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Electronic Supplementary Information

Co-solvent polarity tuned thermochromic nanotubes of cyclic dipeptide–polydiacetylene supramolecular system.

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Contents

1. Experimental section

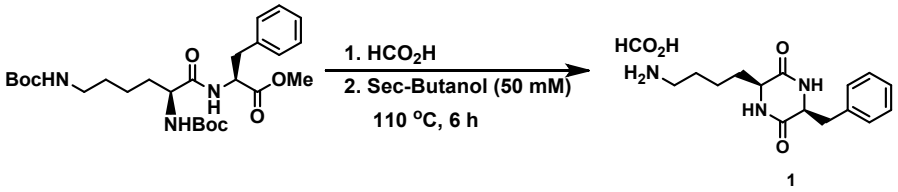
1.1 Materials

L-Phenylalanine, 1-hydroxybenzotriazole hydrate, piperidine, triisopropylsilane and propylphosphonic anhydride (50% in ethyl acetate) were purchased from Sigma Aldrich (Korea). 10,12-Pentacosadiynoic acid (PCDA) was purchased from GFS Chemicals. Thionyl Chloride (1 mol/L in dichloromethane), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride, N,N-diisopropylethylamine, trifluoroacetic acid were purchased from TCI. Triethylamine was purchased from Daejung (Korea). All the other chemicals used were analytical grade reagents.

1.2 Instruments

SEM of nanotube morphology was conducted with a JEOL (JSM-6330F) FE-SEM. TEM investigations were carried out using a JEOL TEM-2100F microscope. The absorption spectra were recorded on a USB2000 miniature fiber-optic spectrometer (Ocean Optics). IR spectra were recorded on a Thermo Nicolet NEXUS 470 FTIR using an ATR accessory (Thermo Fisher Scientific, Inc.). The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unitylnova (300 and 600 MHz) spectrometer at 298 K in $CDCl_3$ and DMSO-d_6. Mass spectra were recorded on a AXIMA MALDI-TOF (SHIMADZU). XRD spectra were recorded with a minFlex600 (Rigaku, Germany). Raman spectra were recorded on a LabRAM HR Evolution Raman Spectrometer (Horiba Scientific, 785nm laser source).

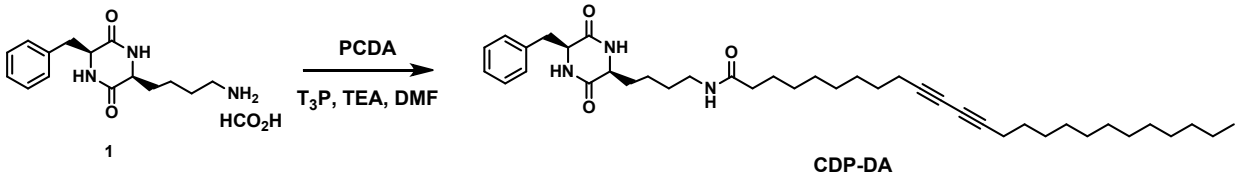
1. Syntheses of CDP [Cyclo(L-Lys-L-Phe)]



1

Syntheses of (*3S,6S*)-3-(4-aminobutyl)-6- benzylpiperazine-2,5-dione) (1). The cyclo (L-Lys-L-Phe) was synthesized by following the previously reported procedure.[1] The dipeptide εN-Boc, αN-Boc-Lys-Phe-OMe (5.1 g, 10.05 mmol) was subjected to Boc deprotection by treating with formic acid. The dipeptide was dissolved in formic acid (80 mL) and stirred at room temperature for 2 h. The reaction was monitored by thin layered chromatography (TLC). After completion of the reaction, all the volatiles were evaporated under reduced pressure. The obtained residue was co-evaporated with toluene (2 × 60 mL) and dried under vacuum for 30 min. Then the residue was re-dissolved in sec-butanol (195 mL, ~50 mM) and allowed to stir at 110 °C in an oil bath for 6 h. After 30 min, the formation of a white precipitate was observed, and a thick curdy white precipitate was formed with time. After 6 h, the reaction was stopped and brought to room temperature. Then the maximum amount of volatiles was evaporated using a rotary evaporator under reduced pressure and a thick white suspension was obtained. The thick white suspension was filtered under vacuum using a sintered funnel and was washed with dichloromethane. The white precipitate was dried under vacuum to obtain the pure product as a white solid (2.0 g, 67% yield) and was characterized by ^{1}H &^{13}C NMR and HRMS analysis.

