

Curriculum vitae

Present Status

4th-year Integrated Ph.D., Scholar (MS-PhD), Department of Chemical Sciences, IISER Kolkata, India
(Master's CGPA: 9.43)
(2018-Current)
Under the Supervision of **Prof Rahul Banerjee**, Department of Chemical Sciences, IISER Kolkata.

Educational Qualifications

Degree/Certificate	School/College	Board/University	Year of Passing	Percentage/CGPA
Integrated Ph.D. Semester 6 (Masters)	Indian Institute of Science Education and Research Kolkata	Indian Institute of Science Education and Research Kolkata	2020	9.43 CGPA
B.Sc. Chemistry(H)	Jhargram Raj College	Vidyasagar University	2018	77%
WBCHSE (10+2)	Garhraiipur High School (H.S.)	WBCHSE Board Exam	2012	78.6%
WBBSE (10th)	Nepura Kumarara S.B. High School	WBBSE Board Exam	2010	82.75%

Research Interest

- ❖ Porous Organic Framework Materials (POCs, COFs, and CONTs)
- ❖ Photocatalysis & Electrocatalysis
- ❖ Photophysical Properties of Porous Organic Materials
- ❖ Device Application of Porous Organic Materials (Li/Na/K-ion battery and solar cell)
- ❖ Membrane Application of Porous Organic Materials (Water purification and gas separation)

Research Experience

- ❖ Junior research fellow (2020-2021) at IISER Kolkata
- ❖ Research project on "Porous Covalent Organic Nanotubes and their self-assembly into loops and toroids" at IISER Kolkata (2019-2021)
- ❖ Research project on "Design and synthesis of isorecticular Covalent Organic Nanotubes" at IISER Kolkata (2021-current)
- ❖ Research project on "Design and synthesis of porphyrin based Covalent Organic Nanotubes for photocatalytic CO₂ reduction to value-added products" at IISER Kolkata (2021-current)

Achievements & Awards

- ❖ Qualified Joint Admission Test for M.Sc., (JAM) in Feb 2018 (AIR-425)
- ❖ Qualified Graduate Aptitude Test in Engineering (GATE) in 2021 (GATE Score-469)
- ❖ Gold Medalist in Bachelor of Science (B.Sc.) in Chemistry in 2018, Vidyasagar University



Porous covalent organic nanotubes and their assembly in loops and toroids

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Carbon nanotubes, and synthetic organic nanotubes more generally, have in recent decades been widely explored for application in electronic devices, energy storage, catalysis and biosensors. Despite noteworthy progress made in the synthesis of nanotubular architectures with well-defined lengths and diameters, purely covalently bonded organic nanotubes have remained somewhat challenging to prepare. Here we report the synthesis of covalently bonded porous organic nanotubes (CONTs) by Schiff base reaction between a tetratopic amine-functionalized triptycene and a linear dialdehyde. The spatial orientation of the functional groups promotes the growth of the framework in one dimension, and the strong covalent bonds between carbon, nitrogen and oxygen impart the resulting CONTs with high thermal and chemical stability. Upon ultrasonication, the CONTs form intertwined structures that go on to coil and form toroidal superstructures. Computational studies give some insight into the effect of the solvent in this assembly process.

In the construction of reticular frameworks of any dimension the geometry and bonding capability of the building units, and the self-correction capability of the reversible linkages between them, are crucial aspects^{1,2}. Through dynamic covalent chemistry, a wide variety of organic cages (zero-dimensional) and two- and three-dimensional covalent organic frameworks have been synthesized^{3–6}. However, controlling the periodic arrangement of covalent bonds in extended one-dimensional solids is still in its infancy. Nanotubes are one group of such covalently bonded structures where limited synthetic approaches have been developed^{7,8}. These one-dimensional hollow tubular nanostructures are attractive for applications in electronic devices, energy storage, catalysis, membrane separation and biosensors^{9–11}. Carbon nanotubes (CNTs) are the most explored members of this family due to their electronic and mechanical properties. CNTs are generally synthesized by rolling two-dimensional graphite sheets along their edges by various methods, including arc discharge, electrolysis, chemical vapour deposition, plasma torch and hydrothermal techniques^{12–18}. These methods demand harsh reaction conditions and high temperatures. Furthermore, the incorporation of predesigned functionalities is difficult due to the insolubility of CNTs in common organic solvents.

Although self-assembly and disassembly have been shown to lead to such nanotubular architectures^{19–21}, it has remained challenging to control their size on the nanoscale, and to control their morphology and composition. One of the main challenges in the bottom-up synthesis of such self-assembled nanostructures is the need to simultaneously control their structure and their morphology. In particular, a variation in composition of the building blocks can alter the system's nanoscopic assembly and in turn the overall morphology

of the resulting structures—making the systematic tuning of their size or shape difficult^{22,23}. A supramolecular strategy also often leads to substantial structural alterations during functionalization because functional groups alter the interactions between the building blocks.

In this article we present the synthesis of covalently bonded porous organic nanotubes, using organic building blocks designed to assemble into one-dimensional covalent organic nanotubes (CONTs) through dynamic covalent chemistry. A tetratopic triptycene derivative with a dihedral angle of $\sim 120^\circ$ was combined with linear ditopic ligands by a reversible Schiff base reaction, leading to the formation of CONTs. The formation of either the thermodynamically or the kinetically stable product was favoured by adjusting the reaction conditions. The reversibility of the Schiff base reaction imparts error-correction capability to the system, which under thermodynamic control allowed the selective formation of the ordered porous covalent one-dimensional tubular framework over a random polymeric structure. Due to the high strength and stability of the covalent bonds, the synthesized CONTs display excellent chemical and thermal stability. These extended nanotubes (up to several micrometres in length) with subnanometre diameter exhibit porosity as high as $321 \text{ m}^2 \text{ g}^{-1}$. This one-pot reaction strategy for CONT synthesis may also be suitable for large-scale synthesis.

