Electronic Supplementary Material (ESI) for Nanoscale.

SUPPORTING INFORMATION

Design and Fabrication of Supramolecular Semiconductor Nanowires Formed by Benzothienobenzothiophene (BTBT)-Conjugated Peptides

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Synthesis of BTBT Precursors (BTBT-C_3-COOH and C_8-BTBT-C_3-COOH) for Covalent Peptide Attachment

All reagents were purchased from commercial sources and used without further purification unless otherwise noted. Anhydrous THF and toluene were distilled from Na/benzophenone. Conventional Schlenk techniques were used and reactions carried out under N_2 unless otherwise noted.

Methyl 4-([1]Benzothieno[3,2-b][1]benzothiophen-2-yl)-4-oxobutanoate (BTBT-CO-C_2-COOMe): Into a solution of [1]Benzothieno[3,2-b][1]benzothiophene (1) (250 mg, 1.04 mmol) in dry dichloromethane (25 mL) at -10 °C was added $AlCl_3$ (378.58 mg, 2.84 mmol) under nitrogen, Then, methyl 4-chloro-4-oxobutyrate (187.9 mg, 1.248 mmol) was added dropwise, and the mixture was stirred for 1h at the same temperature. The reaction mixture was allowed to stand without cooling and stirred for 24h at room temperature. The reaction mixture was next poured into ice-cooled water (150 mL) and the product was extracted with chloroform. The organic phase was washed with water, dried over Na_2SO_4, filtered, and evaporated to dryness. The crude product was then purified by column chromatography on silica gel with chloroform as the eluent, affording methyl 4-([1]Benzothieno[3,2-b][1]benzothiophen-2-yl)-4-oxobutanoate (2) as a white solid (160 mg, 43.4% yield).^{1}H NMR ($CDCl_3$): δ 2.85 (t, 2H, J = 7.0 Hz), 3.45 (t, 2H, J = 7.0 Hz), 3.74 (s, 3H), 7.49 (m, 2H), 7.96 (m, 3H), 8.09 (dd, 1H, J = 1.6 Hz, 8.8 Hz), 8.60 (d, 1H, J = 0.8 Hz) ppm; m.p. 189-190 °C.

4-([1]Benzothieno[3,2-b][1]benzothiophen-2-yl)butanoic acid (BTBT-C_3-COOH): A mixture of methyl 4-([1]Benzothieno[3,2-b][1]benzothiophen-2-yl)-4-oxobutanoate (2) (470 mg, 1.33 mmol), potassium hydroxide (296.68 mg, 5.29 mmol), hydrazine hydrate (50-60%, 1.12 mL, 17.98 mmol) in diethylene glycol (50 mL) was heated to 110 °C for 1 h and then further heated at 210 °C for 5 h. The mixture was then allowed to cool to room temperature and acidified with 4M HCl. Then, water (50 mL) was added and the product was extracted with ethyl acetate. The organic phase was washed with water, dried over Na_2SO_4, filtered, and evaporated to dryness. The crude product was then purified by column chromatography on silica gel with ethyl acetate as the eluent, affording 4-([1]Benzothieno[3,2-b][1]benzothiophen-2-yl)butanoic acid (3) as a white solid (150 mg, 35% yield). ^{1}H NMR (d6-DMSO): δ 1.90 (m, 2H), 2.27 (t, 2H, J = 8.0 Hz), 2.78 (t, 2H, J = 8.0 Hz), 7.37 (d, 1H, J = 8.0 Hz), 7.50 (m, 2H), 7.96 (d, 1H, J = 8.0 Hz), 7.98 (s, 1H), 8.02 (d, 1H, J = 7.0 Hz), 8.14 (d, 1H, J = 8.0 Hz), 12.08 (s, 1H) ppm; ^{13}C NMR (d6-DMSO): δ 26.9, 33.5, 34.9, 121.9, 122.0, 124.2, 124.9, 125.8, 126.7, 130.9, 132.6, 132.9, 133.2, 140.0, 141.9, 142.4, 174.7 ppm; m.p. > 400 °C; MS(ESI) m/z ($[M-H]^+$): calcd. for $C_{18}H_{14}O_2S_2$, 325.04; found, 325.02491.

([1]benzothienopheno[3,2-b]benzothienophene-2-yl)octan-1-one (C_7-CO-BTBT): Into a solution of [1]Benzothieno[3,2-b][1]benzothiophene (1) (2.0 g, 8.32 mmol) in dry dichloromethane 90 mL) at -10 °C was added $AlCl_3$ (1.44 g, 10.82 mmol) under nitrogen, Then, octanoyl chloride (1.73 mL, 9.99 mmol) was added dropwise, and the mixture was stirred for 1h

at the same temperature. The reaction mixture was allowed to stand without cooling and stirred for 24h at room temperature. The reaction mixture was next poured into ice-cooled water (150 mL) to give a precipitate. The precipitate was collected by filtration and washed consecutively with water and methanol. The crude product was then purified by column chromatography on silica gel with chloroform as the eluent, affording ([1]benzothienopheno[3,2-b]benzothienophene-2-yl)octan-1-one (4) as a white solid (2.0 g, 65.6% yield). ^{1}H NMR ($CDCl_3$): δ 0.91 (t, 3H, J = 7.0 Hz), 1.29-1.44 (m, 8H), 1.81 (m, 2H), 3.07 (t, 2H, J = 7.2 Hz), 7.48 (m, 2H), 7.94 (m, 3H), 8.05 (dd, 1H, J = 1.5 Hz, 8.0 Hz), 8.55 (s, 1H); m.p. 179-180 °C.

2-octyl[1]benzothieno[3,2-b][1]benzothiophene (C_8-BTBT): A mixture of ([1]benzothienopheno[3,2-b]benzothienophene-2-yl)octan-1-one (4) (1.45 g, 3.96 mmol), potassium hydroxide (611.04 mg, 10.89 mmol), hydrazine hydrate (50-60%, 3.15 mL, 50.49 mmol) in diethylene glycol (50 mL) was heated to 110 °C for 1 h and then further heated at 210 °C for 5 h. The mixture was then allowed to cool to room temperature and filtered to give a crude solid. The crude solid was washed with methanol and dried under vacuum to yield a white solid (1.2 g, 86.3% yield). ^{1}H NMR ($CDCl_3$): δ 0.91 (t, 3H, J = 7.0 Hz), 1.30-1.41 (m, 10H), 1.71 (m, 2H), 2.79 (t, 2H, J = 8.0 Hz), 7.30 (d, 1H, J = 8.0 Hz), 7.41 (d, 1H, J = 8.0 Hz), 7.47 (d, 1H, J = 8.0 Hz), 7.74 (d, 1H, J = 8.0 Hz), 7.80 (d, 1H, J = 8.0 Hz), 7.88 (d, 1H, J = 8.0 Hz), 7.92 (d, 1H, J = 8.0 Hz); m.p. 111-112 °C.

