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Supporting Information

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Efficient Multiple Healing Conductive Composite via Host-Guest Inclusion

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General information

Materials.

All solvents and reagents were used as supplied except the following. Dimethylformamide (DMF) was dried and distilled over calcium chloride anhydrous under reduced pressure and stored under an argon atmosphere. 1-Pyrenebutylic acid (Py-CH_2-CH_2-CH_2-CH_2-COOH, M_n=288.34) was purchased from Sigma-Aldrich Co., Inc. SWNTs(d ~ 1 nm) was purchased from Aldrich Chemical Co. The branched structure of polyethylenimine (PEI, M_w=1800) was procured from Polysciences Inc. β-cyclodextrin (β-CD) and 1-Adamantaneacetic acid(Ad-CH_2-COOH)(98.5%) were purchased from Aladdin Chemistry Co.Ltd. 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDCI), N-Hydroxysuccinimide (NHS), 4-(dimethylamino) pyridine (DMAP)and all the other starting materials were purchased from local chemical company.

Instruments.

The ^{1}HNMR spectra was measured on an Advance Bruker 600NMR spectrometer at 600 MHz. Scanning electron microscopy (SEM) observations were performed on a Jeol JSM-5900LV electron microscope at an accelerating voltage of 20kV. UV-Vis-NIR absorption spectra was recorded with WFM UV-2800H, 2D-FTIR spectrometer was measured on GX, Perkin-Elmer, CA, USA. Both the real and imaginary parts of the complex permittivity and permeability of the sample were measured by a vector network analyzer system (HP8722ES). Tensile strength measurements at room temperature were carried out on a universal tensile tester (INSTRON 5567). The strain rate was 0.5mm • min^{-1} in all experiments. The water content and electrical conductivity test under different humidity were measured in constant temperature and humidity chamber (Noske-Kaeser KSP 252)

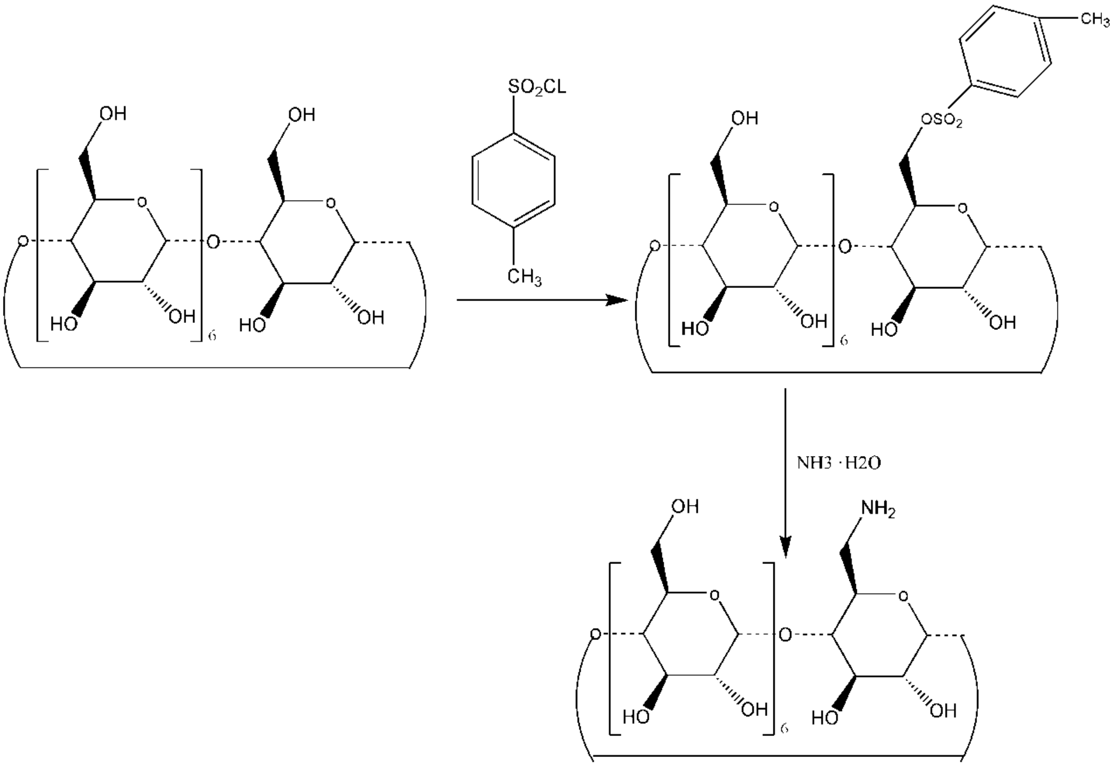
Experimental details

Mono-6-deoxy-6-amino—cyclodextrin(6-NH2-β-CD).[1]

β-Cyclodextrin (120.0 g, 105.8 mmol) was dispersed in 1000 ml deionized water, and 40 ml NaOH (13.14 g, 328 mmol) aqueous solution was added dropwise slowly. The suspension became homogeneous and slightly yellow before the addition of NaOH aqueous solution was completed. *p*-Toluenesulfonyl chloride (20.16 g, 105.8 mmol) in 60 ml of acetonitrile was added dropwise over 10 min, causing immediate formation of a white precipitate. After vigorous stirring for 6 h at room temperature, diluted HCl (1 mol/L) solution was added dropwise until the reaction solution was adapted to pH=8 to terminate the reaction. Product solution refrigerated overnight at 4 ^oC, then the white precipitate was obtained. The white precipitate was recovered by suction filtration and then it was in diethyl ether (Et_2O) for 48 h to remove the unreacted *p*-Toluenesulfonyl chloride. After recovered by suction filtration, the white precipitate was further purified by recrystallization from deionized water. We got 6-OTs-β-CD. ^{1}HNMR (600

Hz, DMSO), 2.41(s, 3H, Ar-CH_3)4.30–4.50 (m, 7H, O(6)H of -CD), 4.75–4.90 (m, 7H, C(1)H of -CD), 5.60-5.78 (m, 14H, O(2)H and O(3)H of -CD), 7.4-7.7 (Ar-H).

