Electronic Supplementary Information

Multi-mode Waveguides From Ultra-long Self-assembled Hexagonal Faceted Microtubules From a Benzothiadiazole Molecule

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1. Materials and Methods

A. Self-assembly protocol: Phase transfer method

All solvents were used as received from the suppliers. The synthesis of **1** has been described elsewhere.[1] The self-assembly of **1** was carried out using a phase-transfer method[2]. A stock solution (~0.3 mM) of **1** in chloroform was first prepared. A known volume of this stock solution was then added in a long testing tube (16 x 150 mm). Following this a large excess (~5-10x the original volume of **1** in chloroform) of methanol was carefully added atop the chloroform layer so that two-layers of the solutions with different density and miscibility do not mix rapidly. The tube was then left undisturbed for 2-3 days. It must be noted here that the aggregate formation took more than 4-6 hours to initiate (small precipitates at the interface). The completion of the growth is observed by the quenching of free molecule emission. The resulting aggregates were then analyzed for their morphological characteristics using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The fluorescence and wave guiding characteristics were analyzed using a combination of UV-Visible spectroscopy, fluorescence spectroscopy, optical, polarized, and fluorescence (polarized) microscopy.

B. Important notes about the self-assembly of 1

N1. The sonication (less than 30 s) of the ultra-long (3-5 cm) microtubules results in a lengthwise cutting of the microtubules (shortening of the microtubules).

***N2.* Length controlled self-assembly of 1:** It must be noted here that the longer lengths of the self-assembled structures require longer times (e.g., 2-3 cm lengths of self-assembled structures could be completed in 3 days, while the 5 cm long self-assembled structures takes about 5 days (the top layer is always refreshed with methanol owing to the loss of evaporation overnight and care is taken when the fresh addition is performed).

C. Characterization

UV-Visible was performed using Cary 5000. Appropriate sample holders were used to measure the solution and solid-state spectra. Fluorescence measurements with polarization were acquired using a PTI instrument fitted with liquid and solid state cells. SEM was performed using FEI quanta microscope operated at a working voltage of 30 kV. The samples were lightly sputtered by gold before morphological inspection. The self-assembled structures were cast on Si surface and allowed to dry before gold sputtering and SEM analysis. For evaluation of the waveguide characteristics the as cast microtubules were analyzed under an optical microscope and were excited using a 405 nm laser source. The out coupled light was collected using a fiber optic and the spectra were recorded using an ocean optics detector.

2. Optical properties of 1

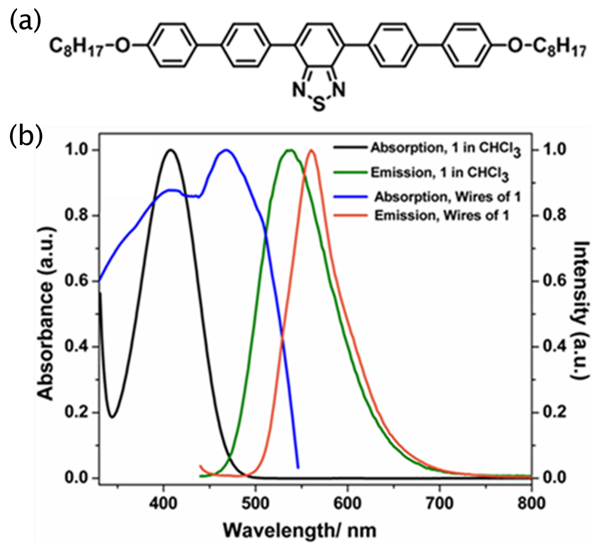

Figure S1. (a) Chemical structure of the BTD Absorption and emission characteristics of the BTD molecule in homogeneous solution state (black and green curves) and assembled state (blue and red).

3. Ultralong microtubules: Images from the growth tubes

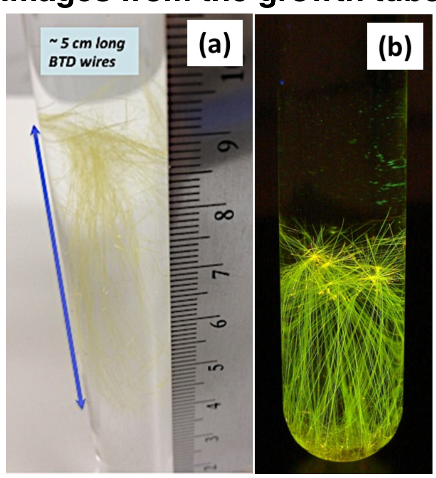

***Figure S2**.* Growth of ultra-long microtubules using the phase-transfer method (a) from **1**. These ultra-long self-assembled microtubules display strong emission (b) upon excitation under UV-lamp.