Methyl 4-(2-octyl[1]benzothieno[3,2-b][1]benzothiophen-2-yl)-4-oxobutanoate (C_8-BTBT-CO-C_2-COOMe): Into a solution of 2-octyl[1]benzothieno[3,2-b][1]benzothiophene (5) (1.1 g, 3.12 mmol) in dry dichloromethane (50 mL) at -10 °C was added $AlCl_3$ (1.14 g, 8.52 mmol) under nitrogen, Then, Methyl 4-chloro-4-oxobutyrate (0.56 g, 3.74 mmol) was added dropwise, and the mixture was stirred for 1h at the same temperature. The reaction mixture was allowed to stand without cooling and stirred for 20h at room temperature. The reaction mixture was next poured into ice-cooled water (150 mL) and the product was extracted with chloroform. The organic phase was washed with water, dried over Na_2SO_4, filtered, and evaporated to dryness. The crude product was then purified by column chromatography on silica gel with chloroform as the eluent, affording methyl 4-(2-octyl[1]benzothieno[3,2-b][1]benzothiophen-2-yl)-4-oxobutanoate (6) as a white solid (700 mg, 48% yield).^{1}H NMR ($CDCl_3$): δ 0.90 (t, 3H, J = 7.5 Hz), 1.35 (m, 10H), 1.75 (m, 2H), 2.84 (m, 4H), 3.51 (t, 2H, J = 7.5 Hz), 3.76 (s, 3H), 7.33 (d, 1H, J = 8 Hz), 7.77 (s, 1H), 7.85 (d, 1H, J= 8 Hz), 7.93 (d, 1H, J = 8 Hz), 8.09 (d, 1H, J = 8 Hz), 8.60 (s, 1H) ppm; m.p. 144-145 °C.

4-(2-octyl[1]benzothieno[3,2-b][1]benzothiophen-2-yl)butanoic acid (C_8-BTBT-C_3-COOH): A mixture of methyl 4-(2-octyl[1]benzothieno[3,2-b][1]benzothiophen-2-yl)-4-oxobutanoate (6) (700 mg, 1.50 mmol), potassium hydroxide (335 mg, 5.97 mmol), hydrazine hydrate (50-60%, 1.26 mL, 20.28 mmol) in diethylene glycol (50 mL) was heated to 110 °C for 1 h and then further heated at 210 °C for 5 h. The mixture was then allowed to cool to room temperature and acidified with 4M HCl. Then, water (50 mL) was added and the product was extracted with chloroform. The organic phase was washed with water, dried over Na_2SO_4, filtered, and

evaporated to dryness. The crude product was then purified by column chromatography on silica gel with ethyl acetate as the eluent, affording 4-(2-octyl[1]benzothieno[3,2-b][1]benzothiophen-2-yl)butanoic acid (7) as an off-white solid (140 mg, 21.3% yield). ^{1}H NMR (d6-DMSO): δ 0.86 (t, 3H, J = 7.0 Hz), 1.31 (m, 10H), 1.65 (m, 2H), 1.90 (m, 2H), 2.70 (t, 2H, J = 7.5 Hz), 2.75 (m, 4H), 7.35 (m, 2H), 7.94 (m, 4H) ppm. m.p. 186-187 °C; MS(ESI) m/z ([M-H]$^+$): calcd. for $C_{26}H_{30}O_2S_2$, 437.17; found, 437.25624.

Synthesis of BTBT-Peptide Molecules

All peptide molecules were synthesized by using solid phase peptide synthesis (SSPPS) method. The synthesis were performed on MBHA Rink Amide resin and 2 equivalents of fluorenylmethyloxycarbonyl (Fmoc) protected amino acids, 1.95 equivalents of O-Benzotriazole-N,N,N',N'-tetramethyl-uroniμM-hexafluoro-phosphate (HBTU) and 3 equivalents of N,N-diisopropylethylamine (DIEA) for 6 h. Fmoc protecting groups were removed by 20% of piperidine in dimethylformamide for 20 minutes. The peptides were cleaved from the solid Resin by a mixture of trifluoroacetic acid: triisopropylsilane: H2O in the ratio of 95:2.5:2.5 for 2 h. The product was collected into a round bottom flask by washing the resin with DCM. The DCM was evaporated by rotary evaporation and cold ether was poured to precipitate the peptide. The final product was collected by centrifuging and then lyophilizing for 72 h to get a white powder.

Synthesis of BTBT-Peptide molecule: In the last step of the synthesis, 1.5 equivalents of BTBT-C_3-COOH were used and the coupling was left for 24 h.

Synthesis of C8-BTBT-Peptide molecule: In the last step of the synthesis, 1.5 equivalents of C_8-BTBT-C_3-COOH were used and the coupling was left for 24 h.

Preparative High Performance Liquid Chromatography: In purification of positively charged peptide molecules, reverse phase silica column (C18) and 0.1% TFA in water and 0.1% in ACN were used as eluents.. Preparative Liquid Chromatography System (Prep-HPLC Agilent 1200 series) integrated with a sample collector was used.

Liquid Chromatography-Mass Spectrometry (LC-MS): After purification of the peptide molecules by Prep HPLC, the purity of the molecules were determined by Agilent Technologies 6530 Accurate-Mass Q-TOF LC-MS. Zorbax SB-C18 column and 0.1% formic acid in water and 0.1% formic acid in acetonitrile were used as mobile phase for positively charged molecules. All peptides were obtained with high purity.

UV-Vis Spectroscopy

The peptide solutions were prepared in a 3 mL quartz cell having 1 cm path length. Stock solutions of BTBT-peptide and C_8-BTBT-peptide were prepared in dd water. 3 mL of BTBT-peptide and C_8-BTBT-peptide having a concentration of 860 μM was prepared from stock

solution. The pH of solutions was adjusted to 2 by addition of 1M HCl and to 10 by addition of 1M NaOH .The absorbance values were recorded on CaryBio100 instrument.

