synthesis. Additionally, due to the high strength and stability of the covalent bonds, the synthesized CONTs display unprecedented chemical and thermal stability. These extended nanotubes (up to several microns in length) with sub-nanometer diameter exhibit porosity as high as $321 \text{ m}^2\text{g}^{-1}$. Apart from the synthesis, we have performed a thorough investigation of the morphological evolution of CONTs. The time-dependent electron microscopic studies prove the transformation of isolated tubular morphologies to intertwined structures. Interestingly, the nanotubular structures of CONTs can be further transformed into a more complicated toroidal structure.

Results And Discussion

We have focused on an angular tetraamine and a linear dialdehyde to construct the covalent organic nanotubular architecture (Fig. 1). The tetraaminotriptycene (TAT) possesses its opposite terminal pairs at a dihedral angle of $\sim 120^\circ$, which mandates the construction of one-dimensional (1D) CONTs (Fig. 1a). The precise orientation of amine functionalities in the TAT units enables the propagation of covalent linkages in one dimension. Our model structure (Fig. 1c) indicates that the two geminal imine bonds connected with a triptycene unit are trans to each other. TAT units' orientation ensures the framework's tubular propagation during the condensation, keeping the non-functionalized benzene ring towards the tube wall. To check the reaction's feasibility, we have first synthesized a monomeric unit by reacting the TAT with 2-methoxy benzaldehyde. High-resolution mass spectrometry (HRMS) analysis indicates that the stoichiometric condensation of TAT and 2-methoxy benzaldehyde results in a mixture of three products. These products are monomer-1; with two imidazole rings, monomer-2; with one imidazole ring and two imine bonds, and monomer-3; with four imine bonds (Supplementary Section 2). By carefully examining the monomers, we concluded that imidazole formation is the competitive reaction preventing the nanotube formation. Thus, to suppress the imidazole formation, we have used argon atmosphere, room temperature condition, high dilution, and dropwise addition of TAT during the CONT synthesis.

We have synthesized two CONTs (CONT-1 & CONT-2) *via* imine condensation reactions by combining a mixture of one equivalent of TAT (15.7 mg, 0.05 mmol) and two equivalents of 2,5-dimethoxybenzene-1,4-dicarboxaldehyde (DMDA) (19.4 mg, 0.1 mmol) for CONT-1 and two equivalents of terephthalaldehyde (TA) (13.4 mg, 0.1 mmol) for CONT-2. The dropwise addition of amine solution in dichloromethane (DCM) into the aldehyde solution (in DCM) in presence of 0.5 mL 6 (M) acetic acid results in the cloudy precipitate (Supplementary Section 1). The resulting precipitate was collected by centrifugation followed by washing with anhydrous THF and then evacuated at 120°C for 12 hours to yield 25.05 mg of CONT-1 and 13.3 mg of CONT-2 [78%, and 51% yield of CONT-1 and CONT-2 respectively based on TAT] as off-white solid. The FTIR spectra of both CONTs show the characteristic peaks at 1610 cm^{-1} , which are

characteristic -C=N- stretching modes for imine bonds (Fig. 2a, Supplementary Figure 3). Solid-state Cross-Polarization Magic angle Spinning (CPMAS) NMR spectroscopy of the ^{13}C and ^{15}N nuclei was performed to validate the formation, connectivity, and atomic level construction of the CONT-1 backbone (Fig. 2b, Supplementary Figure 4).

Solid-state ^{13}C CP-MAS NMR spectroscopy shows the characteristic peaks of the imine (-C=N-) bonded carbon atoms at 155.5 ppm, whereas the methyl carbon appears at 53.5 ppm. The NMR spectrum also displayed discrete resonances in the aromatic region between 150 and 110.5 ppm (Fig. 2b). Solid-state High-Power Decoupled (HPDEC) ^{13}C spectrum quantifies the number of different carbon atoms in the tube backbone. According to the reaction scheme, the basic unit consists of 20 carbons from TAT and 40 carbons from DMDA. Out of these, 18 carbons from TAT and 32 carbons from DMDA appear in the aromatic and carbonyl region (200 to 100 ppm), two carbons of TAT and eight carbons of DMDA appear in the aliphatic region (~55 ppm) (Fig. 2c). Thus, one would expect an aromatic to the aliphatic carbon ratio of 5:1 for a complete reaction. The ratio obtained from the ^{13}C HPDEC spectrum is close to 5:1. The peak at 186 ppm could be assigned as free aldehyde functionality generated from the defect sites at the nanotube surface (Supplementary Figure 4). The ^{15}N CP-MAS spectrum of CONT-1 displayed two discrete peaks, a resonance at 240 ppm and another at 148 ppm, indicating two distinct nitrogen sites. The characteristic peak at 240 ppm suggests the formation of the imine (-C=N-) bonded nitrogen atoms. The resonance at 148 ppm indicates the presence of N-H group, which could be due to imidazole ring formation at the defect sites (Supplementary Section 17). Thermogravimetric analysis (TGA) of the activated CONT-1 under N_2 atmosphere indicates that the framework has thermal stability up to 400° C, and there is no guest molecule inside the nanotubes (Supplementary Figure 25). The porosity of the CONTs was evaluated by measuring N_2 adsorption isotherm at 77K (Fig. 2d, Supplementary Figure 5). Activated CONTs at 140 °C showed reversible type II adsorption isotherm. The BET surface areas of the activated CONT-1 and -2 were 321 m^2g^{-1} and 52 m^2g^{-1} , respectively (Supplementary Figure 5). The pore size distribution of both the CONTs was calculated based on the nonlocal density functional theory (NLDF) (Fig. 2d and Supplementary Figure 6). The pore size distribution, which indicates two types of pores of 1-2 nm and 3.5-4.5 nm of size, is in good agreement with the theoretically predicted structure (Supplementary Figure 6). The 3.5-4.5 nm pore distribution refers to the main hollow tubular channels running along the length of the CONTs. The 1-2 nm pore distribution corresponds to the side pores located on the nanotubes' walls.