A time-dependent electron microscopic study into the morphological evolution of these CONTs showed that the isolated tubular morphologies go on to form intertwined toroidal structures.

Results and discussion

Design and synthesis of CONTs. We have focused on a tetratopic tetraamine and a linear dialdehyde to construct the nanotubular

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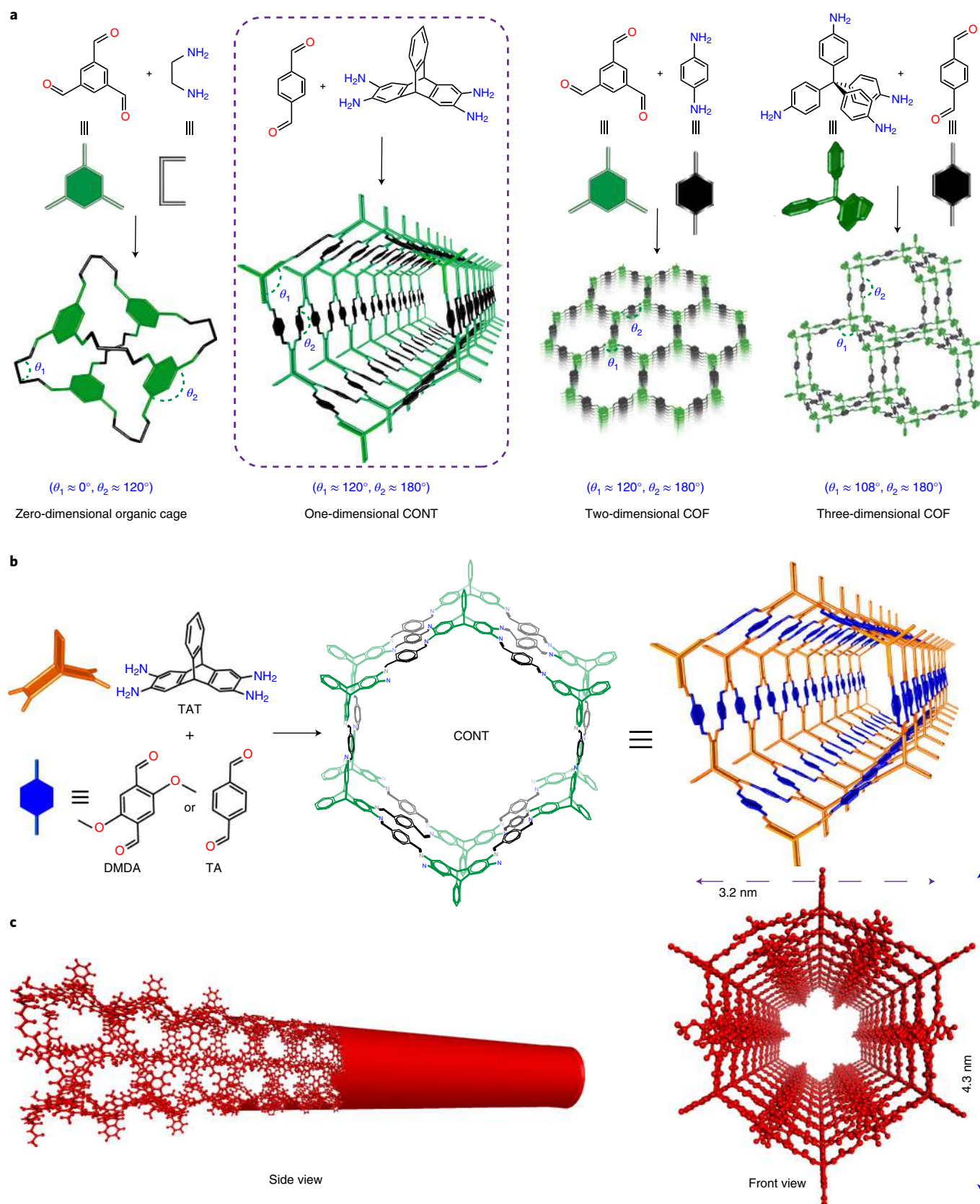


Fig. 1 | Design and synthesis of covalent organic nanotubes. a, Schematic representation of the synthesis of zero-dimensional cages, one-dimensional CONTs, and two- and three-dimensional covalent organic frameworks (COFs) based on the reversible aldehyde-amine condensation. **b**, Structures of the porous CONTs synthesized from TAT and from the linear dialdehydes DMDA and TA. **c**, Schematic representation of the resulting CONTs.