Fluorescence Spectroscopy

The peptide solutions were prepared in a 3 mL quartz cell having 1 cm path length. Stock solution of BTBT-peptide and C_8-BTBT-peptide was prepared in dd water. 3 mL of BTBT-peptide and C_8-BTBT-peptide having a concentration of 860 μM was prepared from stock solution. The pH of solutions was adjusted to 2 by addition of 1M HCl and to 10 by addition of 1M NaOH. The samples were excited at 310 nm with excitation slit and emission slit widths of 5 and 5 respectively. The emission intensities were recorded on Fluorescence Spectrometer (Cary Eclipse) instrument.

Circular Dichroism (CD) Spectroscopy

The peptide solutions were prepared in a 3 mL quartz cell having 1 cm path length. Stock solution of BTBT-peptide and C_8-BTBT-peptide was prepared in dd water. 3 mL of BTBT-peptide and C_8-BTBT-peptide having a concentration of 860 μM was prepared from stock solution. The pH of solutions was adjusted to 2 by addition of 1M HCl and to 10 by addition of 1M NaOH. The samples were measured from 500 nm to 190 nm with 0.1 data pitch, 100 nm/min scanning speed, 1 nm band width and 4 s D.I.T. Average of two measurements were adjusted and sensitivity was selected as standard. All measurements were recorded on Jasco J-815 circular dichroism spectrometer.

X-ray Photoelectron Spectroscopy (XPS)

30 μL of BTBT-peptide and C_8-BTBT-peptide solutions (1 wt %) were dropped on piranha cleaned glass slides (1.5x2 cm^2) and then placed in a sealed container containing 2 mL of NH_4OH solution. After 20 minutes of exposure to NH_3 vapor, the samples were dried at 37 ^oC under vacuum overnight. BTBT-peptide and C_8-BTBT-peptide solutions were prepared at pH 2 then drop casted on glass slides and then dried at 37 ^oC under vacuum overnight. Both assembled and unassembled peptide films were analyzed by Thermo K-alpha monochromatic high-performance X-ray photoelectron spectrometer.

Transmission Electron Microscopy (TEM)

10 μL of BTBT-peptide and C_8-BTBT-peptide solutions were dropped on a carbon grid followed by staining the samples by 2% uranyl acetate solution. Air dried samples were imaged by FEI Tecnai G2 F30 transmission electron microscope.

Atomic Force Microscopy (AFM)

Peptide samples were prepared on silicon wafer using 5 μL of 200 fold diluted from stock solutions (1 % w/v). The pH of peptide solutions were adjusted to 10 by addition of 1M NaOH. After dropping the solution onto a silicon wafer, the samples were air-dried. Tapping mode imaging were used to image topography of the resulting samples, using appropriate cantilevers (force constant of 5 N/m, resonance frequency of f_0=150 kHz). Images were taken in 5 um or 2 um areas at a scan rate of 1.5 Hz and a resolution of 512 x 512 points and lines, respectively.

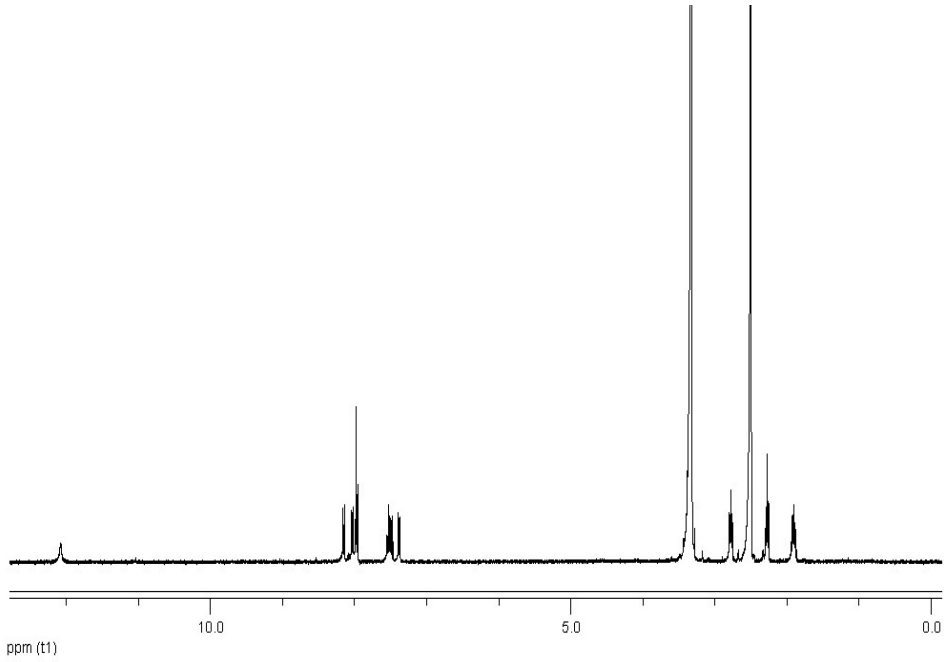


Figure S1. ^{1}H NMR spectra of **BTBT-C_3-COOH** in dimethyl sulfoxide-d_6.

