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ARTICLE TYPE

Formation of double helical microfibrils from small molecules

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5 By a facile vapor-solid route, double helical organic small molecules microfibrils 3, 4, 9, 10-
perylene-tetracarboxylic dianhydride (PTCDA) were synthesized, which was based on spontaneous
twisting of supramolecular microtubes. The averaged diameter of the resulting helical structures was
about 200 nm and overall length of several micrometers. The helices microfibrils which were obtained by
10 coiling the multilayer microtubes from the inner to the outer molecules layers tend to release their internal
rotation stress, so as to present the most stable morphology as indicated by a series of characterizations.
The changed van der Waals contact together with the surface free energy among adjacent microtubes
molecules layer, were the driving forces to induce the formation of helical structure. The obtained results
present an extremely facile strategy for fabrication of small molecular double helical microfibrils with
morphological transformation process.

15 Introduction

Helix is prevalent in living and non-living systems. In biological system, helix is a central structural motif, which ranges from nanoscopic DNA double helix, collagen triple helix to microscopic viruses, bacteria, macroscopic conch, escargots, and galaxy etc.¹⁻³ Materials with double-helix structure have attracted intensive attention due to their elegant morphology and their amazing morphology-related potential applications.⁴⁻⁶ Scientists have long held a fascination, sometimes bordering on mystical obsession for helical structures. Rotational symmetry, chirality and morphology-related applications are just a few attributes associated with helix, which make it special for materials science.^{7,8} Inspired by such sophisticated structures, chemists have been challenged to mimic its unique form and have explored various helical structures by self-assembly at the micro-nanoscale.⁹⁻¹¹ On the basis of metal-ligand interactions,¹² H-bonds,¹³ aromatic-aromatic interactions¹⁴ or π - π interactions¹⁵, etc., different kinds of double helical microstructures have been developed. To date, most of the researches on materials with helical structures have been focused on macromolecules and inorganics, less attention has been paid to organic conjugated small molecules, although the low-molecular-mass organic materials have lot of obvious advantages than the inorganic counterparts due to their promising applications in electronic and optoelectronic micro-nanodevices.¹⁶⁻¹⁸ Because of the difficulty of controlling the structure and interactions of small molecules monomers,^{19,20} it is still a fairly new world to explore of functional small molecules with double-helix micro-architecture.

3, 4, 9, 10-perylene-tetracarboxylic dianhydride (PTCDA) is an archetypal organic semiconducting conjugated small molecule, which is a potential building block for the realization of organic electronic devices.^{21,22} In our previous study (J. Mater. Chem., 2012, 22, 883), the PTCDA microtubes (MTs) were prepared, which were obtained from the curling and seaming of a two-dimensional (2D) lamellar structure, constructed with the cooperation of some noncovalent interactions such as π - π interactions and H-bonds. To the best of our knowledge, report on

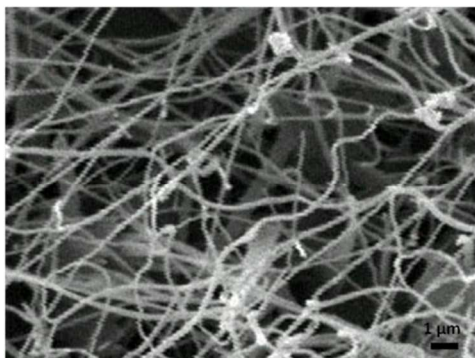
microscale materials with helical architectures has rarely been seen, especially through physical method. In this study, we demonstrate well-defined double helical microfibrils can be readily fabricated undergoing a shape transformation process, which bases on spontaneous twisting of PTCDA microtubes by a simple physical vapour deposition (PVD) on silicon substrates. This is a completely new phenomenon observed for organic small molecule nanostructures. The evolution process of the helices microfibrils was demonstrated by observation under scanning electron microscopy (SEM) and transmission electron microscopy (TEM), which contributed to the experimental evidence for possible to take a look at the formation mechanism. In addition, it is particularly important that alcohol is one kind of central nervous system depressant, drinking a lot of alcohol into the body, it will cause the lack of timely response measures. How effective and efficient monitoring of the concentration of alcohol vapour to stop drunk driving, are all countries in efforts to resolve the issue. Based on PVD technique, here we fabricated PTCDA double helical microfibrils, which have good sensitivity in low concentration of alcohol at room temperature. We believe that the gas sensors might have promising applications in the future and stimulate research for other kinds of nanostructured gas sensors.