Scanning Electron Microscopy (SEM) images of CONTs reveal uniform tubular morphology, with an average diameter of ~5 nm (Supplementary Figure 7). High-Resolution Transmission Electron microscopy (HRTEM) (Fig. 2e) identifies the hollow tubular nature at the interior with a constant diameter of ~5 nm throughout the entire length of the nanotube (Supplementary Figure 8). Atomic Force Microscopy (AFM) further corroborates this finding (Supplementary Figure 9). The AFM height profile shows the uniform diameter of ~5 nm of the single nanotube, which is in good conjunction with the TEM results and nanotubes' theoretically predicted structure (Fig. 2f). Additionally, electronic microscopic images show

that the single-walled CONTs are intertwined, which could be due to their high length to width ratio (~avg. 300:1).

The microscopic analysis further confirms that the individual units of the intertwined nanotubes' diameter having a close match (~5 nm) with isolated single nanotubes (Supplementary Figure 13).

We have isolated the reaction mixtures at different time intervals and characterized them via SEM analysis to shed more light on the CONT-1 formation (Supplementary Figure 10). CONT-1 formation starts within 6 hours of reaction. These CONTs are 100-200 nm in length and ~5 nm in diameter. After 12 hours, the CONTs grow up to 500-800 nm in length with a diameter of ~5 nm (avg. length to diameter ratio 130:1). The intertwining starts after 24-30 hours when the length to diameter ratio of the CONTs increases significantly (~avg. 200:1).

The rapid increase in the length of CONTs induces high flexibility, promoting intertwined structures. After 36 hours of reaction, almost all CONTs become completely intertwined, and no significant morphological changes were observed (Supplementary Figure 11). We speculate that the defect centers could trigger this intertwining (Fig. 3). After 6 hours, two nanotubes uniformly intertwine, following a particular pattern where the twining pitch is 70 (± 10) nm (Supplementary Figures 13, 14). The resulting intertwined nanotube thread again entangles with the available mesh of CONTs. The width of intertwined nanotubes reaches up to ~100 nm (maximum) with time (Supplementary Figures 11, 12, and 15). However, the intertwining pitch remains constant (~70 nm) irrespective of their size and diameter.

To our surprise, the nanotubes retain their morphology in a broad range of solvents of various polarities (Figs. 4a, b). However, the width of intertwined CONT-1 varies with the solvents' nature. The N₂ adsorption isotherm confirms the structural stability in water after seven days (Fig. 4d). We drop-casted the well-dispersed CONTs on a silicon wafer and heated it at different temperatures to validate the material's temperature stability. The morphology remains unaltered even at 150 °C (Fig. 4c).

To obtain a molecular-level insight into the structure and interactions of CONTs, we used multiscale molecular models. First, we simulated the behavior of the CONTs in different conditions.^{16,17} We developed all-atom (AA) models of CONT-1 composed of 15 TAT layers (Fig. 5a). This AA model was immersed in explicit DCM or THF solvent molecules (Fig. 4b) and was then equilibrated via 200 ns of all-atom molecular dynamics (AA-MD) at 20 °C of temperature (Supplementary Section 24). For comparison, we also equilibrated via the AA-MD model of the CONT-1 in water and the absence of solvent (Fig. 5b). The simulations in DCM and THF showed that the CONT-1 equilibrates to configurations just slightly deviating from the initial perfect one (Fig. 5b). This can be inferred by the distributions of the characteristic angles 1 and 2 (Fig. 5a: the angles formed by neighboring TAT units), which equilibrate at values similar to those of the starting conformation (Fig. 5c: green and orange distributions vs. black dotted lines). On the contrary, in water and the absence of solvent, the tubules adopt a much more distorted configuration, as the solvophobic effects are so strong that the CONT-1 structure is compressed (Fig. 5b and Fig. 5c). We then used these AA models as a guideline to develop a minimalistic Coarse-

Grained (CG) model¹⁸ that, although more approximated, allowed us to study the behavior and interaction between the CONTs on a much higher scale. In particular, the CG model is composed of one CG particle per TAT unit in the CONT-1 structure, which are interconnected with each other via explicit bonds (Fig. 5d).