4. Morphological Analysis

A limited number of self-assembled structures appear to be non-hollow (solid cores), while a few of the resulting structures appear to have more than 6 facets (complex crystallization). Amongst these different morphological 1D structures observed here a commonality is that their sizes are rather similar. Also, no morphological structures other than 1D structures could be observed.

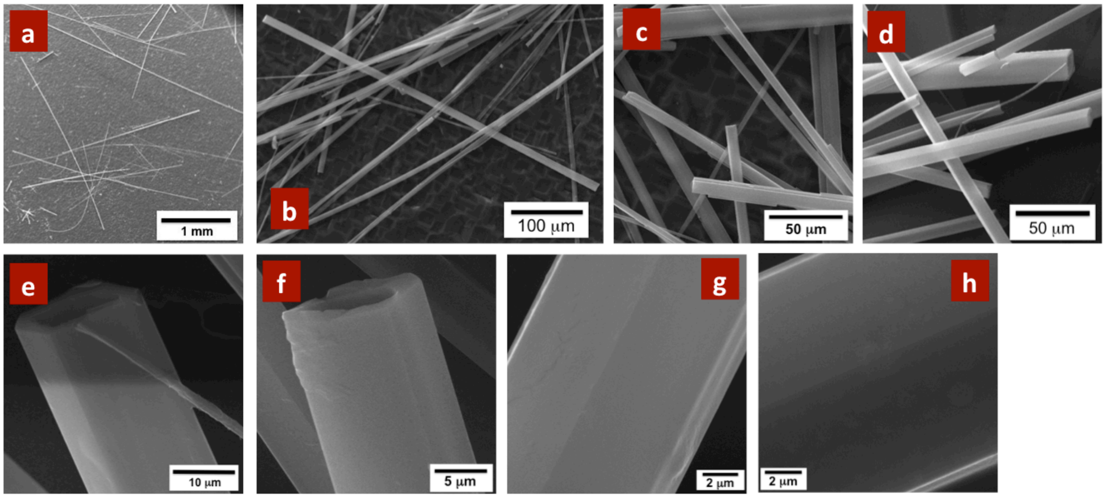

Figure S3. More SEM images of the hexagonal faceted microtubules. The most common morphological characteristic observed in the self-assembled structures are hexagonal facet microtubules.

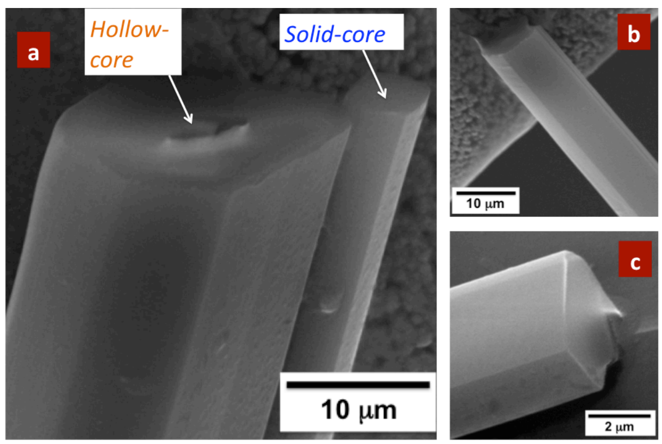

Figure S4. (a-c) Morphological inspection revealing the solid-cores of the microwires. These structures are observed along with the more common microtubule structures shown in **Fig. 1** (main text) and **Fig. S3**.