2. Synthesis of CDP-DA



N-(4-((2S,5S)-5-benzyl-3,6-dioxopiperazin-2-yl)butyl)pentacosa-10,12-diynamide (CDP-DA). To a solution of cyclo(L-lys-L-phe) formic acid salt (250 mg, 0.311 mmol, 1 equiv), 10,12-pentacosadiynoic acid (350 mg, 0.373 mmol, 1.2 equiv) and triethylamine (0.55 mL, 1.245 mmol, 5 equiv) in 10 mL of DMF was added a solution of propylphosphonic anhydride (0.7 ml, 0.467 mmol, 1.5 equiv) at room temperature and stirred overnight at 60 °C. The reaction mixture was cooled at RT, and then solid was collected by filtration and washed with EA. The crude material was triturated /washed with ACN to afford title compound (220 mg, 45%). ^{1}H NMR: (600 MHz, DMSO-d_6): δ 8.13 (d, *J* = 2.4 Hz, 1H), 8.03 (d, *J* = 2.4 Hz, 1H), 7.25 (t, *J* = 6 Hz, 2H), 7.20 (t, *J* = 6 Hz, 2H), 7.15 (d, *J* = 6 Hz, 1H), 4.18 (t, *J* = 6 Hz, 1H), 3.54 (t, J = 6 Hz, 1H), 3.14 (dd, 6 Hz, 12 Hz, 1H), 2.85-2.80 (m, 3H), 2.27 (t, *J* = 6 Hz, 4H), 2.01(t, *J*= 6 Hz, 2H), 1.49-1.41 (m, 6H), 1.32-1.24 (m, 24H), 1.10-1.01 (m, 4H), 0.85 (t, *J* = 6Hz, 3H), 0.77-0.71 (m, 2H), 0.65-0.59 (m, 2H); ^{13}C NMR: (75 MHz, $CDCl_3$) 173.4, 167.4, 166.9, 135.2, 129.8, 129.0, 127.5, 65.2, 56.1, 54.7, 45.5, 39.8, 38.5, 37.6, 36.8, 32.7, 31.9, 30.2, 29.6, 29.4, 29.3, 29.2, 29.1, 29.0, 28.9, 28.8, 28.7, 28.3, 28.2, 25.7, 22.6, 21.3, 19.2, 16.0, 15.2, 14.1; IR (cm^{-1}) *ν*max: 3302, 3190, 3057, 2919, 2848, 1685, 1640, 1541, 1453, 1338, 1253, 1218, 1191, 1102, 820, 744, 721, 697, 576, 480, 447; MS (MALDI-TOF, m/z): calcd. for $C_{40}H_{61}N_3O_3$ $[M+Na]^+$654.46, found 654.19

