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# Supramolecular Non-helical One-dimensional Channels and Microtubes Assembled from Enantiomers of Difluorenol

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Abstract: The design and assembly of photoelectro-active molecular channel structures is of great importance because of their special advantages in charge mobility, photo-induced electron transfer, proton conduction and exciton transport. Besides macrocycle stacking and knot + linker connection, this work rarely provides a fresh strategy for the exquisite design of 1D channel based on a pair of mirror isomers. Racemic 9,9'-diphenyl-[2,2'bifluorene]-9,9'-diol (DPFOH) enantiomers were proved to be utilized as newfashioned building modules for the non-helical 1D channel structures. Although the individual molecule doesn't present any molecular symmetry, two pairs of racemic DPFOH enantiomers can form a  $C_2$ -symmetric closed loop via the stereoscopic herringbone assembly. Thanks to the special symmetry derived from the enantiomer pairs, the multiple supramolecular interactions and the padding from solvent molecules, this conventionally unstable topological structure is achieved. The self-similar relationship of tubular structures spanning from molecular level to microscale level was explained. Finally, the lithium-ion transport performance was demonstrated, showing a significant ion conductivity of 1.77×10<sup>-4</sup> S/cm, indicating the potential research value of this novel 1D channel structure.

Organic frameworks with one-dimensional (1D) channel/column structures have attracted considerable research interest because of their special multi-functionalities in charge mobility, photo-induced electron transfer, proton conduction and exciton transport.<sup>[1]</sup> Furthermore, channel walls modified with active sites allow diversified applications, including catalysis, pollutant adsorption and molecular recognition.<sup>[2]</sup> The organization of 1D channel in organic networks can be deemed as the aligned packing of meshed 2D layers without interpenetration or misregistration, as illustrated by many examples in covalent organic frameworks (COFs) and supramolecular organic involving hydrogen-bonded frameworks (SOFs) organic frameworks (HOFs).<sup>[3]</sup> As a result, the design and construction of channel structures is closely associated with the self-assembly modes based on both the backbone architectures and the bonding forces. Apart from the 1D face-to-face stacking of macrocycle molecules, the most common strategy is utilizing multi-armed monomers with the functional joint to provide directional covalent or non-covalent interactions for the sequential extension of reticular systems.<sup>[4]</sup> For example, diaminotriazine, carboxylic acid, amide, benzimidazolone, imidazole, pyridine and such organic groups with abundant Hbonding interaction sites were considered for the terminal design of assembly units.<sup>[5]</sup> The permutation and combination of the units with different levels of symmetry (C2, C3, C4, C6 and Td) leads to a variety of different topologies covering triangular, tetragonal and hexagonal patterns.<sup>[6]</sup> In addition, the building blocks with asymmetric structures such as steroidal ureas and bile acids can form channels through helical arrangement with supramolecular chirality.<sup>[7]</sup> Despite these strategies, the design of 1D channel is still an intriguing problem which calls for fresh organic modules and assembly modes to enlarge the material library. On the other hand, due to the geometry retention of building units, the prediction of framework motifs is feasible at the molecular level. But the further understanding of the relationship between 1D channel structures and their crystal morphologies in micro/nanoscale has been rarely reported.

Herein, we exhibit an unprecedented supramolecular 1D nonhelical channel structure based on racemic 9,9'-diphenyl-[2,2'bifluorene]-9,9'-diol (DPFOH) enantiomers. Although the individual molecule doesn't present any molecular symmetry, two pairs of racemic DPFOH enantiomers can form a  $C_2$ symmetric closed loop via the stereoscopic herringbone assembly. Thanks to the special symmetry derived from the enantiomer pairs, the multiple supramolecular interactions (C-H...π, π...π and H-bonding forces) and the padding from solvent molecules, this conventionally unstable topological structure is achieved. The etching of solvent in 1D channels leads to the formation of microtubes. Finally, the lithium-ion transport performance was demonstrated, showing a significant ion conductivity of  $1.77 \times 10^{-4}$  S/cm.



**Figure 1.** Molecular structures of (*R*, *R*)-DPFOH and (*S*, *S*)-DPFOH. (a) Chemical molecular structures of (*R*, *R*)-DPFOH and (*S*, *S*)-DPFOH. (b) Crystal molecular structures of ((*R*, *R*)-DPFOH) and ((*S*, *S*)-DPFOH) mirroring each other.