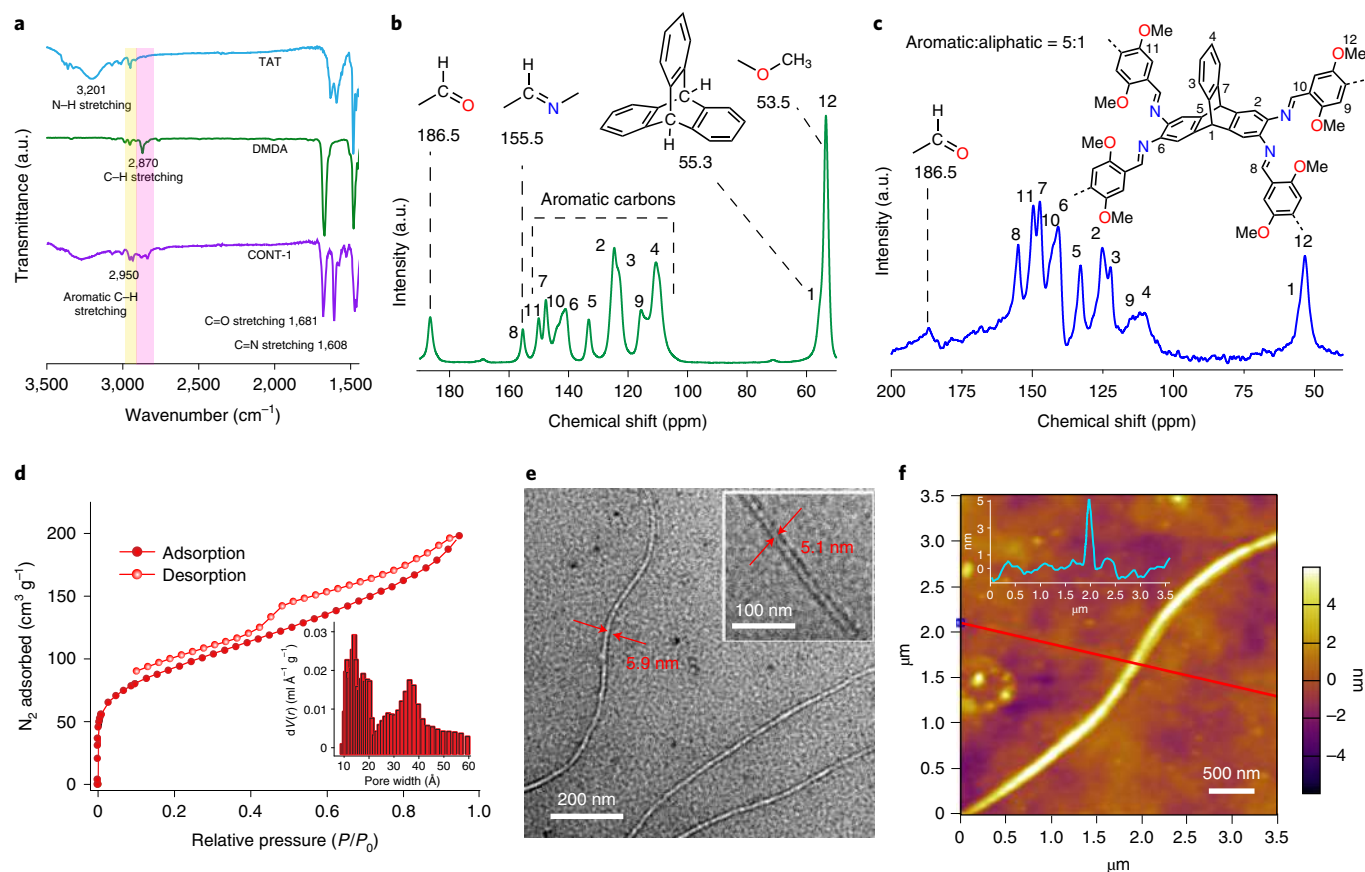


Fig. 2 | Characterization of nanotubes. **a**, FTIR spectra of TAT, DMDA and CONT-1. **b**, ^{13}C Solid-state CP-MAS NMR spectrum of CONT-1. **c**, Solid-state HPDEC ^{13}C NMR spectrum of CONT-1 for quantitative analysis of the carbonyl group. **d**, Nitrogen adsorption isotherm of CONT-1 at 77 K. Inset: NLDFT pore size distribution from the nitrogen adsorption analysis showing the microporous (1.2–2.0 nm) and mesoporous (3.5 nm) nature of the nanotubes (V and r are the cumulative pore volume and radius of the pore). **e**, TEM image of isolated single nanotubes (red arrows indicate the inner diameter of nanotubes). Inset: the hollow interior of ~ 5 nm of CONT-1 (this 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 (the red line signifies the movement of AFM tip).

covalent organic architecture (Fig. 1). The tetraaminotriptycene (TAT) features two opposite terminal amine pairs at a dihedral angle of $\sim 120^\circ$ (Fig. 1b), and it is this orientation of amine functionalities in the TAT units that promotes the formation of covalent linkages in one dimension. The building blocks (Fig. 1b) were chosen for their geometry and energy optimization, which on aldehyde–amine condensation favour the formation of two geminal imine bonds that are *trans* to each other. This in turn ensures that the framework forms in one dimension because the non-functionalized benzene rings are kept towards the inner wall of the resulting nanotube.

To check the reaction's feasibility, we first synthesized a monomeric unit by reacting the TAT with 2-methoxybenzaldehyde (MB). High-resolution mass spectrometry analysis indicates that the stoichiometric condensation of TAT and MB results in a mixture of three products: monomer-1 (diimidazole–triptycene, with two imidazole rings), monomer-2 (diimine–monoimidazole–triptycene, with one imidazole ring and two imine bonds) and monomer-3 (tetraimine–triptycene, with four imine bonds) (Supplementary Information section 2). By carefully examining the monomers, we concluded that imidazole formation is the competitive reaction preventing nanotube formation. Thus, imine bond formation was optimized to reduce imidazole formation with sequential modifications of the synthetic conditions (Supplementary Table 1 and Supplementary Figs. 3–8).

We then synthesized two CONTs (CONT-1 and CONT-2) via imine condensation reactions by combining a mixture of

1 equiv. of TAT (15.7 mg, 0.05 mmol) and 2 equiv. of either 2,5-dimethoxybenzene-1,4-dicarboxaldehyde (DMDA) (19.4 mg, 0.1 mmol) for CONT-1 or 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 the presence of 0.5 ml 6 M acetic acid results in the cloudy precipitate (Supplementary Information section 1). The resulting precipitate was collected by centrifugation followed by washing with anhydrous THF and then evacuated at 120°C for 12 h 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 an off-white solid.