References

1. C. Balachandra, T. Govindaraju, *J. Org. Chem.,* 2020, **85**, 1525–1536.

3. NMR and MALDI-TOF spectra for CDP-DA

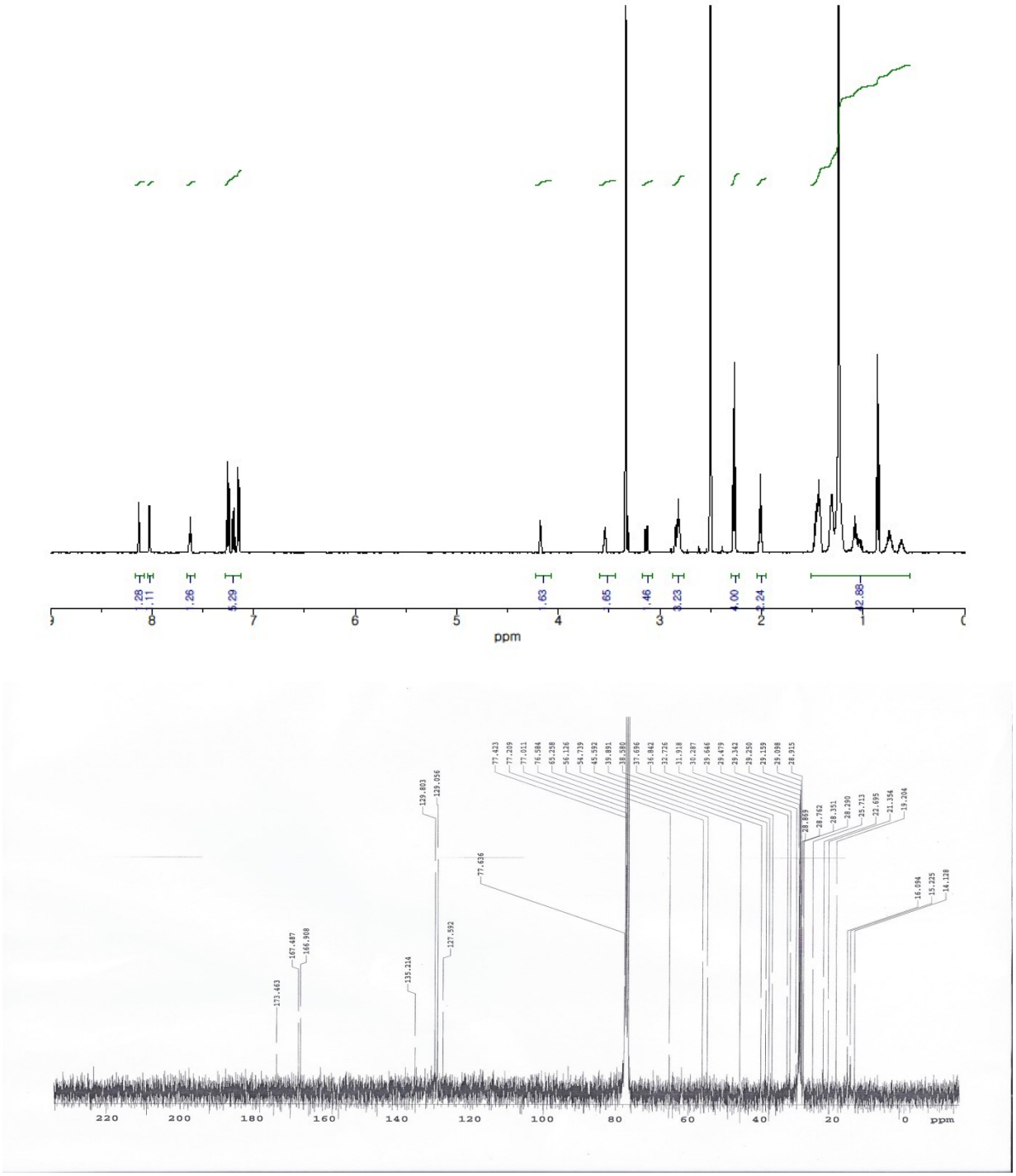


Figure S1. ^{1}H (top, 600 MHz, DMSO-d_6) and ^{13}C (bottom, 75 MHz, $CDCl_3$) NMR spectra of N-(4-((2S,5S)-5-benzyl-3,6-dioxopiperazin-2-yl)butyl)pentacosa-10,12-diynamide (CDP-DA).