DPFOH is a wide-bandgap semiconductor material which could be synthesized through a Suzuki coupling reaction as stated in Supporting Information (SI, Scheme S1). With the thin-layer chromatography (TLC) experiment in Figure S1, we found that DPFOH is composed of two kinds of diastereomers: raceme (*rac*-DPFOH) and mesomer (*meso*-DPFOH), and the *rac*-

DPFOH were purified as characterized by 1H NMR in Figure S2. It is well known that the rac-DPFOH include a pair of enantiomers,<sup>[8]</sup> (R, R)- and (S, S)-DPFOH, and their chemical structures are shown in Figure 1a. Colorless rod-like single crystals of rac-DPFOH were obtained by slow solvent diffusion of ethanol (EtOH) into chloroform (CHCl<sub>3</sub>) solution. Through single-crystal X-ray diffraction(XRD), the crystal structure was disclosed as a tetragonal space group I-4 with eight molecules in a unit cell (Table S1), and (R, R)- and (S, S)-DPFOH enantiomers show a 1:1 ratio in it. The crystal molecular structures of (R, R)- and (S, S)-DPFOH are exhibited in Figure 1b. The individual molecule doesn't present any axisymmetric or centrosymmetric properties, instead there is a strict mirror symmetry between a pair of (R, R)- and (S, S)-DPFOH molecules. Both of them include a C-C connected fluorenyl dimer acting as the coaxial rod-like backbone with a synconformation where a slight twist occurs between two fluorene planes (the corresponding dihedral angle is 21.86°). Two benzene rings lie on the opposite side of the fluorene backbone with large dihedral angles of 82.09° and 85.93°, and two hydroxyls locate at the other side of the backbone relative to the benzene rings. To distinguish the mirror isomers, (R, R)-DPFOH is marked in light blue and (S, S)-DPFOH is marked in pink, and the benzene rings are marked in dark blue or yellow respectively, in order to explain their stacking manner in the next section.



**Figure 2.** Crystal structure analysis of *rac*-DPFOH crystal (light blue: (*R*, *R*)-DPFOH, pink: (*S*, *S*)-DPFOH, red: hydroxyl). (a) The top view of a single layer from *c*-axis exhibits the pore structures. (b) The side view of a single pore shows the stereoscopic herringbone arrangement and the connecting interactions from *b*-axis. (c) The relative position and interactions of two adjacent pores viewed from *c*-axis. (d) The aligned packing of *rac*-DPFOH and the corresponding schematic diagram (four different colors stand for four different layers) along [001] direction across four layers represent the 1D channel structure.

The crystalline structures of rac-DPFOH are illustrated in Figure 2 via different viewpoints to make the organic framework clear. Viewed from c-axis, two kinds of pores with internal diameters of 9.6 Å and 3.8 Å can be observed in a single layer (Figure 2a). Unlike the knot + linker strategy in which one branched knot molecule may contribute to the construction of several pores, here two pairs of enantiomer molecules form a relatively closed pore structure (9.6 Å) without extended terminals. Furthermore, each pore is contacted by four neighboring ones with a small misalignment, generating a smaller pore (3.8 Å) surrounded by four larger pores. To figure out the construction feature of this pore structure, a side view of the larger pore in Figure 2b reveals an unusual stereoscopic herringbone assembly. Four linear (R, R)- and (S, S)-DPFOH molecules are standing obliquely on the ab-plane and connected with each other head to tail along a circular route. Specifically, the dark blue benzene ring of (R, R)-DPFOH interacts with the yellow benzene ring of (S, S)-DPFOH through a C-H...π interaction of 2.838 Å. Similarly, the yellow