Structural characterization. The Fourier transform infrared spectra of both CONTs show peaks at 1610 cm^{-1} that are characteristic $\text{C}=\text{N}$ stretching modes for imine bonds (Fig. 2a and Supplementary Fig. 9). Solid-state cross-polarization magic angle spinning (CP-MAS) 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 and Supplementary Fig. 10). Solid-state ^{13}C CP-MAS NMR spectroscopy shows the characteristic peaks of the imine ($\text{C}=\text{N}$) 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). The solid-state high-power decoupled (HPDEC) ^{13}C spectrum quantifies the

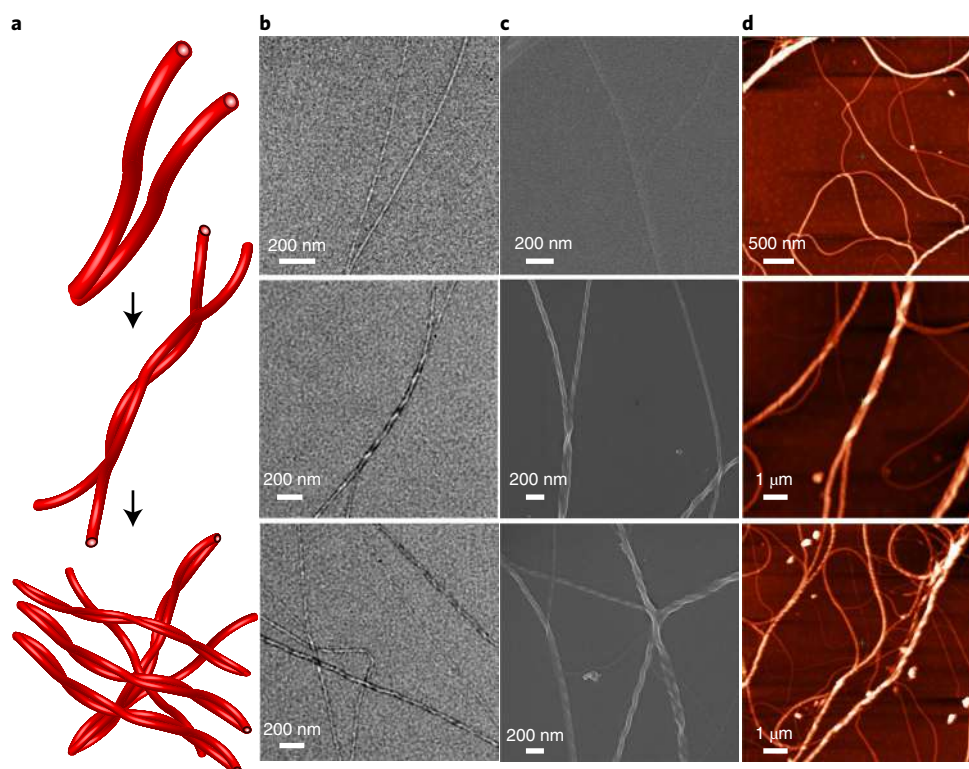


Fig. 3 | Intertwining of the CNTs. **a**, Graphical representation of the increasing intertwining of the nanotubes, from top to middle to bottom. **b–d**, Characterization by HRTEM (**b**), SEM (**c**) and AFM (**d**) of each of the situations represented in **a**. In **d** two flexible CNTs interconnect first at a single point (top); this interconnection leads to the formation of intertwined structures with a characteristic average pitch (middle); this in turn generates the assemblies shown in the bottom panel.

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. Of these, 18 carbons from TAT and 32 carbons from DMDA appear in the aromatic and carbonyl region (200–100 ppm), and 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 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 was assigned as free aldehyde functionality generated from the defect sites at the nanotube surface (Supplementary Fig. 10). Although the optimized condition for the model system results in no imidazole formation, the nanotube contains a meagre percentage (6–8%) of aldehyde moieties as defects in the framework. We have recorded multiple solid-state HPDEC ^{13}C NMR spectra with different synthetic scales (yielding 150 mg and 280 mg of CONT-1) in two different instruments to quantify the defects in CONT-1. All the spectra consistently show 6–8% defects in the nanotube framework (Supplementary Information section 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 ($-\text{C}=\text{N}-$) bonded nitrogen atoms. The resonance at 148 ppm indicates the presence of an $\text{N}-\text{H}$ group, which may be due to imidazole ring formation at the defect sites (Supplementary Information section 16). Thermogravimetric analysis of the activated CONT-1 under a nitrogen atmosphere indicates that the framework has thermal stability up to 400 °C, and there is no guest molecule inside the nanotubes (Supplementary Fig. 34). The porosity of the CNTs was evaluated by measuring the nitrogen adsorption isotherm at 77 K (Fig. 2d and Supplementary Fig. 11). Activated CNTs (after degassing at 140 °C for 10 h)

showed a reversible type II nitrogen adsorption isotherm. The Brunauer–Emmett–Teller surface areas of the activated CONT-1 and CONT-2 were 321 and 52 m^2g^{-1} , respectively (Supplementary Fig. 11). The pore size distribution of both CONT-1 and CONT-2 was calculated based on the non-local density functional theory (NLDFT) (Fig. 2d and Supplementary Fig. 12). The pore size distribution, which indicates two types of pores of 1–2 nm and 3.5–4.5 nm in size, is in good agreement with the theoretically predicted structure (Supplementary Fig. 12). The 3.5–4.5 nm pore distribution refers to the main hollow tubular channels running along the length of the CNTs. The 1–2 nm pore distribution corresponds to the side pores located on the walls of the nanotubes.