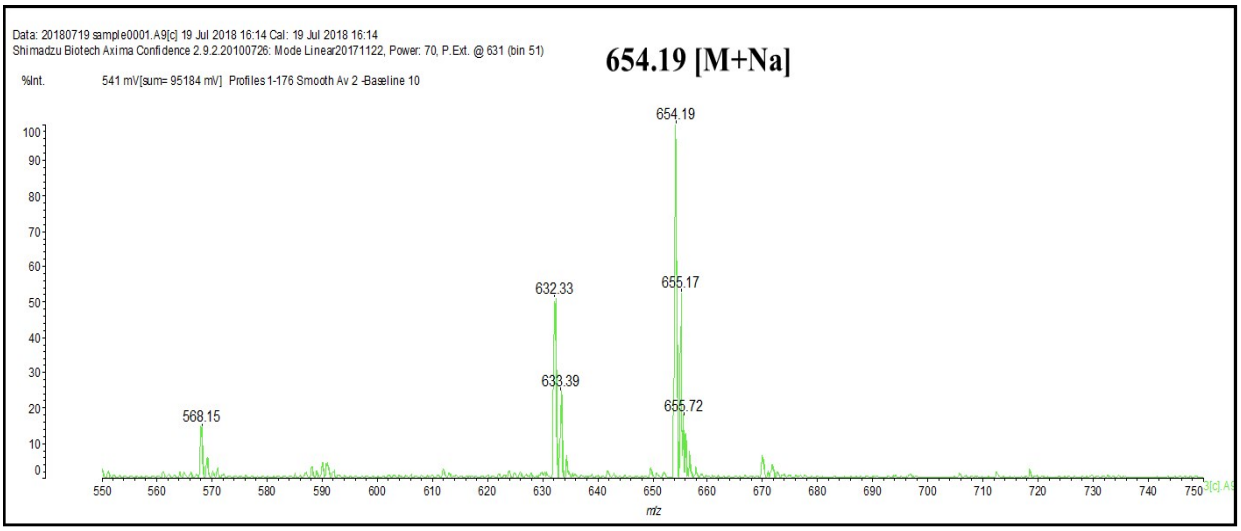


Figure S2. MALDI-TOF spectrum of N-(4-((2S,5S)-5-benzyl-3,6-dioxopiperazin-2-yl)butyl) pentacosa-10,12-diynamide(CDP-DA)**.** MS (MALDI-TOF, m/z): calcd. for $C_{56}H_{90}N_2O_6$ [M+Na] 654.46, found 654.19

4. Table for morphologies of CDP-DA in the different volume ratio of chloroform/ methanol mixture

	Chloroform	Chloroform Methanol (3 : 1)	Chloroform Methanol (2 : 1)	Chloroform Methanol (1 : 1)	Chloroform Methanol (1 : 2)	Chloroform Methanol (1 : 3)	Methanol
Phase	Clear gel	Solution	Solution	Nanotube + Plate	Nanotube	Nanotube	Nanotube
Polymerization	X	X	X	O (Blue)	O (Blue)	O (Blue)	O (Blue)

Table S1. Morphology of CDP-DA in the different volume ratio of chloroform/ methanol mixture

5. SEM images of CDP-DA in various solvents

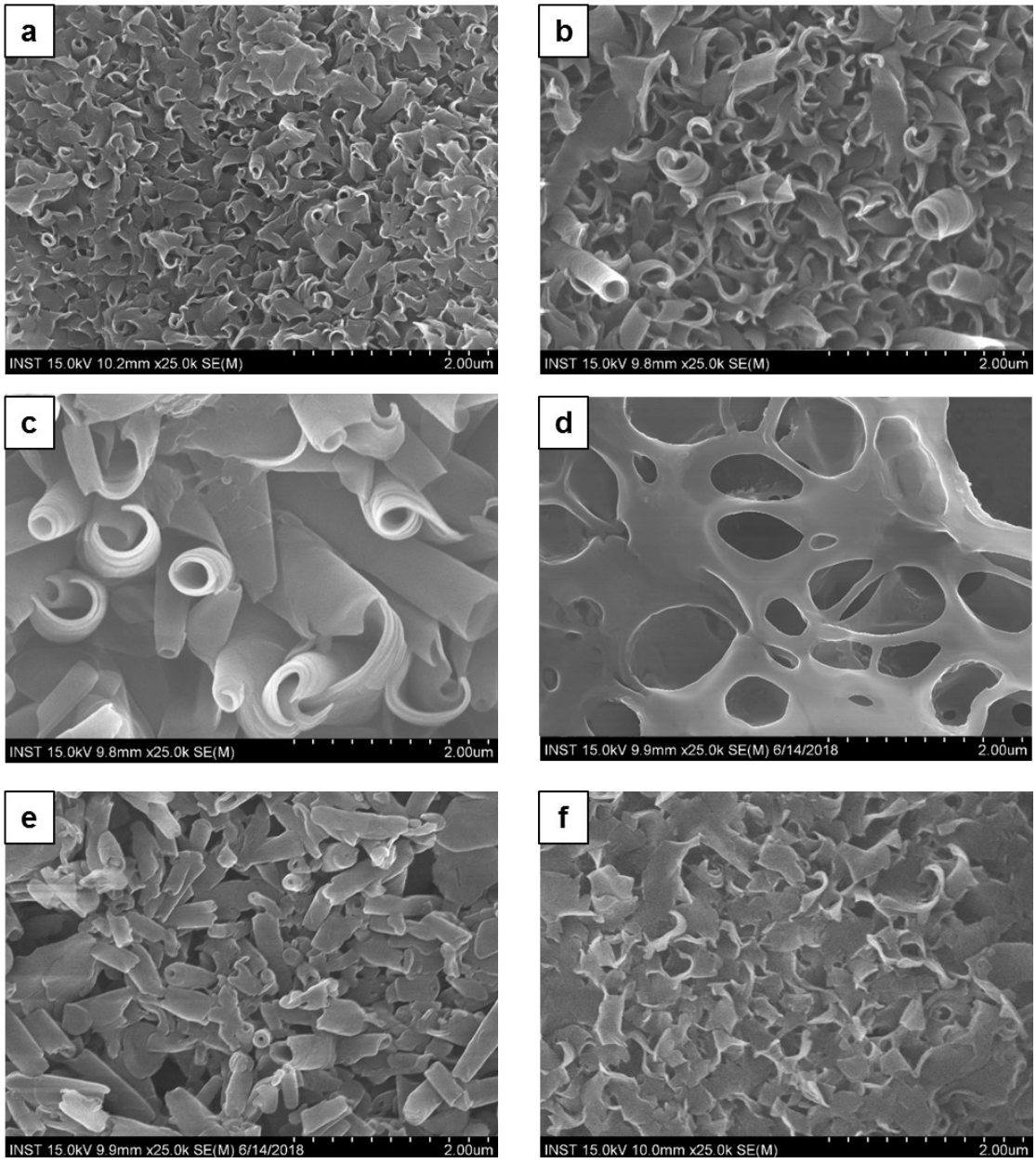
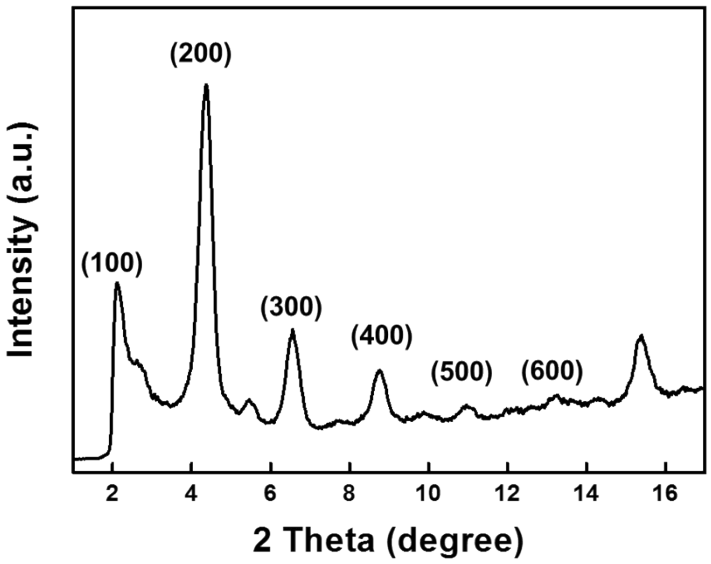