Results and discussion

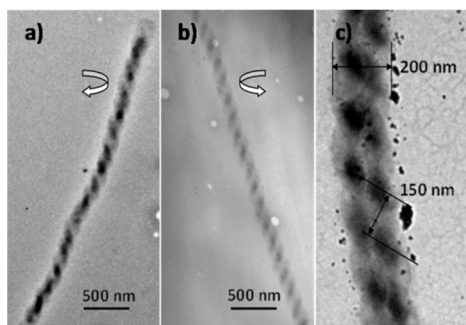
75 On a silicon substrate, the helical microfibrils were achieved by thermal evaporation of PTCDA powders (20 mg) in an Ar ambient at a vapor-flow rate of 50 sccm (standard cubic centimetres per minute) deposited. The typical growth process was conducted at 550 °C for 50 mins, and condensation of the vapor on the substrate at temperature of 410 °C, then the substrate was cooled with 4 °C min⁻¹. A high density of helices structure could be seen from the representative overview SEM image (Figure 1). Studies on the transmission electron microscopy (TEM) (Figure 2) revealed that both left- (Figure 2a) and right-handed (Figure 2b) double helices microfibrils existed in the sample, in each helix, the chirality was always consistent. These superstructures (Figure 2c) had diameters of approximately 200



nm and a pitch of 150 nm and the extended length of several micrometers.



5 Figure 1. Representative overview SEM image of the as-synthesized PTCDA double helical microfibrils by deposited on the silicon substrate.

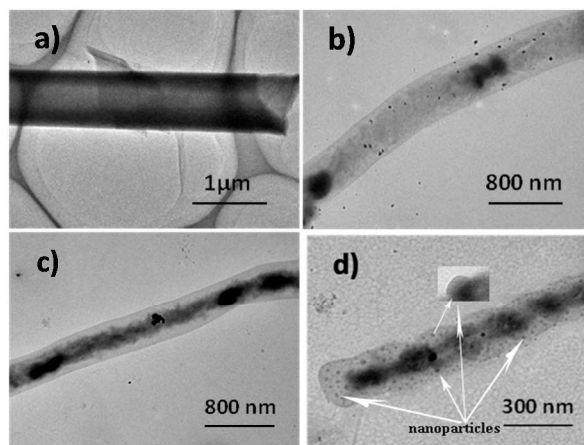


10 Figure 2. TEM images of PTCDA double helical microfibrils showing different chirality: a) left-handed, b) right-handed, c) diameters and pitch of the helical structure.

The dominated factors which are crucial to the growth of PTCDA helical microfibrils, are the sublimation temperature of the PTCDA molecules and the silicon substrate temperature. The preferential formation of microtubes instead of other microstructures, such as microwires, is achieved when the sublimation temperature of the PTCDA at 500–550 °C, the temperature of the substrates (TOS) and the sublimation temperature of the PTCDA molecules (TS) complies with the expression: $0.65 TS < TOS \leq 0.7 TS$, as it is shown in Figure S2. When the deposition process is carried out at TS closed to 550 °C and TOS > 0.7 TS, the PTCDA molecules tend to form a one-dimensional (1D) helical structure on the substrate.

The growth morphology of the microstructures can be critically affected by the temperature of the substrate. A vertically positioned substrate was used, so that the temperature across the entire substrate would be constant in the tube furnace. In order to better understand the process of forming of well-defined double helical microfibrils, the sublimation temperature of the PTCDA molecules during the deposition was maintained at 550 °C, and the corresponding transformations of morphology with four TOS [about 360 °C (Figure 3a), 380 °C (Figure 3b), 400 °C (Figure 3c) and 410 °C (Figure 3d)] for TEM observation are presented in Figures 3a-d, respectively. It is obvious that different morphologies are formed in the four substrates. As shown in Figure 3a, microtubes with diameters of approximately 1 μm and lengths up to several micrometers can be synthesized at the substrate temperature of 360 °C. According to our previous studies (J. Mater. Chem., 2012, 22, 883), these PTCDA microtubes are constructed via curling and seaming of a 2D lamellar structure which assembled by layer-by-layer technique. This result implies that PTCDA microtubes together with the