Morphology of nanotubes. Scanning electron microscopy (SEM) images of CNTs reveal uniform tubular morphology, with an average diameter of ~5 nm (Supplementary Fig. 13). 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 Fig. 14). Atomic force microscopy (AFM) further corroborates this finding (Supplementary Fig. 15). The AFM height profile shows a uniform diameter of ~5 nm for the single nanotube, which is in good agreement with the TEM results and with the theoretically predicted structure of the nanotubes (Fig. 2f). Additionally, electron microscopy images show that the single-walled CNTs are intertwined, which might be due to their high length-to-width ratio (average, ~300:1). The microscopy analysis further confirms that the individual units of the intertwined nanotubes have diameters very similar (~5 nm) to those of isolated single nanotubes (Supplementary Fig. 15). We have isolated the reaction mixtures at different time intervals and characterized them via SEM

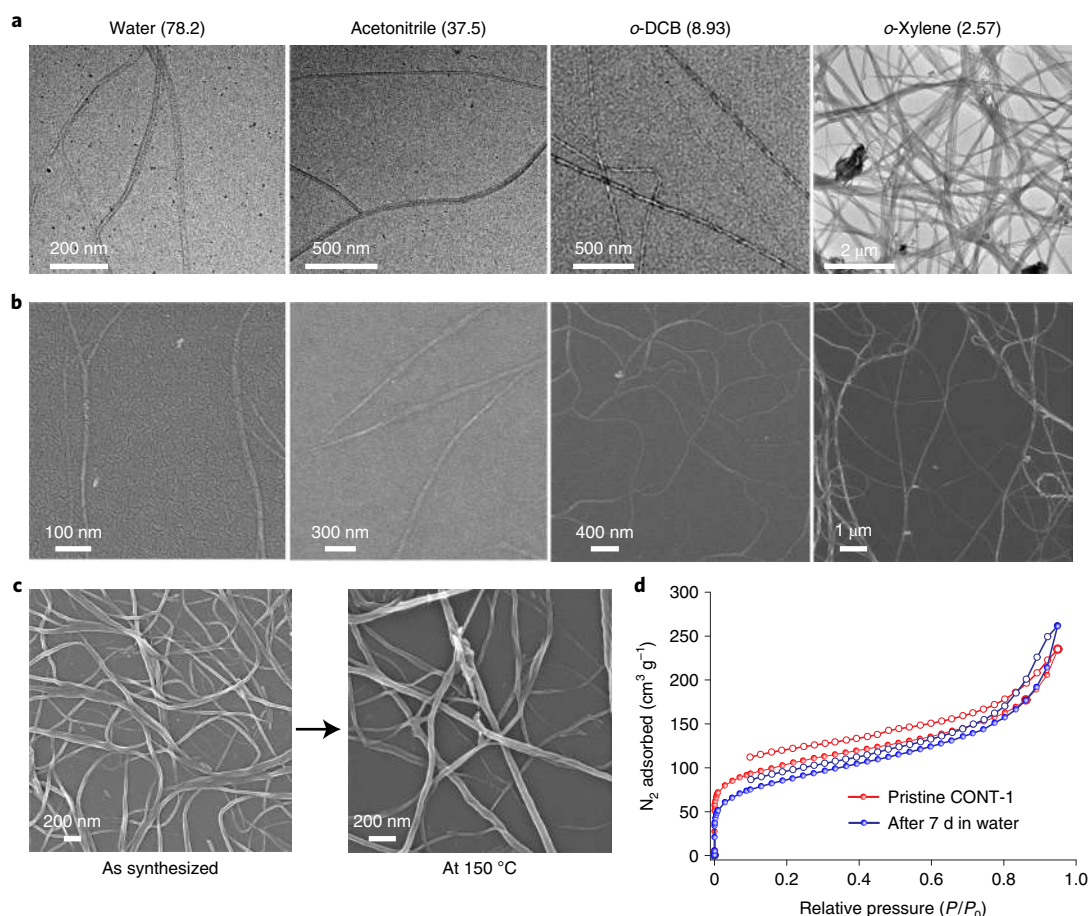


Fig. 4 | Stability of CONT-1. **a, b**, TEM (**a**) and SEM (**b**) images of CONT-1 immersed in water, acetonitrile, o-DCB and o-xylene for 7 d showing its stability in the solvents. The numbers in parentheses are the dielectric constants of the solvents. **c**, SEM images of CONT-1 before and after heat treatment at 150 °C showing the tube's high thermal stability. **d**, Nitrogen adsorption isotherm of CONT-1 before and after water treatment (immersion in water) for 7 d.

analysis to shed more light on CONT-1 formation (Supplementary Fig. 16). CONT-1 formation starts within 6 h of reaction. These CONTs are 100–200 nm in length and ~5 nm in diameter. After 12 h, the CONTs grow up to 500–800 nm in length with a diameter of ~5 nm (average length-to-diameter ratio, 130:1). The intertwining starts after 24–30 h when the length-to-diameter ratio of the CONTs increases substantially (average, ~200:1).

The rapid increase in the length of CONTs induces high flexibility, promoting intertwined structures. After 36 h of reaction, almost all CONTs become completely intertwined, and no notable morphological changes are observed (Supplementary Fig. 16). We speculate that defect centres could trigger this intertwining (Fig. 3). After 6 h, two nanotubes uniformly intertwine, following a particular pattern where the twining pitch is 70 ± 10 nm (Supplementary Figs. 19 and 20). 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 Figs. 16–18). However, the intertwining pitch remains constant (~70 nm) irrespective of the size and diameter of the nanotubes.

Stability of CONTs. To our surprise, the nanotubes retain their morphology in a broad range of solvents of various polarities (Fig. 4a,b). The nitrogen adsorption isotherm confirms the structural stability in water after 7 d (Fig. 4d). We drop-cast the well-dispersed CONTs on a silicon wafer and heated this at different temperatures to validate the material's temperature stability. The morphology remained unaltered even at 150 °C (Fig. 4c). However,

the width of intertwined CONT-1 varied with the nature of the solvents due to the solvent environment apparently affecting the interaction among the CONTs.