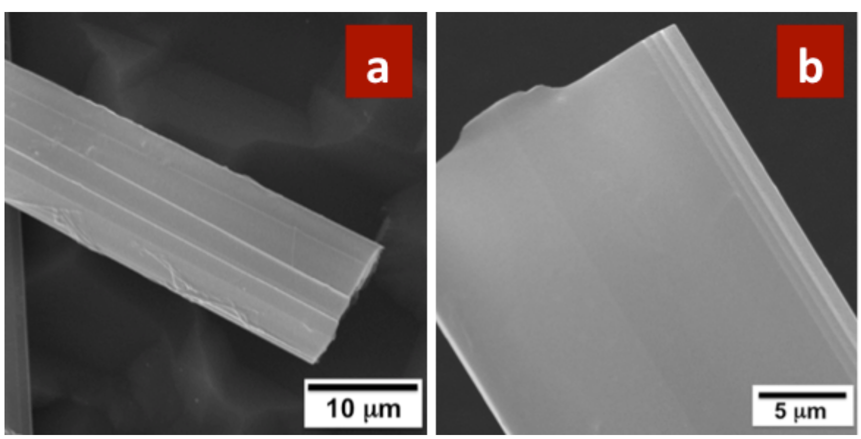

Figure S5. (a-b) SEM revealing multi-faceted (> 6) microtubes. These structures are observed along with the ones shown above (**Fig. S3 and S4**).

5. Energy minimized structural view of 1 using *MMFF94* calculations

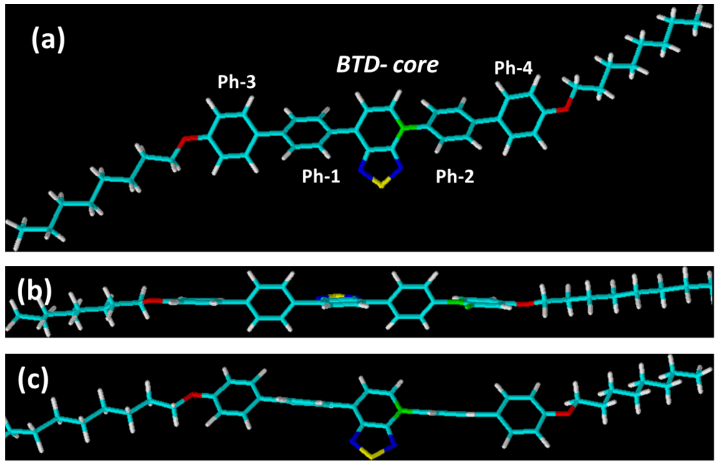

Figure S6. **(a)** 3D energy minimized structure of **1**. The energy minimization is performed using MMFF94 (Chem. draw 3D, 12.0). **(b)** A 3D view of the molecule showing near planarity of the BTD-core with the Ph-3 and Ph4, the two phenyl groups at the end of the BTD molecule used in the self-assembly of the 1D microtubules. **(c)** A 3D view of the molecule showing the near planarity of the Ph-1 and Ph-2.

6. Strong emission from microtubules and polarization dependent emission

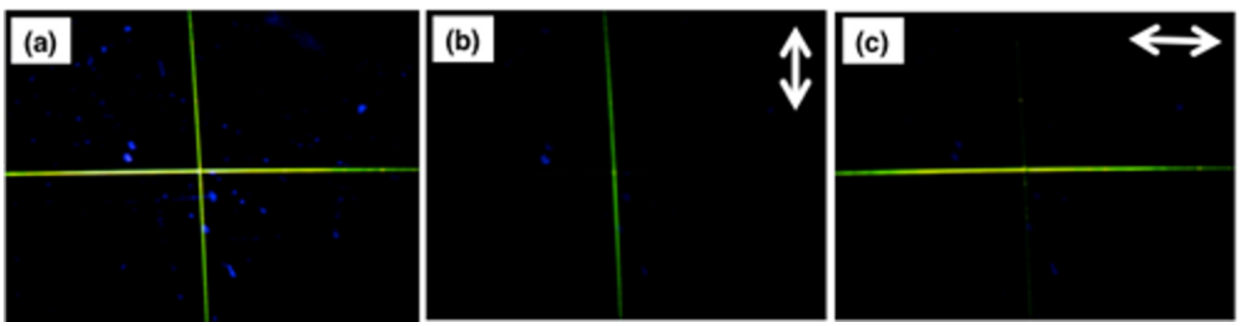

Figure S7. Polarized fluorescent emission image from two strategically placed ultra-long microtubules of **1** under excitation from UV-lamp taken from a microscope (a). The strategically placed microtubules emitted linear polarized light. Arrows show the transmission axis of the polarizer placed in front of the camera (b and c).