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benzene ring of (R, R)-DPFOH links with the dark blue benzene ring of another (S, S)-DPFOH by the same C-H... $\pi$  interaction and in this way a closed single pore is formed. The bonding forces between the pores are still C-H...π interactions as shown in Figure 2c (see Figure S3 for details). In addition, some EtOH molecules decorated inside the channels with hydrogen bonds stabilize the pore structure to some extent (see Figure S4 for details). The 1D tubular assembly is displayed in the left part of Figure 2d with a nonplanar zigzag-shaped orifice, which is undoubtedly distinct from the traditional bicontinuous arrangement of the collection of right- and left-handed helices.<sup>[9]</sup> The molecules in every layer parallel to each other and align precisely along c-axis without any misalignment between layers. The interlayer supramolecular forces involve C-H...π, π-π interactions and hydrogen bonds S5). (Figure The corresponding schematic representation in the right part of Figure 2d more clearly demonstrates the 1D cylindrical channel features through this special stereoscopic herringbone packing mode. It is worth noting that in our crystalline network the single building block is asymmetric, indicating the realizability of asymmetric racemic molecules for the building of in-plane reticular architectures. The theoretical Connolly surface area of rac-DPFOH crystals was calculated using Materials Studio with a 1.82 Å probe radius for N<sub>2</sub>, which is determined to be 649.71  $m^2/g$ , comparable to the previously reported organic frameworks.[10]



**Figure 3.** The morphologies and crystallographic structures of *rac*-DPFOH microtubes. (a) SEM, (b) TEM images of the microtubes. Inset in (a): the SEM image of a single microtube. Inset in (b): the SAED pattern of the corresponding microtubes and the electron beam direction is [110]. (c) The schematic diagram of the microtube with indexed crystal faces and the molecular arrangements of  $(1\overline{10})$  and (001) crystal faces.

The hollow channel structures are not only reflected at the molecular level, the micro/nano morphologies of *rac*-DPFOH are also investigated through a facile reprecipitation method, which turn out to be tubular morphologies as well. The morphology and structure of the *rac*-DPFOH microcrystals are shown in Figure 3a and 3b by SEM (scanning electron microscopy) and TEM (transmission electron microscopy) with high morphological purity. The microtubes have smooth surfaces and varied size, with the average length is about 182.4  $\pm$  24.8 µm, the edge length 7.6  $\pm$  1.5 µm, and the wall thickness 0.3  $\pm$  0.1 µm. Some microtubes are tend to aggregate into bundles and stand on the substrate, so the hollow nature can be clearly observed by the open-ended rectangular cross-sections (inset in Figure 3a), which is also confirmed by the TEM image in Figure 3b. The crystal structures of the microtubes were examined by powder

X-ray diffraction (PXRD), and the patterns are consistent with the rac-DPFOH single crystal, indicating the same crystalline structures (Figure S6). The largest exposed crystal faces of the rac-DPFOH single crystal/microcrystal are assigned to 4 equivalent sets of {hh0} planes, inducing the strong diffraction from {hh0} family different from the simulated pattern. The selected-area electron diffraction (SAED) patterns (inset in Figure 3b) of the microtubes can be indexed to  $(2\overline{2}0)$  and (001)faces, and the axial growth orientation is confirmed to be [001] direction. Based on the above results, the schematic illustration of a single microtube is revealed in Figure 3c with assigned tube walls as {110} family, which is consistent with the Bravais Friedel Donnay Harker (BFDH) simulation of rac-DPFOH crystal and the attachment energies of {110} facets (Figure S7). By observing the molecular accumulation of the microtube, it can be found that the hollow direction of the microtube is consistent with the axial of the 1D molecular channel.



**Figure 4.** SEM images of rac-DPFOH samples after growing for (a) 10 min, (b) 30 min and (c) 12 h. (d) The proposed formation process of the microtubes. (e) Kinetic simulation of molecular diffusion of EtOH molecules from (001) crystal face occurred at 0 ps, 10 ps, 50 ps and 100 ps, respectively. (f) The corresponding distance-concentration curve.