Theoretical investigation of the self-assembly. To obtain a deeper insight into the molecular factors that drive CONT self-assembly in different solvents, we used multiscale molecular models to simulate the CONTs in different solvent conditions. Following well-established approaches^{24,25}, we developed an all-atom (AA) model of CONT-1 composed of 15 TAT layers (Fig. 5a). This AA model was immersed in explicit DCM or THF solvent (Fig. 4b) and equilibrated via 200 ns of molecular dynamics (AA-MD) at $T = 20$ °C (Supplementary Information section 26). For comparison, we also equilibrated this CONT-1 model in water and in the gas phase (that is, in the absence of solvent). The AA-MD simulations showed that in DCM and THF the CONT-1 equilibrates to configurations slightly deviating from the initial perfect one (Fig. 5b), as also demonstrated by the distributions of angles 1 and 2 (Fig. 5c). On the contrary, in water, the tubules tend to compress along the longitudinal axis due to strong solvophobic effects (Fig. 5b,c, see also Supplementary Information section 26). A similar structural compression is also seen in the gas phase. In all cases, the diameter of the AA CONT models remains compatible with that estimated experimentally (Fig. 4a,b). We then used these AA models as a guideline to develop a minimalistic coarse-grained (CG) model²⁶ that, while more approximated, allowed us to study the behaviour and interactions between the CONTs on a larger scale.

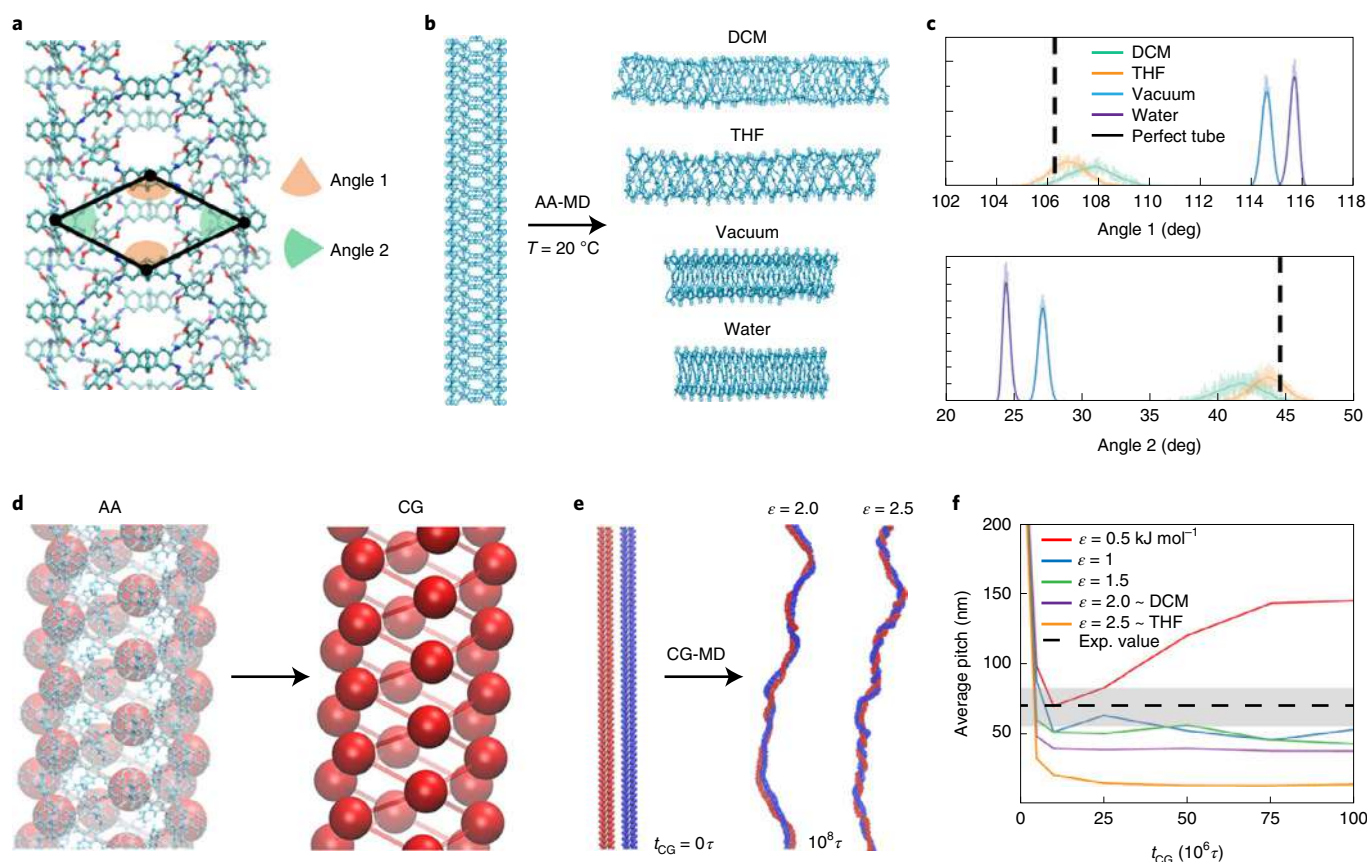


Fig. 5 | Multiscale molecular models of the CONT-1 system. **a**, AA model of CONT-1. The two characteristic angles (angles 1 and 2) formed by the TAT moieties in the CONT structure are highlighted in orange and green. **b**, MD snapshots of the AA model of the initially perfect CONT-1 (left) and the equilibrated CONT-1 tube (after 200 ns of AA-MD) in DCM, THF, vacuum and water. **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 coloured distributions indicate the most probable values for the angles in the various environments. **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, t , 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 (ϵ values of 2 and 2.5 correspond to the CONT-CONT interaction in DCM and THF, respectively).