7. Waveguide characterization: Relevant information

N3. Important criteria for π-rich self-assembled structures as waveguides: For obtaining high quality waveguides from the π-rich organic structures, the self-assembled structures must satisfy the following conditions:[3]

(i) Self-assembled structures with various dimensions must be of appropriate size (crystal dimensions) relevant to the desired propagating wavelength; The number of modes in a waveguide is approximately equal to $M = 2\pi A(n_1^2 - n_2^2)/\lambda^2$ **(Eq. 1)**, where A is the area of the structure, λ is the wavelength, n_1, and n_2 are refractive indices of the crystal and surrounding;

(ii) Highly crystalline (preferably single-crystalline), low defect density, and a smooth surface interface (reducing scattering losses) are desirable;

(iii) The guiding material must have a higher refractive index than its surrounding cladding material in order for total internal reflection to occur;

(iv) The characteristic absorption and emission of the self-assembled structure must be spectrally isolated to avoid propagation losses due to re-absorption.

These characteristics are often manifested in the self-assembled structures (typically with size (widths) of mm range) by the manner in which the molecules are organized.

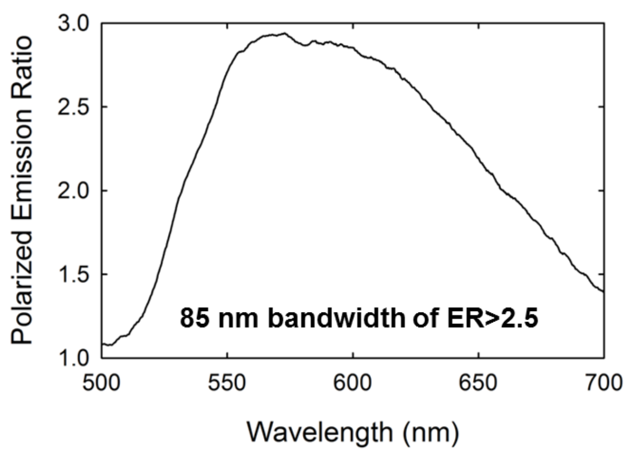

Figure S8. Measurement of polarization dependent emission spectrum from the self-assembled microtubules. The polarization ratio is defined to be the ratio of the intensity of linear polarized light in direction of highest linear polarized light intensity to the intensity of linear polarized light 90 degrees from the same direction.

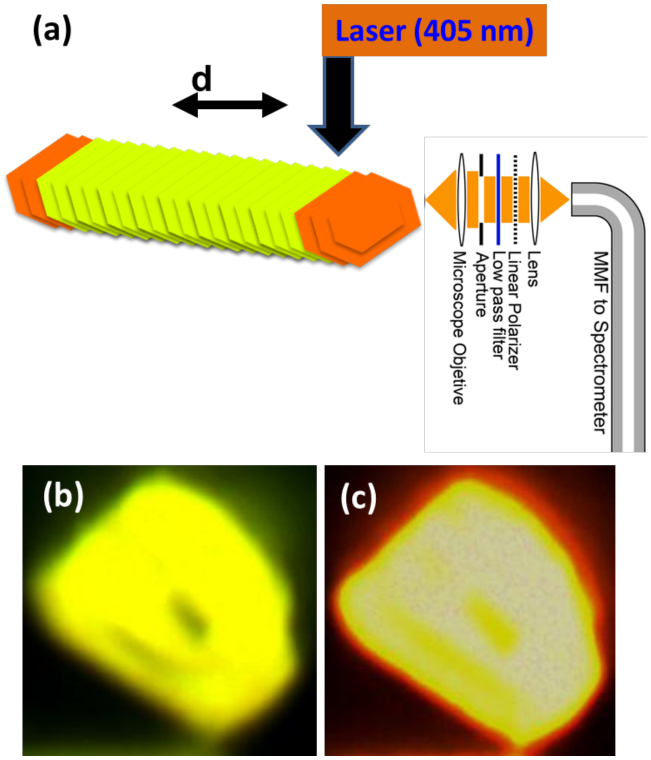

Figure S9. (a) Setup for measuring the waveguide characteristics from the self-assembled microtubules. The light guiding characteristics observed at the end of the microtubule upon excitation from 0.5 mm from near the end (b) and 5 mm (c) from the end of the microtubule. The orange-yellow color at the end of the tubules (as also shown in **Fig. 3b** (main text)) is evident at longer excitation distance from the end is a direct result of the self-absorption of light by the microtubule structure.

8. References: ESI

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2. K. Balakrishnan, A. Datar, T. Naddo, J. Huang, R. Oitker, M. Yen, J. Zhao and L. Zang, *J. Am. Chem. Soc.*, 2006, **128**, 7390.
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