We parametrized this CG model consistently with the behavior observed through the AA-MD simulations (Supplementary Section 24). Such CG model allowed us to simulate long CONT-1 composed of 500 TAT hexagonal layers, corresponding to a tubule length of ~820 nm (Fig. 5c). Thus, we compared via CG-MD simulations the behavior of two long CONT-1 tubules that interact between them in different conditions. In particular, the non-bond interaction between the CG particles that compose the two CONT models (modeled by a Lennard-Jones, LJ, potential in the CG model) was changed to modulate the nanotube-nanotube interaction. This allowed us to simulate the effect of the solvent's change on the system by increasing/decreasing the solvophobic interactions between the CONTs. In particular, for ϵ (depth of the LJ potential, determining the strength of non-bonding the interaction between the CG particles) values below 1.0 kJ mol⁻¹, the two CONTs interacted only in an unstable way, and no intertwining was observed. Instead, for $\epsilon \geq 2$ kJ mol⁻¹, we could observe stable interaction between the CONTs and inter-tubule wrapping. As indicated by umbrella sampling¹⁹ calculations showed (Supplementary Section 24), the CG models with ϵ values of 2 and 2.5 kJ mol⁻¹ provided a CONT-CONT attraction compatible with that of AA models in explicit DCM and THF solvents, respectively (Supplementary Figure 29). In these cases (Figs. 5e-f), the CG-MD showed an average intertwining pitch consistent with that observed experimentally (~70±10 nm). Umbrella sampling results also demonstrated that the CONT-CONT interactions of the AA model in water, or in the absence of solvent, are compatible with much higher ϵ values in the CG model (stronger solvophobic effects). However, CG-MD simulations showed that at $\epsilon > 2.5$ kJ mol⁻¹, the intertwined CONTs are not stable on their own, and the tubules tend to fold multiple times further.

The intertwined CONTs further self-assemble to form a toroidal superstructure upon ultrasonication (Figs. 6a-c).²⁰⁻²² We have observed that tetrahydrofuran (THF) is the best solvent to obtain the toroids in high yields (up to 60%) (Supplementary Figure 21). Toroidal micro ring formation also proceeds in other solvents like o-xylene and o-dichlorobenzene (DCB), with a yield of ~5%. The toroids are purified from the mixture of intertwined nanotubes by filtering through a Whatman 42 filter paper (pore size of 2.5 μ m) (Supplementary Section 17). The Dynamic Light Scattering (DLS) study of the filtrate provides the average outer diameter of 600 nm at 20 °C with a polydispersity index less than 0.15 (Fig. 6d). FESEM images show that the toroid diameters ranging from 300 nm to 900 nm (Fig. 6f). However, the rings' thickness remains constant (~50 nm) around their circumference (Supplementary Figure 21).

Topographical analysis using AFM further confirms the same toroidal morphology (Supplementary Figure 23). HRTEM images of toroids prove that the walls of toroids are composed of intertwined hollow nanotubes with a ~5 nm individual tube diameter and a constant pitch of ~70 nm (Supplementary Figure 22). Detailed SEM, TEM, and AFM analyses reveal that the intertwined nanotubes first bend to form non-uniform loops (diameter 100-1000 nm) (Fig. 6f). The most probable mechanism involves the creation of bubbles in THF.²³ The bubbles act as the template for hydrophobic CONTs, which eventually orient

themselves around such bubbles' circumference. Being bent at the bubble–THF interface, nanotubes form loops when the bubble collapses. The untied intertwined nanotubes coil up in both the transverse and longitudinal directions to create a closed and coiled loop-like structure of various diameters (0.1–1 μm). These spiral loop structures were later transformed into toroidal structures (Fig. 6f).

Conclusion

In summary, we have designed covalently connected and porous single-walled covalent organic nanotubes (CONTs). The efficient synthetic protocol results in functionalizable porous nanotubes with high chemical and thermal stability. The intertwined nanotubes transform into a highly demanded superstructure, toroids. Our mechanistic understanding demonstrates that the intertwined nanotubes coiled up to construct toroid-shape-superstructure under the influence of solvent and mechanical stimuli. We could separate the toroids from intertwined nanotubes by their size distribution. Interestingly, all the characteristic features of CONTs, including flexibility, intertwining nature, and toroids formation, are similar to the CNTs. We believe that this work will significantly boost the repertoire issues associated with CNTs and other nanotubes chemistry. The unique opportunity of functionalization and their high chemical and thermal stability could facilitate the exploration of nanotube chemistry; yet unattainable; in catalysis, electrochemistry, and biochemistry.