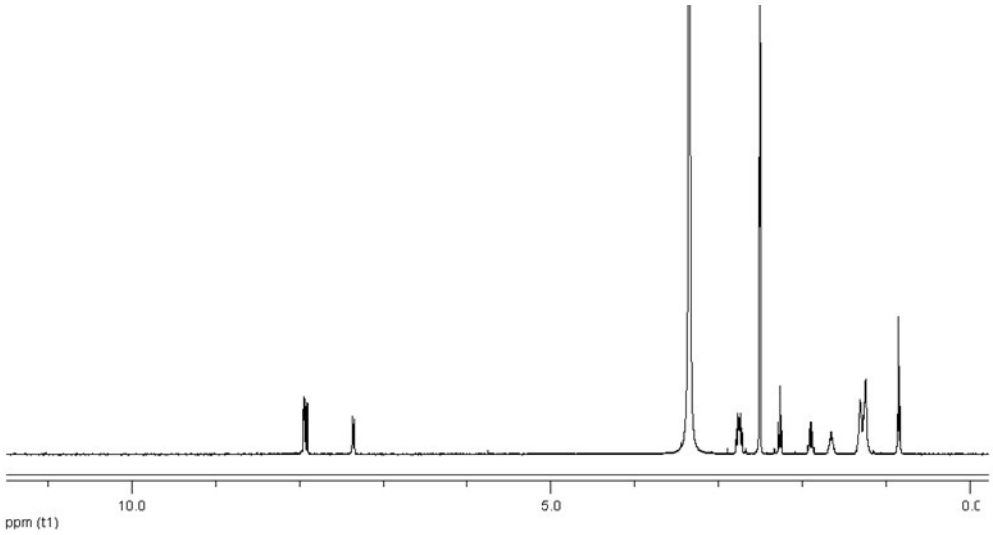


Figure S2. ^{1}H NMR spectra of **C_8-BTBT-C_3-COOH** in dimethyl sulfoxide-d_6.

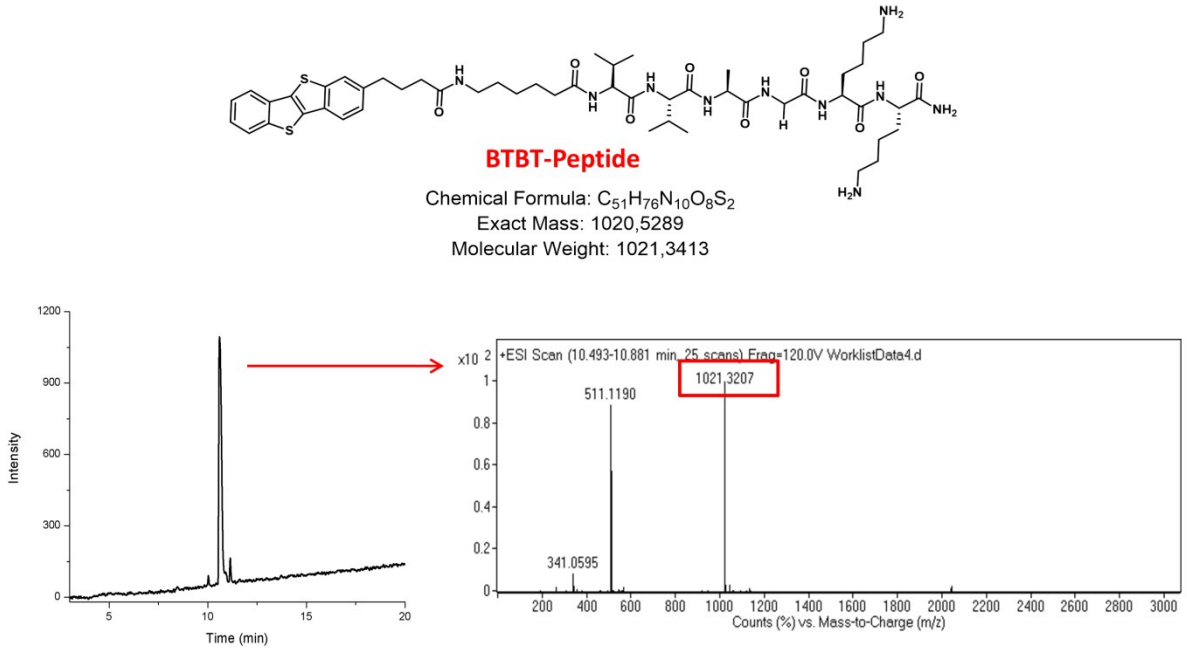


Figure S3. Chemical structure of **BTBT-peptide** molecule (top). Liquid chromatogram (left) and mass spectrum (right) of BTBT-Peptide molecule.

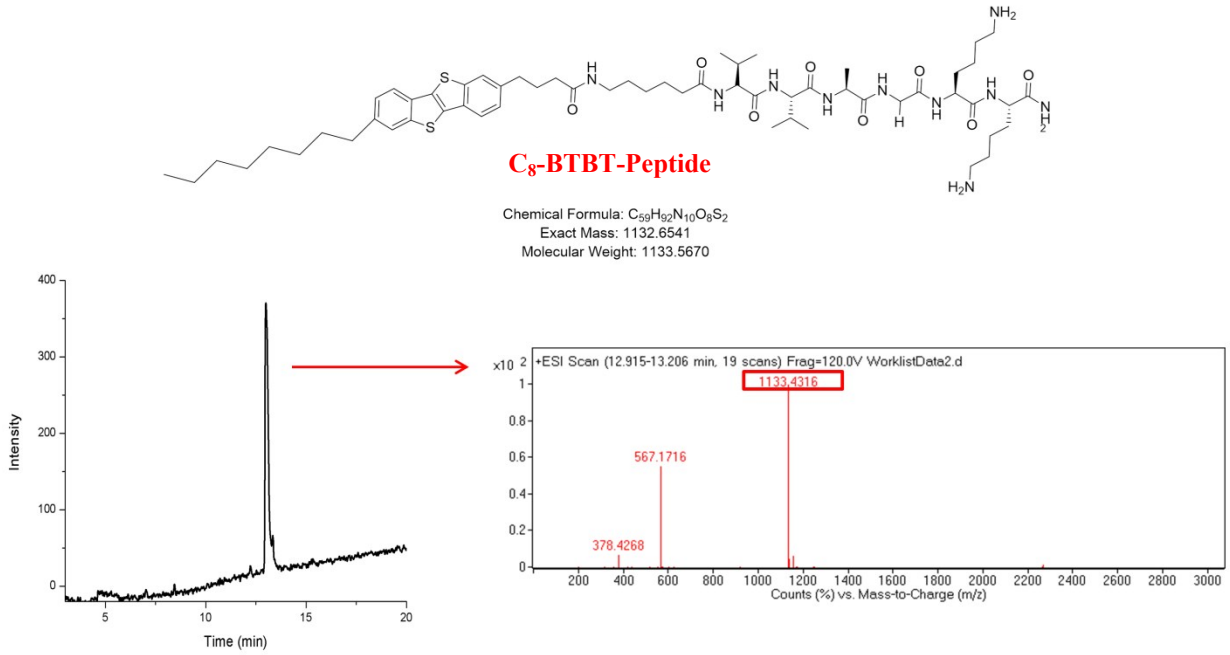


Figure S4. Chemical structure of **C_8-BTBT-peptide** molecule (top). Liquid chromatogram (left) and mass spectrum (right) of C_8-BTBT-Peptide molecule.