In this CG model, each TAT unit in the CONT-1 structure is represented by a single CG particle, interconnected with the other neighbour TAT particles via harmonic bonds (Fig. 5d). The CG particles interact with each other via a simple Lennard–Jones potential. The parameters of this CG model were initially optimized to obtain a behaviour consistent with that of the AA CONT-1 model in explicit DCM solvent (Supplementary Information section 26.2). This allowed us to simulate with reasonable accuracy the behaviour of long CONT models composed of 500 TAT layers (Fig. 5c: tubule length, ~ 820 nm). Starting from a system configuration with two separated, initially parallel tubes, we ran CG-MD simulations in which the depth of the Lennard–Jones potential (ϵ) acting between the CG beads was systematically varied, modulating the nanotube–nanotube interaction to model a change of solvent in the system (ϵ sets the strength of the non-bonded interaction between the CG particles of the CONTs: see Supplementary Information for details). Comparison with the AA models allowed us to relate the stronger/weaker CONT–CONT interactions in the CG models to the effect of increased/decreased solvophobicity of the tubules in different realistic solvent conditions. For ϵ values < 1 kJ mol $^{-1}$, the two CONTs interacted only weakly and intermittently, and no intertwining was observed during the CG-MD (weak solvophobicity). Instead, for

$\epsilon \geq 1$ kJ mol $^{-1}$, we observed persistent interactions and intertwining of the two CONTs. As indicated by umbrella sampling²⁷ calculations (Supplementary Information section 26), ϵ values in the CG models of 2 and 2.5 kJ mol $^{-1}$ provided a CONT–CONT interaction compatible with that obtained with the AA models in explicit DCM and THF solvents, respectively (Supplementary Fig. 38). In these cases (Fig. 5e–f), the CG-MD showed an average intertwining pitch consistent with that observed experimentally ($\sim 70 \pm 10$ nm). These results also demonstrated that the interactions between the CONTs in water (stronger solvophobic effects) or in the gas phase are compatible with higher ϵ values in the CG model. However, at $\epsilon > 2.5$ kJ mol $^{-1}$, the formation of well-defined helices becomes less favoured, and the CONTs tend to interact further, generating tighter and less-defined hierarchical assemblies. In general, these CG-MD results indicate that the combination of solvophobic effects with the geometric structure and flexibility of the CONTs is a determining factor controlling the intertwining observed experimentally.

Formation of toroids. The intertwined CONTs further self-assemble to form a toroidal superstructure upon ultrasonication (Fig. 6a–c)^{28–30}. We have observed that THF is the best solvent to obtain the toroids in high yields (up to 60%) (Supplementary

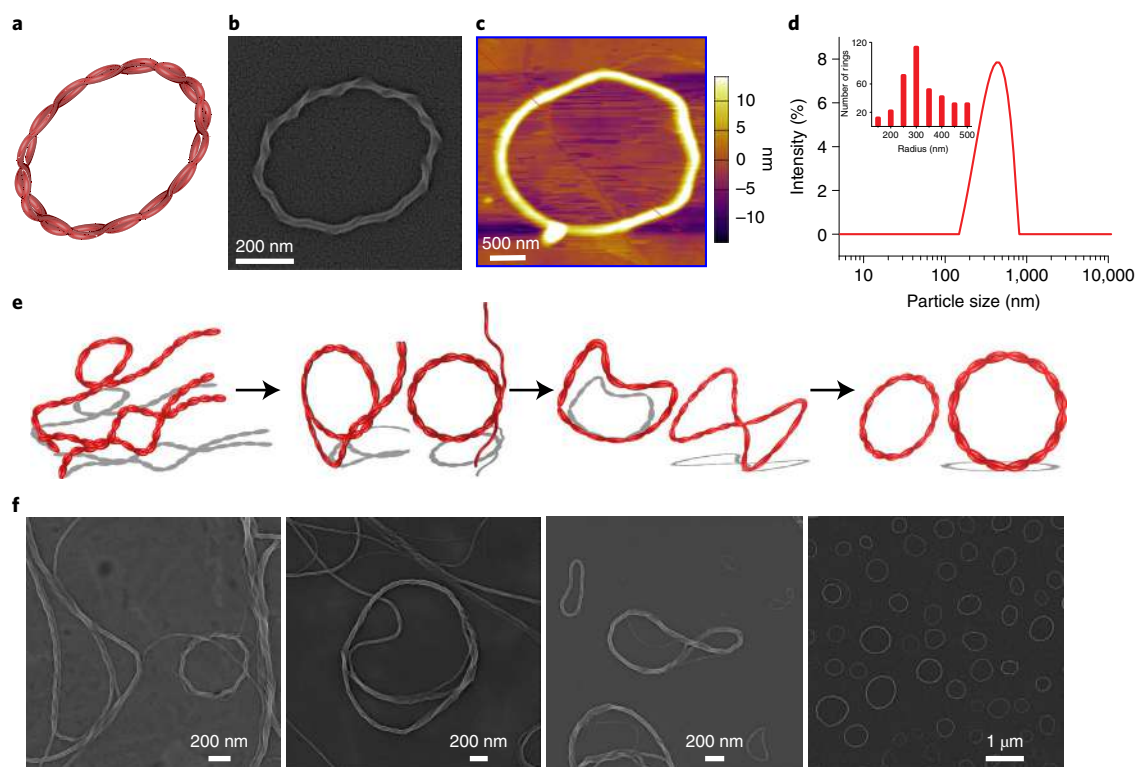


Fig. 6 | Characterization of toroidal structures. **a**, Schematic representation of toroids. **b,c**, SEM (**b**) and AFM (**c**) images of toroids. **d**, Dynamic light scattering study of the toroids after separating them from the nanotubes. Inset: histogram of contour length of rings measured directly from SEM images. **e,f**, Schematic illustration (**e**) and SEM characterization (**f**) of intertwined nanotubes that gradually form toroidal architectures.