Declarations

Data availability

All data supporting the findings of this study, including synthesis, experimental procedures, and compound characterization, are available within the Article and its Supplementary Information.

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Contributions

Designing and choosing building blocks have been made by KK, SK, and RB. KK and ShK synthesized all the materials. SEM, TEM and AFM performed by KK. SSNMR was done by NT and TGA. AFM images in Fig. 1 and Supplementary Figure 9 were collected by MM and MB. The nanotube architecture was constructed by SK. Theoretical calculation of intertwining and solvents' role was done by CP, LL, LP, RC, and GMP. All experiments were planned by KK, SK, ShK, SuK, and RB. RB supervised the whole project. KK, SK, SuK, and RB analyzed all the results and co-wrote the manuscript taking inputs from all co-authors.

Additional information

Supplementary Information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to R. B.

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Competing interests

The authors declare no competing financial interests.

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Figures

Figure 1

Strategy for design and synthesis of covalent organic nanotubes: a) Schematic representation of the one-dimensional covalent organic nanotube (CONT). CONT has been compared with the imine-based zero-dimensional covalent organic cage, two- and three-dimensional covalent organic framework. b) & c) A general strategy for design and construction of purely covalent bonded one-dimensional porous covalent organic nanotubes (CONTs) via condensation of aldehyde (DMDA/TA) and amine (TAT). d) & e) Represent front and side view of CONTs, respectively.

Figure 2

Characterization of nanotubes: a) FTIR spectra of TAT, DMDA, and CONT-1. b) ¹³C Solid-state CP-MAS NMR spectrum of the CONT-1. c) Solid-state High-Power Decoupled (HPDEC) ¹³C NMR spectrum of the CONT-1 for quantitative analysis of carbonyl group. d) N₂ adsorption isotherm at 77 K of CONT-1. The NLDFT pore size distribution from the N₂ adsorption analysis (inset) shows the micro (1.2-2.0 nm) and mesoporous (3.5 nm) nature of the nanotubes. e) TEM image of isolated single nanotubes. Inset shows the hollow interior of ~5 nm of CONT-1. (Inset image is a zoomed portion from another CONT). f) AFM image of a single nanotube, showing the nanotube length of ~4.5 μm. Height profile indicates a uniform diameter of 5 nm.

Figure 3

Mechanism of intertwining: Two flexible CNTs interconnect first at a single point. This interconnection leads to the formation of intertwined structures with a characteristic average pitch. The convoluted CNTs then hierarchically generate network-like superstructures.

Figure 4

Stability of CONT-1: a) TEM and b) SEM images of CONT-1 treated with different solvents (the dielectric constants are mentioned in the bracket) indicate its solvent stability. c) SEM images of CONT-1 before and after heat treatment at 150° C show the tube's high thermal stability. d) N₂ adsorption isotherm of CONT-1 before and after water treatment (seven days).

Figure 5

Multiscale molecular models of the CONT-1 system. a) AA model of CONT-1. The two characteristic angles (Angles 1 and 2) formed by the TAT moieties in the CONT structure are highlighted in orange and green colors. b) MD snapshots of the AA model of the initially perfect CONT-1 (left) and the equilibrated CONT-1 tube (after 200 ns of AA-MD) in different solvents: in DCM, THF, vacuum (VAC), and in water (WAT). c) Distributions of the angles 1 and 2 in the structure of the equilibrated CONT-1 computed along the AA-MD in the different environments. Black lines indicate the value of angles 1 and 2 in the initially perfect conformation of the tube, the peaks of the colored distributions indicate the most probable values for the angles in the various solvents. d) Mapping of the AA structure of the model into the CG CONT model (interconnected red CG beads). e) Spontaneous intertwining of two CONTs during CG-MD simulations. Starting from initially parallel CONTs (left), different average intertwining pitches are obtained during the CG-MD as a function of the interaction strength (ϵ) between the CG beads (simulation time is expressed in CG-MD integration time steps units, τ). f) Average intertwining pitch as a function of CG-MD simulation time, measured for different values of ϵ (values of ϵ of 2-2.5 correspond to the CONT-CONT interaction in DCM and THF, respectively).

Figure 6

Characterization of toroids and mechanism of their formation. a) Schematic representation of toroids. b) & c) SEM and AFM images of toroids, respectively. d) DLS study of the toroids after separating them from the nanotubes. Inset indicates a histogram of contour length of rings measured directly from SEM images. e) & f) Mechanism of formation of toroids from the intertwined nanotubes.

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