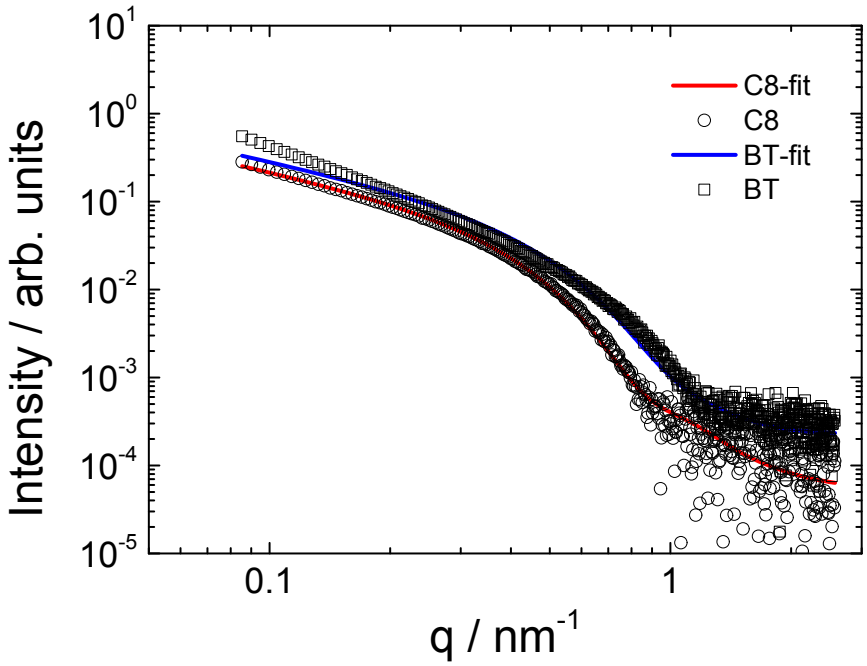


Figure S5. SAXS data measured for solutions of **BTBT-peptide** and **C_8-BTBT-peptide** (open symbols) along with form factor fits (lines) using a core-shell cylinder model (described in the text).

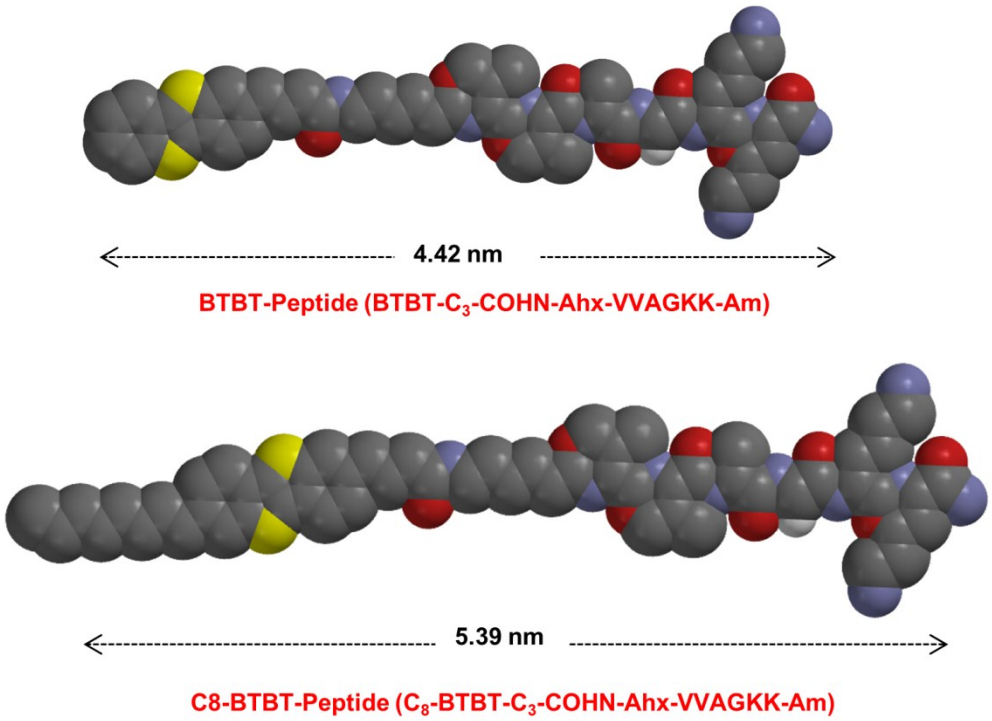


Figure S6. Computed (DFT, B3LYP/6-31G**) molecular lengths of **BTBT-peptide** and **C_8-BTBT-peptide** in their fully extended molecular conformations.

Conductivity Measurements

30 µL of BTBT-peptide and C_8-BTBT-peptide solutions (1 wt%) were dropped on piranha cleaned glass substrates with 1.5 x 2 cm^2 dimensions and then placed in a sealed container containing 2 mL of NH_4OH solution. After 20 minutes of exposure to NH_3 vapor, the samples were dried at 37 ^oC under vacuum overnight. Deposited peptide films were used for electrical characterization. 20 pairs of Au electrodes are formed on each film by thermal evaporation of Au through shadow masks. The channels have 10 or 20 µm length and 1 mm or 4 mm width (Figure S6 and S7). Gold is chosen as the electrode material as it is commonly used with similar organic films. The shadow masks are obtained from Ossila Ltd. Au is evaporated on the films at a rate of 0.2 nm/s in a thermal evaporation chamber under 3.5×10^{-6} Torr pressure. The final electrode thickness is 50 nm. The electrodes without a channel show resistance levels of a few Ω that is orders of magnitude smaller than the film resistance between the electrodes which is expected to be more than MΩ. For electrical measurements, two tungsten needles attached to separated micro-manipulators are used to touch the Au electrodes with dimensions of 1x1 mm^2 under a probe station. Current through the channel is measured by monitoring the current leaving/entering the probes while sweeping the voltage difference across the electrodes from 0 to 20 V (Figure S8). Current- voltage (I-V) characteristics are then plotted for resistance analysis.