tubular structures deposition process on glass substrates follow a general similar folding behaviour which can be obtained via physical vapour deposition process. Similar results are also found in other small organic molecules materials.^{18,23} The increase of the TOS (380 °C) can result in a dramatic change of the shape of the PTCAD tubes. The TEM image (Figure 3b) of the sample revealed that the inner conformation of the PTCDA microtubes tend to conglomeration. When the TOS was upgraded to 400 °C, it was observed that the inner space of the as-grown PTCDA microtubes continued to spirally grow (Figure 3c). During this process, the diameter of microtubes significantly decreased from approximately 1 μm to 0.5 μm. It was the sequential morphological transformation provided strong evidence that PTCDA microtubes were formed via assemble of 2D lamellar structure by the cooperation of noncovalent interactions such as π - π interactions and H-bonds. It is reasonable to assume that the contraction of inner space induces the geometrical curvature required for twisting its shape, to make the whole system stable. The distort multilayer lamellar microtubes were just the intermediates in the formation of the final double helical microfibrils which further evolved into PTCDA microtubes by grown on the silicon substrate at 410 °C (Figure 3d). The as-grown products have the diameter range from 200 to 300 nm and the length larger than 10 μm.



15 Figure 3. TEM images of PTCDA microstructures deposited on silicon substrates at different substrate temperatures: a) 360 °C, b) 380 °C, c) 400 °C, d) 410 °C and the inset is the TEM image of nanoparticles of the microfibrils.

It is well known that the formations of organic micro- and nanostructures with different morphology were determined by the different dominant intermolecular interactions. It is those noncovalent forces such as H-bond, π - π interaction, and van der Waals contact, etc., play decisive roles in the formation of organic low-dimensional structures. By PVD methods, many inorganic helical micro-materials, such as helical carbon, SiO₂, ZnO, and MgB₂,²⁴⁻³⁰ have been prepared at high temperature. While much progress has been made in assembling small molecules to form supramolecular helical microstructures via multiple noncovalent interactions, success has been limited by chemical technique. Similar right- and left-handed twisted microfibers have also been prepared by the polymerization of aniline with ammonium persulfate in water in the presence of D- and L-CSAs as the dopant. Yan et al. believed that helical polyanilines self-assemble to form superhelices with a helical bias, which originated from the polyaniline helicity induced by the dopants.³¹ The current case could be different, because no microscopic chirality at the atomic scale exists, and PTCDA is

planar molecule structure, which cannot form macroscopic double-helical morphologies without introducing defects by only supramolecular assembly. For our experiment, the strong π - π interaction between PTCDA molecules was not broken during PTCDA microtubes conversion into helical microfibrils. However, we do not believe that π - π interaction is the only force that responsible for the helical structure formation. For example, in order to reach thermodynamic equilibrium states by such morphology evolution, the van der Waals contact together with the surface free energy change taking place in vapor-solid process, which may play a crucial role

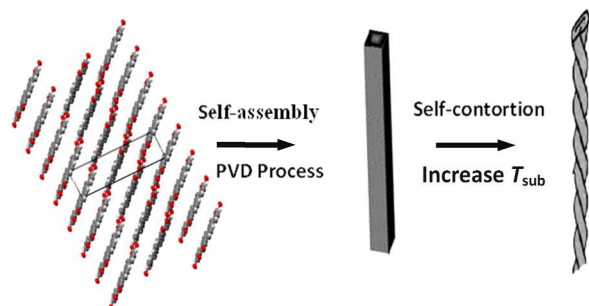


Figure 4. Illustration of the formation of the PTCAD double helical microfibrils.

The experimental results indicated that the double helical microfibrils experienced a self-twist procedure. The possible mechanism of helical formation is discussed (as indicated in Figure 4). It was considered that the increase in TOS accompanied by an increase in surface free energy, causes the change of van der Waals contact between PTCDA monolayer sheets, and then facilitated the formation of layer-layer loose microtubes. Therefore, we speculate that this changed van der Waals contact among adjacent PTCDA molecules layer is the original driving force for the double-helical structure formation. The as-grown loose multilayer microtubes with the same-handed rotation coil on themselves release the internal stress and achieve a more stable morphology from inner to outer molecules layer. This leads to a reduction in microtube diameter, which competed with the increase in surface free energy for reach equilibrium states, thereby suggesting the twisted tubes into helical conformation can distribute the energy effectively. The PTCDA double-helical microstructure can be achieved by the balance between the van der Waals contact and the changed surface free energy among adjacent microtubes molecules layers. Such a unique and complicated driving force could also be responsible for the fleet formation process. The morphology evolution is very similar to the formation of the double helical Si microtubes, but it is different from the formation of the Si double-helical by the balance between the inner pressure of the melt and the viscosity of the melt.³² However, an in-depth investigation of the mechanism of the helical microstructures formation is still in progress.