Figure S3. SEM images of CDP-DA in different solvent systems (a) tetrahydrofuran (b) ethyl acetate (c) isopropyl alcohol (d) dichloromethane (e) DMSO : Water (3:1 v/v) (f) acetone

6. Powder X-ray diffraction pattern of CDP-DA

a



b

2Θ	d (Å)	
2.12	**41.6**	**(100)**
4.36	**20.8**	**(200)**
5.46	16.2	
6.56	**13.7**	**(300)**
7.66	11.5	
8.76	**10.8**	**(400)**
10.82	**8.2**	**(500)**
13.2	**7.0**	**(600)**
15.4	5.5	

Figure S4. Powder X ray diffraction

Figure S4. Powder X-ray diffraction of CDP-DA (a) powder X-ray diffraction spectrum (b) Table of calculated 2θ theta values.

7. Thermochromic response of CDP-PDA

Figure S5. Thermochromic response of CDP-PDA 30 ^{o}C to 200 ^{o}C.

8. SEM images of CDP-PDA before and after heating

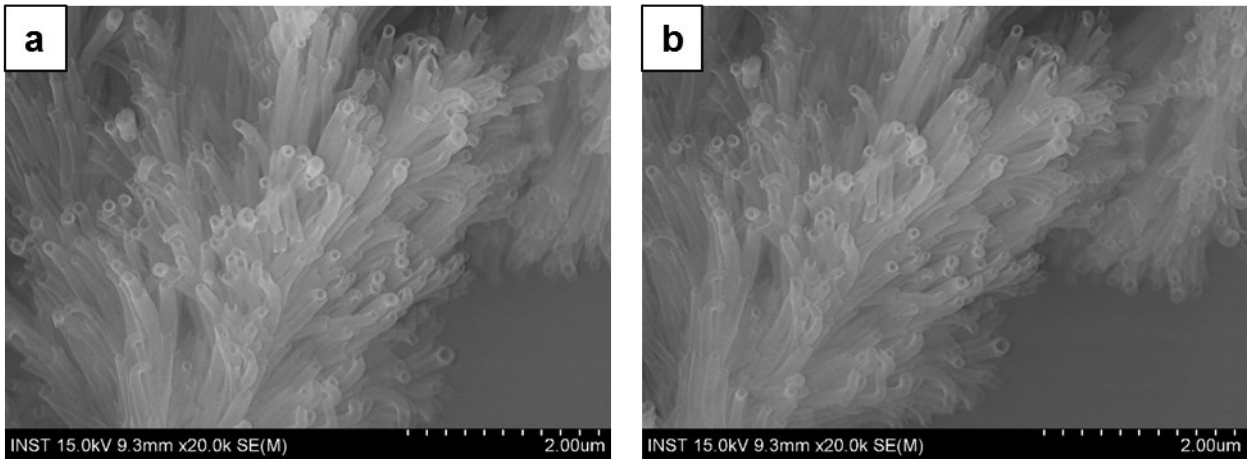


Figure S6. SEM images of CDP-PDA nanotubes (a) before and (b) after heating at 150 ^{o}C for 5 minutes.

9. ^{1}H NMR and FT-IR spectra for hydrogen bonding effect of CDP-DA

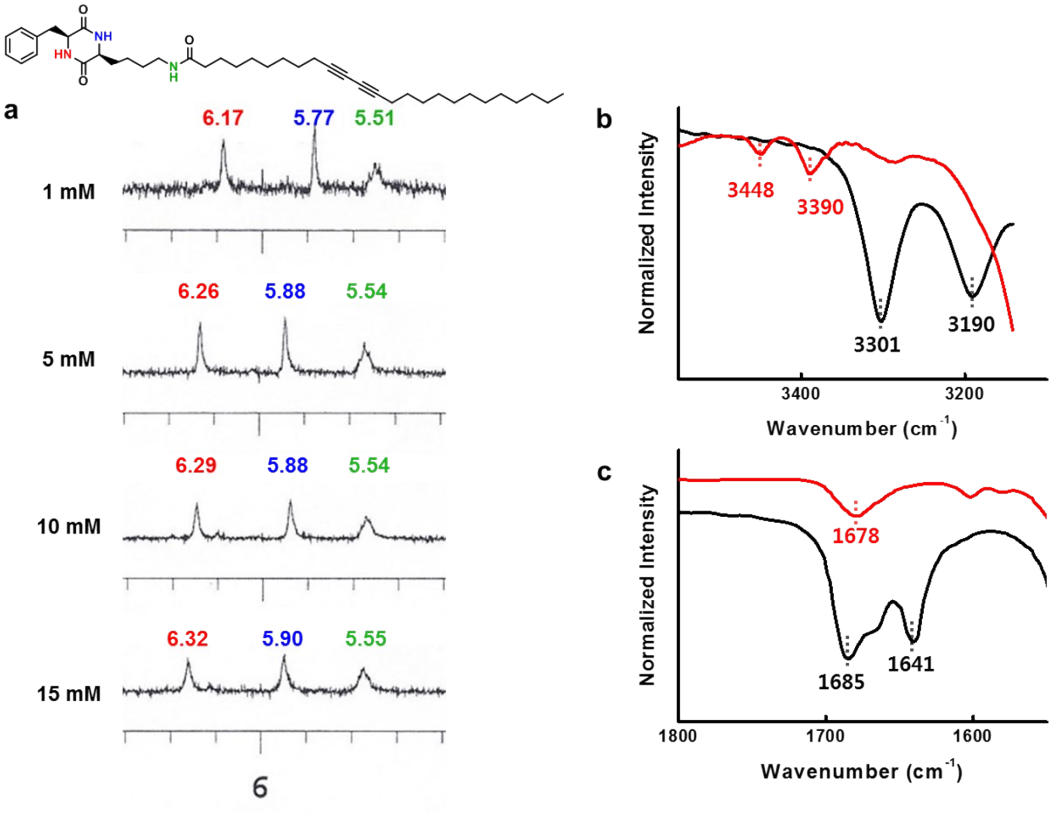


Figure S7. (a) ^{1}H NMR ($CDCl_3$) peak shift of CDP-DA solution dependent on concentration. (b, c) FT-IR spectra of CDP-DA solution in chloroform (red) and powder (black).