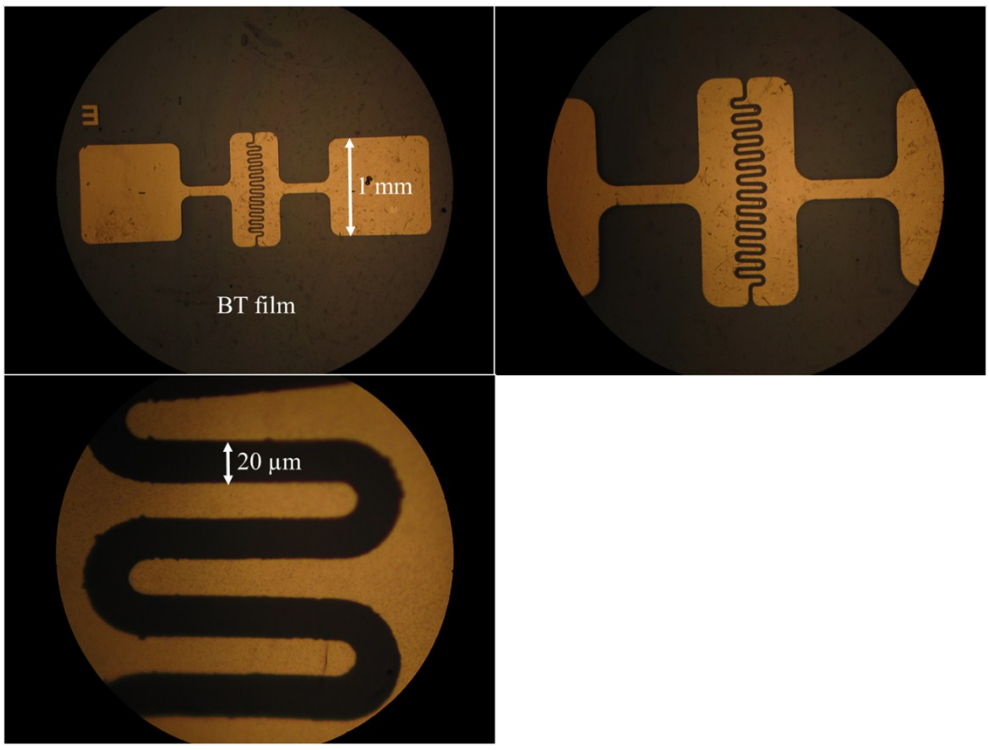


Figure S7. Optical microscope images of Au contacts on **BTBT-peptide** film with L = 20 µm and W= 4 mm.

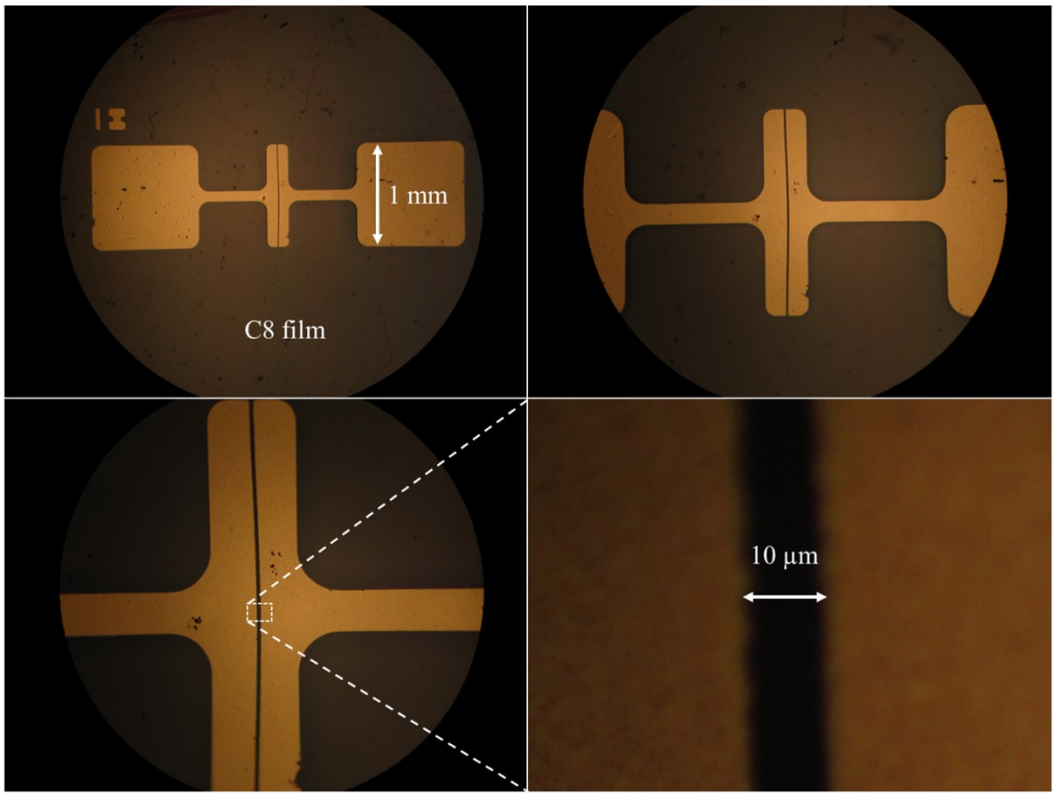


Figure S8. Optical microscope images of Au contacts on **C_8-BTBT-peptide** film with L = 10 µm and W= 1 mm.

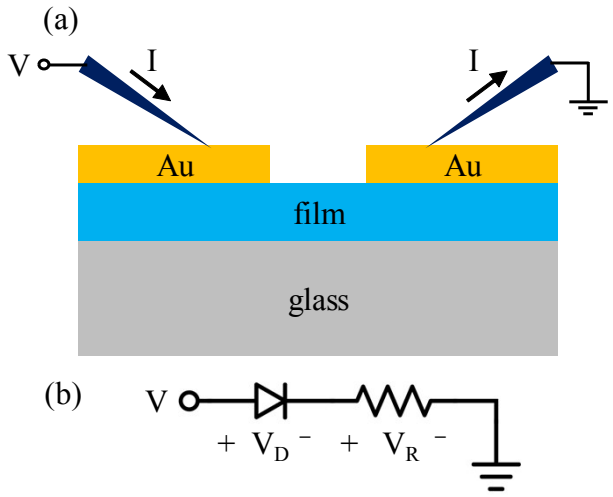


Figure S9. (a) Electric bias/current configurations on cross section illustration of a channel separating Au electrodes. (b) Electrical circuit model of the channel.