As far as we know, Au is known for forming Ohmic contact with p-type organic semiconductor because the work function of the metal must be close to or larger than the sum of the electron affinity and the bandgap energy. It can be seen that both curves have a linear relationship with the variation of the applied voltage, which proves that good Ohmic contacts are achieved for Au/PTCDA/Au. Room-temperature measurement processing (MP) shows linear I-V characteristics whereas the high-temperature (MP) significantly alters the contact properties and effectively changes Ohmic to Schottky contact³³. When the PTCDA double helical microfibrils were exposed to air and

different concentration ethanol at room temperature, the resistance in the air (Ra) and in the test gas (Rg) (as shown in Table 1 respectively) are obtained by combined the DC voltage (-10 to +10 V) on the material mounted on gold electrodes, and the SEM image of PTCDA microfibrils embedded into the two Au electrodes at both ends in the test device is shown as Figure 5, which indicate the Ohmic contacts have been realized as the previous work of our group³⁴.

Due to their large ratio of surface area to volume and unique microstructure, most microfibers have good gas sensitivity, especially for the detection of the ethanol. The gas sensing properties were measured by mounting the device in a housing having a volume of 300 cm³. The resistance variations were recorded with a Keithley 4200-SCS system on exposure to ethanol vapor. Figure 6a is the typical response curves when the single PTCDA double helical microfibrils were exposed to different concentration ethanol at room temperature. When ethanol vapour of 5–20 ppm, is introduced into and removed from the testing atmosphere, the response of the single PTCDA microfibrils-based sensors increases drastically and decreases rapidly in each cycle. The present PTCDA microstructures showed a remarkable response ($S = 4.85$) at 20 ppm ethanol vapour. As shown in Figure 6b, response calibration curves of the as-obtained products are indicated. Moreover, the double helical microfibrils-based sensor offers a fine response (Figure 6c), recovery time (Figure 6d), and the sensitivity of sensor resistance at room temperature (Figure 6e). The enhancement of ethanol gas response should be understood in relation to the electron donation from ethanol through electron-donor-electron-acceptor complexation with PTCDA molecules. We believe that such π - π stacking may strongly change the molecular properties like exciton and charge transport which are of importance for applications of π -conjugated molecules in the design of novel organic optoelectronic devices and sensors. Figure 7 is the TEM images of the fibrils and tubes before (Figures 7 a) and after (Figures 7 b) adsorption of ethanol are shown in the following two figures. From the imagines, we could perceive there was not effect on the morphology mainly due to the pure physical change instead of chemical reaction (inertness of ethanol), indicating good reproducibility and stability.

Table R1. Current–voltage characteristics of PTCDA microfibrils on gold electrodes

Concentration Of Alcohol (ppm)	0	5	10	20
Ra ($\times 10^5$)	1.51	1.53	1.55	1.57
Rg ($\times 10^5$)	—	5.17	6.76	7.61
Ra/Rg	—	3.38	4.36	4.85

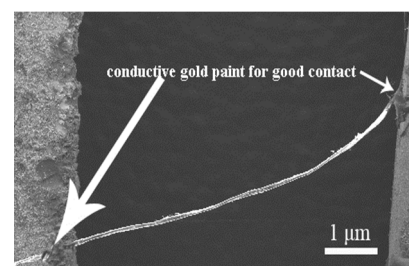


Figure 5. The representative overview SEM image of the PTCDA double helical microfibrils on the gold electrode.