Previous works including cyclic peptide nanotubes<sup>[11]</sup> and porphyrin hollow hexagonal nanoprisms<sup>[12]</sup> indicate that there is a self-similar relationship between micro/nano tubular structures and the corresponding 1D channel molecular packings, which may concern the tube-forming mechanism. To reveal the growth mechanism, the time-dependent evolution was performed as shown in Figure 4a-c. The nanorods with an edge length of about 270 nm can be obtained by growing for 10 min (Figure 4a). Then the nanorods were growing with the edge length increasing to about 500 nm, and the sharp open ends appeared in some nanorods (Figure 4b). After that, the hollowing and the growing processes were continued for 12 h, almost all of the rods transformed into tubes with varying sizes (Figure 4c). These phenomena indicate that the etching along with growing simultaneously leads to the formation of the hollow structures. EtOH molecules are found in the molecular channels of rac-DPFOH crystals, therefore it is supposed that the etching process is caused by EtOH. The schematic diagram of the etching process is shown in Figure 4d. EtOH molecules are absorbed on the two ends of the rods with high attachment energies (Figure S7) and gradually dissolve the (001) and  $(00\overline{1})$ planes until the hollow tubes completed.<sup>[14]</sup> Additional, theoretical calculations are introduced to describe the etching mechanism. The kinetic process was simulated by the Forcite module of Materials Studio software, which presents the diffusion of EtOH molecules into 1D channels from (001) (Figure 4e), (110) and  $(1\overline{1}0)$  crystal faces (Figure S8). With longer diffusion time, more and more EtOH molecules filled the channel from (001) face, while few EtOH molecules can enter the crystal interior from (110) and  $(1\overline{1}0)$  crystal faces. Moreover, from the comparison of the distance-concentration curves of 0 ps and 100 ps, it can be seen that with time increasing, the concentration of EtOH molecules on the right side of the curve declines, while on the left rises, indicating that the EtOH molecules from the external

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environment have diffused into the channel (Figure 4f). On the contrary, the distance-concentration curves of 0 ps and 100 ps from (110) and (110)crystal faces remain unchanged (Figure S9), reflecting there is no entry of EtOH molecules. This result is in line with the conclusions we derived from experimental results. It is hereby verified that the non-helical channels and self-similar microtubes in our study are different from the traditional helical tubes of amphiphiles with a twisted secondary structure.<sup>[15]</sup>



Figure 5. Nyquist plot of rac-DPFOH microtubes at 25°C in a relative humidity (RH) of ~65%.

The crystalline channels are idealized structures for ion and molecule transport due to the excellent regularity and designability. Several promising candidates have been explored such as COFs,<sup>[16]</sup> metal-organic frameworks (MOFs)<sup>[17]</sup> and HOFs<sup>[18]</sup> to deliver ions, especially protons. Compared with the well-investigated proton conduction behavior, the lithium-ion transport in supramolecular channel structures has been much less explored. Here the lithium-ion conductivity of rac-DPFOH microtubes was performed through electrochemical impedance spectroscopy (EIS). 4.28 g LiCIO<sub>4</sub> was dissolved in 7.95 g acetonitrile to prepare a solution with a mass fraction of 35%. The microtubes was immersed in the solution for 24 hours, then washed with acetonitrile and dried. The lithiated sample was pressed into a thin pellet and sandwiched between two stainless steel electrodes for conduction measurement. Nyquist plot of the pellet exhibited a ion conductivity of  $1.77\times 10^{\cdot4}$  S/cm, which could be comparable to the conventional solid polymer electrolytes ( $\sim\!10^{-4}$  S/cm).^{[19]} The stability of the samples has been evaluated by cyclic EIS tests. The impedance spectra of the lithiated sample keep almost the same within 5 cycles with each time interval of 15 min, indicating the stable transport behavior of the channels (Figure S10). The polar hydroxyl groups are supposed to interact with lithium ions and promote the dissociation of lithium salt.<sup>[20]</sup> Although the mechanism of ion transfer is indeterminate, the hydrogen-bonding network within the channels may act as the conducting pathway, learning from the proton transport process.<sup>[21]</sup> In addition, based on the blue light-emitting material DPFOH, the channel structure is promising as a proof-of-concept platform for the further research of ion-exciton interaction.

In summary, *rac*-DPFOH enantiomers were proved to be utilized as newfashioned building modules for the non-helical 1D channel structures. Besides macrocycle stacking and knot + linker connection, this work provides a fresh strategy for the design of 1D channel based on mirror isomers. The self-similar relationship of tubular structures spanning from molecular level to micron level was explained. Furthermore, the supramolecular channel structures displayed high lithium ion conduct properties, indicating the potential research value of this novel 1D channel

structure. We believe that this new-type channel structure could be developed with high designability from structural and functional aspects to disclose more secrets of racemic crystals in addition to Wallach's Rule in chiral-photophysics.<sup>[22]</sup>

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**Keywords:** supramolecular interaction • non-helical channel • enantiomers • self-similar structure • ion conductivity

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#### Table-of-Contents

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