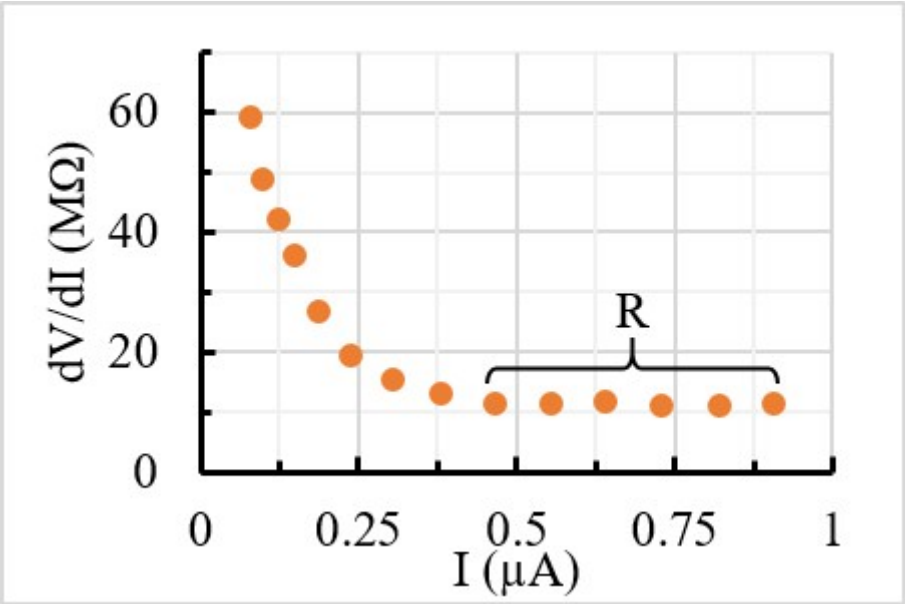


Figure S10. Derivative resistance of **BTBT-peptide** film between two Au electrodes.

The peptide film thickness was obtained from the AFM images of peptide films scratched by tungsten needles under microscope (Figure S11). The thickness of scratched peptide films was obtained by contact mode imaging using a contact tip with spring constant of 0.2 N/m and resonant frequency of 13 kHz. Images were taken in 80 x 80 um areas at a scan rate of 0.35 Hz, scan angle of 90°, deflection set point of 0.5 V and all images were acquired at a resolution of 512 x 512 points and lines, respectively. Asylum Research MFP-3D model AFM was used for imaging.

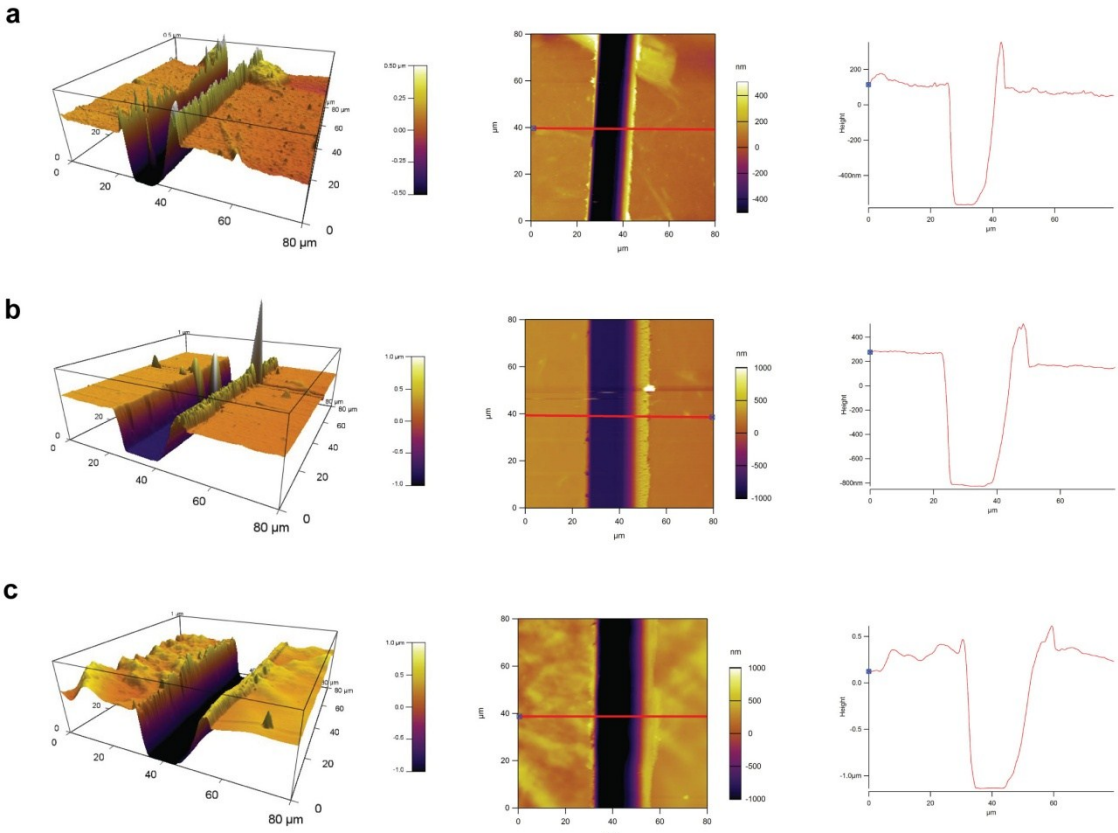


Figure S11. 3D images (left), height retraces (middle) and height profiles (right) of **BTBT-peptide** film (a), **C_8-BTBT-peptide** film (b) and **BTBT-peptide** film with Al contacts (c).

Table S1. Channel dimensions and electrical properties of 7 devices (D) on **BTBT-peptide** and **C_8-BTBT-peptide** films.