Fig. 31). Toroidal micro-ring formation also proceeds in other solvents such as *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, 2.5 μm) (Supplementary Information section 17). A dynamic light scattering study of the filtrate gives an average outer diameter of 600 nm at 20 °C with a polydispersity index of <0.15 (Fig. 6d). Field emission SEM images show that the toroid diameters range from 300 to 900 nm (Fig. 6f). However, the rings' thickness remains constant (~50 nm) around their circumference (Supplementary Figs. 27 and 28). Topographical analysis using AFM further confirms the same toroidal morphology (Supplementary Fig. 29). 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 Fig. 28). Detailed SEM, TEM and AFM analyses reveal that the intertwined nanotubes first bend to form non-uniform loops (diameter, 100–1,000 nm) (Fig. 6f). The most probable mechanism involves the creation of bubbles in THF³¹. We propose that the bubbles act as the template for hydrophobic CNTs, which eventually orient themselves around the bubbles' circumference. Being bent at the bubble-THF interface, nanotubes would form loops when the bubble collapses (Supplementary Fig. 30). The untied intertwined nanotubes would then 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

We have designed covalently connected and porous single-walled CNTs. The efficient synthetic protocol results in porous nanotubes with high chemical and thermal stability, which we anticipate will be amenable to functionalization. The nanotubes then further

assemble into a toroidal superstructure. Our proposed mechanism involves the intertwining of the nanotubes, which then coil up to construct toroidal superstructures under the influence of solvent and mechanical stimuli. The toroids were distinguished from intertwined nanotubes by their size distribution. The main characteristic features of CNTs, including their flexibility, and their capacity to intertwine and form toroids, are similar to those of carbon nanotubes. We hope that this work will lead to the synthesis and functionalization of other organic nanotubes with high chemical and thermal stability, which could facilitate their exploration for application in fields such as catalysis, electrochemistry or biochemistry.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at <https://doi.org/10.1038/s41557-022-00908-1>.

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Methods

Synthesis of monomer. For a typical monomer synthesis, 2-methoxybenzaldehyde (27.2 mg, 0.2 mmol) was placed in dry DCM in the presence of 6 M AcOH as the catalyst. Dilute DCM solution of TAT (15.7 mg, 0.05 mmol) was then added to the reaction mixture and stirred for 24 h. The dry yellow powder was collected after the evaporation of DCM. The powder was dissolved in methanol and characterized by high-resolution mass spectrometry.

Synthesis of CONT-1. DMDA (19.4 mg, 0.1 mmol) was dissolved in 100 ml CH_2Cl_2 (dry, degassed), and 0.5 ml of 6 M AcOH was added directly into the yellow homogeneous solution as a catalyst for the Schiff base reaction. A solution of TAT (15.7 mg, 0.05 mmol) in 50 ml CH_2Cl_2 (dry, degassed) was added dropwise using a dropping funnel with stirring at room temperature under argon atmosphere for 24 h. The resulting cloudy precipitate was filtered and washed with excess anhydrous methanol. Yield, 25 mg, 78% (calculated with respect to TAT).

Synthesis of CONT-2. TA (13.4 mg, 0.1 mmol) was dissolved in 100 ml dry degassed DCM, and 0.5 ml of 6 M AcOH was added directly into solution as a catalyst for the Schiff base reaction. A solution of TAT (15.7 mg, 0.05 mmol) in 50 ml dry DCM was added dropwise using a dropping funnel with stirring at room temperature under argon atmosphere for 24 h. The resulting cloudy precipitate was filtered and washed with excess anhydrous methanol. Yield, 13.3 mg, 51% (calculated with respect to TAT).

Synthesis of toroid. Intertwined CONT-1 (2 mg) was placed in 50 ml anhydrous THF and sonicated at room temperature for 20 min. The nanotubes transformed into toroids. The as-synthesized toroids were separated from the mixture of intertwined nanotubes by simple filtration with Whatman 42 filter paper (pore size, 2 μm).

Computational methods. All simulations were performed with GROMACS 2018 software^{32,33} equipped with PLUMED2.5^{34,35} (for the umbrella sampling simulations and systems analysis). The AA CONT-1 model was parameterized based on the General Amber Force-Field (GAFF)³⁶, setting the partial charges via the Restrained Electrostatic Potential and using PM6 and Hartree–Fock (with the 6-31g* basis set) levels of theory³⁷ for geometry optimization. The organic solvent molecules (DCM and THF) were parameterized compatibly with the GAFF, and the TIP3P model was used for water³⁸. The CG CONT model was constructed to fit with the AA one³⁹. Details on the modelling and on the set-up of the AA-MD and CG-MD simulations are reported in the Supplementary Information.

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. Structure and parameter files for the AA and CG models of the CONT-1 tubules used in the simulations are available at <https://doi.org/10.5281/zenodo.5769788> (ref. 40). 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. Source data are provided with this paper.

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Author contributions

K.K., Sharath Kandambeth and R.B. designed and choose the building blocks. K.K. and Shayan Karak synthesized all the materials. K.K. performed the SEM, TEM and AFM. N.T. and T.G.A. performed the solid-state NMR. M.M. and M.B. collected the AFM images in Fig. 1 and Supplementary Fig. 15. Sharath Kandambeth constructed the nanotube architecture. C.P., L.L., L.P., R.C. and G.M.P. undertook the theoretical calculation of intertwining and the role of the solvents. K.K., Sharath Kandambeth, Suvendu Karak and R.B. planned all the experiments. R.B. supervised the whole project. K.K., Sharath Kandambeth, Suvendu Karak and R.B. analysed all the results and co-wrote the manuscript with input from all co-authors.

Competing interests

The authors declare no competing interests.

Additional information

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