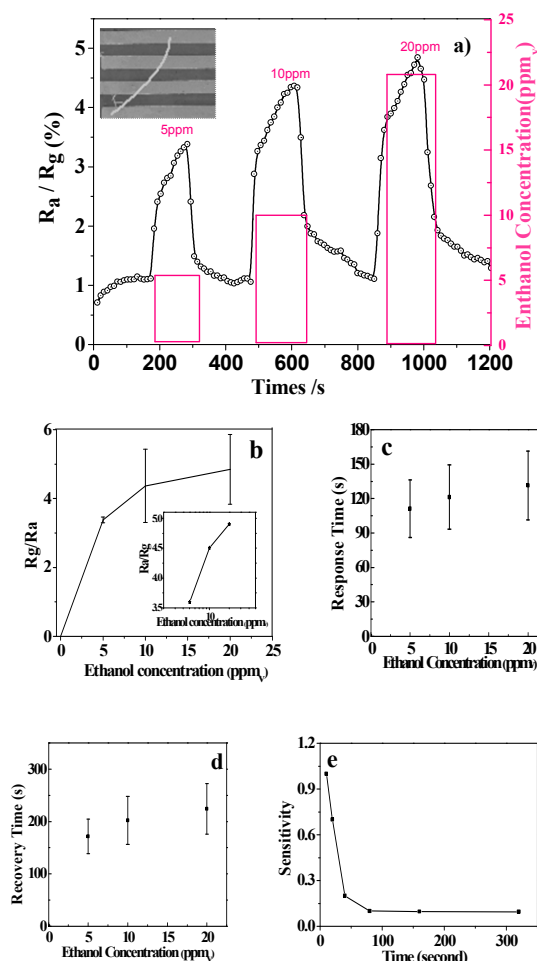


Figure 6. (a) Dynamic response-recovery curves of ethanol vapour (5-20 ppm) sensing at room temperature. The inset is the SEM image of the single PTCDA microfibril assembled on the Au electrodes. (b) calibration curve (c) response time, and (d) recovery time of PTCDA microfibrils on Au microelectrodes toward ethanol at different concentrations. (e) the sensitivity of sensor resistance at room temperature.

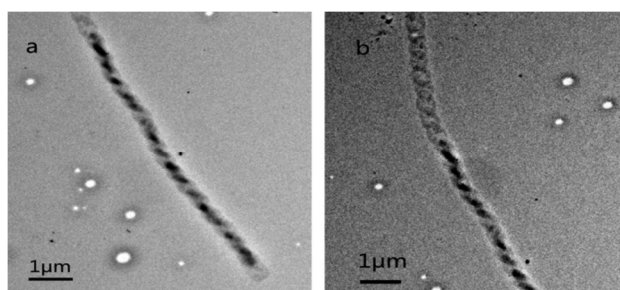


Figure 7. Representative overview TEM image of the as-synthesized PTCDA double helical microfibrils by deposited on the silicon substrate (a) before adsorption and (b) after adsorption.

Conclusions

In summary, we demonstrate for the first time that the supramolecular PTCDA microtubes can self-twist into well-defined double helical microstructure with the PVD method. Studies on the factors controlling revealed that TOS played a crucial role in the growth of PTCDA helical microfibrils. The evolution process of the PTCDA double helices structure was

demonstrated by observation under SEM and TEM images, which provided the experimental evidence for the origin of double helical microfibrils, and accomplished by PTCDA microtubes twisted. The formation of the double helical microfibrils may be realized by balance complex interplay between van der Waals contact among adjacent PTCDA molecules layer and free energy as well as π - π interactions on supramolecular microtubes. This work may provide a new alternative approach to the design and construction of helical microstructure and well-ordered one-dimensional organic small molecule assemblies.

Experimental section

Preparation PTCDA microfibrils. The PTCDA microfibrils were fabricated by a physical vapour deposition method. PTCDA powder was purchased from Sigma-Aldrich and was used without further treatment. In a typical preparation, the quartz boat loaded with the PTCDA powder was then put into the centre of a quartz tube which was inserted into a horizontal tube furnace. The vapourized temperature of PTCDA was heated to 550 °C at a heating rate of 20 °C·min⁻¹ under Ar flow of 50 sccm, controlled by a needle valve and measured using a rotameter. The silicon substrates were thoroughly rinsed with acetone and ethanol and dried with N₂ and were put along the downstream side of the flowing Ar to collect the products, and the substrate temperature was measured using a thermocouple. After the furnace system was kept at 50 min, the substrates were cooled with 4 °C·min⁻¹, the PTCDA source was physically deposited onto the substrates and some wool-like products were obtained.

Characterization. The size and morphology of the as-prepared PTCDA double helix were investigated by using scanning/transmission electron microscopy (SEM/TEM, JSM5600LV/JEOL2010).

Device Fabrication and Characterization. PTCDA microfibrils-based device for resistance (R)-time (t) measurement was assembled on Au electrodes by dielectrophoresis. For dielectrophoresis, an DC voltage with 10 V and 50 kHz was applied to the Au electrode. The response of sensors to ethanol was measured by mounting the device in a housing having a volume of 300 cm³. The resistance variations were recorded with a Keithley 4200-SCS system on exposure to ethanol vapor. The sensor sensitivity to ethanol gas is defined as $S = R_a/R_g$, where R_a and R_g are the resistance in air and in test gas, respectively.

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Notes and references

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