BTBT-peptide	**D1**	**D2**	**D3**	**D4**	**D5**	**D6**	**D7**
R (MΩ)	11.8	16.6	11.5	9.2	20.3	31.7	8.9
L (μm)	20	20	20	20	20	20	20
W (mm)	4	4	4	4	4	4	4
t (μm)	0.67	0.81	0.88	0.88	1.19	1.15	1.20
ρ (kΩ.m)	1.6	2.7	2.0	1.6	4.8	7.3	2.1
σ (S/cm)	6.3×10^{-6}	3.7×10^{-6}	4.9×10^{-6}	6.2×10^{-6}	2.1×10^{-6}	1.4×10^{-6}	4.7×10^{-6}
C_8-BTBT-peptide	**D1**	**D2**	**D3**	**D4**	**D5**	**D6**	**D7**
R (MΩ)	630	283	317	399	335	367	670
L (μm)	10	10	10	10	10	10	20
W (mm)	1	1	1	1	1	1	1
t (μm)	0.47	1.59	1.31	1.35	1.30	1.34	1.09
ρ (kΩ.m)	29.7	44.9	41.6	54.0	43.6	49.1	36.4
σ (S/cm)	3.37×10^{-7}	2.23×10^{-7}	2.40×10^{-7}	1.85×10^{-7}	2.30×10^{-7}	2.04×10^{-7}	2.75×10^{-7}

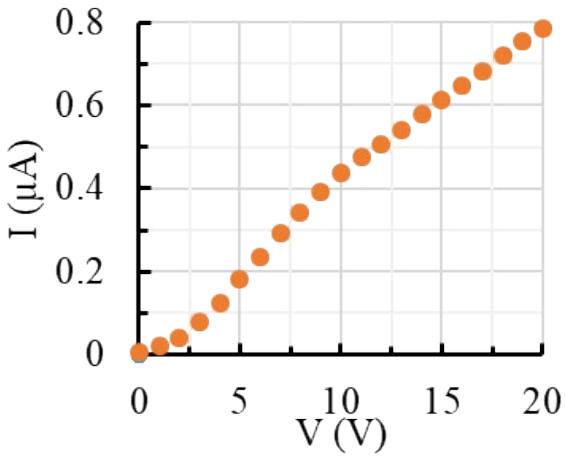
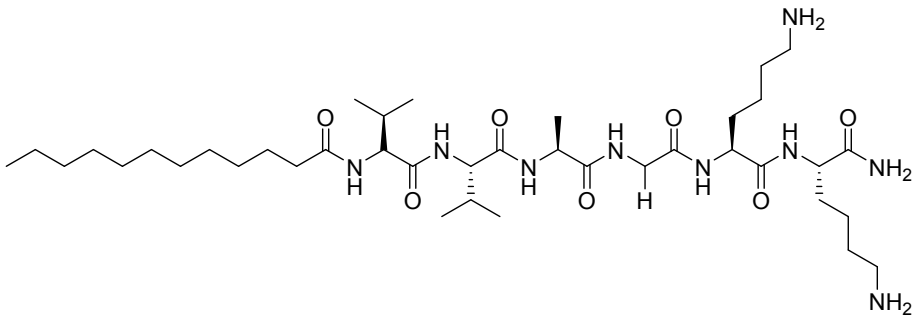


Figure S12. I-V characteristics of **BTBT-peptide** film between two Al electrodes.

Molecule	Morphology	Electrode	Conductivity (Scm^{-1})	Reference
PTCDI	Single nanobelt	Gold	0	30
TTF	Nanofibrous film	Pt	$< 3 \times 10^{-10}$	31
TTF-FF-NH2	Nanofibrous film	Gold	1.9×10^{-10}	32
T1	Random microstructures	Unknown	$< 10^{-9}$	33
BTBT-peptide	Nanofibrous film	Gold/Al	6.0×10^{-6}	This study

Table S2. Comparison of conductivity values for different self-assembled nanostructures in their non-doped states reported in the literature.



Chemical Formula: $C_{39}H_{75}N_9O_7$
Exact Mass: 781.5789
Molecular Weight: 782.0850

Figure S13. Chemical structure of KK molecule.

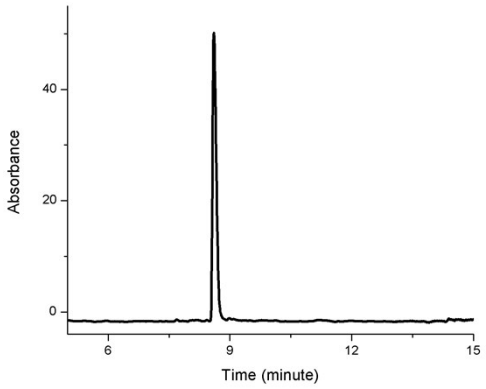


Figure S14. Liquid chromatogram of KK molecule.

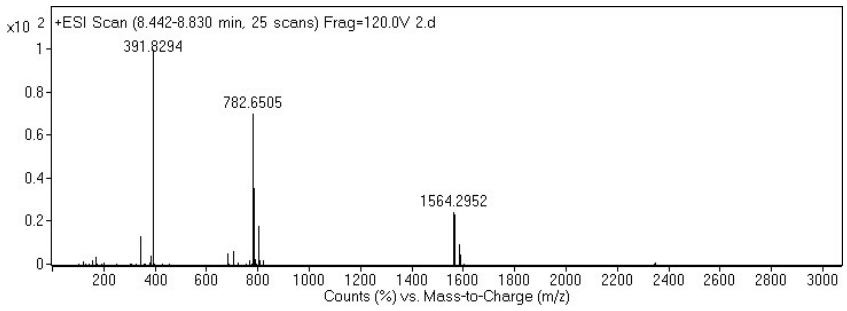


Figure S15. Mass spectrum of KK molecule.

Table S3. Channel dimensions and electrical properties of 6 devices on KK film. The average conductivity value is 1.7×10^{-8} S/cm with 0.6×10^{-8} S/cm standard deviation.

KK	D1	D2	D3	D4	D5	D6
R (GΩ)	2.59	2.04	1.89	2.14	2.1	2

L (μm)	20	20	20	20	20	20
W (mm)	4	4	4	4	4	4
t (μm)	1.6	1.7	0.9	1.3	2.0	1.7
ρ (kΩ.m)	828.8	693.6	340.2	556.4	840.0	680.0
σ (S/cm)	1.2×10^{-8}	1.4×10^{-8}	2.9×10^{-8}	1.8×10^{-8}	1.2×10^{-8}	1.5×10^{-8}