Powdered 6-OTs-β-CD was dissolved in a substantial excess of ammonia at 75 °C. After stirring for 4 h at 75 °C, the reaction solution was cooled to room temperature. Added appropriate amount of acetone into the solution, a mass of white precipitate separated out immediately. After recovered by suction filtration, the white precipitate was dissolved in mixed solution of H_2O/CH_3OH (v/v=3:1) and precipitated by acetone. This operation was repeated several times to remove the unreacted 6-OTs-β-CD and ammonia. The white precipitate was recovered by suction filtration and dried at 50 °C in vacuum for 3 day. We got 6-NH_2-β-CD. ^{1}HNMR (600 Hz, D_2O) 5.01–5.07 (m, 7H, C(1)H of -CD), 3.5-4.0 (m, CD-H), 3.51 (t, 1H); 3.08 (d, 1H, H-6^A); 2.85 (d, 1H, H-$6'^A$).[2]

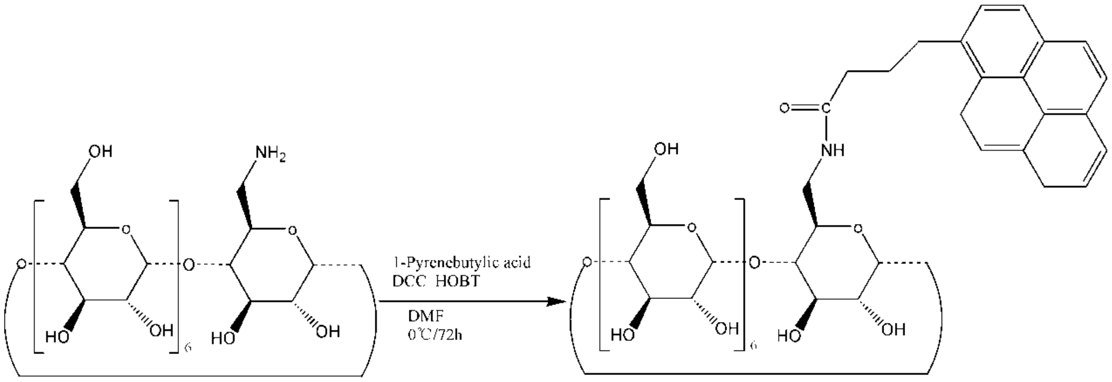


Scheme S1. The synthetic route of 6-NH_2-β-CD.

Synthesis mono-6-(2-pyrenebutylamino)-6-deoxy-β-CD (Py-β-CD).[3]

To DMF solution (15 mL) including 6-NH_2-β-CD (1500 mg, 1.32 mmol) and 1-pyrenebutylic acid (760 mg, 2.62 mmol), DCC (1500 mg, 7.28 mmol) and HOBt (500 mg, 3.7 mmol) were added at 0 °C under argon atmosphere (Scheme S2). The temperature of the mixture was allowed to rise at room temperature and the reaction mixture was stirred overnight. After removal of insoluble salts by filtration, the filtrate was reprecipitated using acetone. The precipitate was washed with water several times to remove 6-NH_2-β-CD. After drying under vacuum, Py-β-CD was obtained. ^{1}H NMR (600 MHz, DMSO-d6) δ2.00 (m, 2H, -$CH_2CH_2CH_2$-), 2.29 (t, 2H, -CH_2CO-), 3.00–3.84 (m, β-

CD and 2H, Py-$CH_2CH_2CH_2$-), 4.40–4.50 (m, 7H, O(6)H of β-CD), 4.78–4.90 (m, 7H, C(1)H of β-CD), 5.65–5.74 (m, 14H, O(2)H and O(3)H of β-CD), 7.66 (br, 1H, -CONH-), 7.92–8.34 (m, 9H, pyrene group). ^{13}C NMR (100 MHz, DMSO-d6) δ173.02 (C of –CONH-), 137.07, 131.34, 130.90, 129.75, 128.63, 127.92, 126.95, 125.41, 125.27, 124.7, 123.96 (C of pyrene group), 102.48 (C(1) of β-CD), 82.13 (C(4) of β-CD), 73.51 (C(3) of β-CD), 72.89 (C(2) of β-CD), 72.51 (C(5) of β-CD), 60.38 (C(6) of β-CD), 35.24(C of –CH_2CH_2CO-), 32.67(C of Py–$CH_2CH_2CH_2$-), 27.96 (C of Py–$CH_2CH_2CH_2$-). Mass Spectrum m/z = 1427 (M+Na), m/z = 1403 (M-H). FT-IR (KBr) 3329cm^{-1}(s, —OH), 1647cm^{-1}(s, C=O).



Scheme S2 . The synthesis strategies for pyrene-labelled β-cyclodextrin (Py-β-CD).

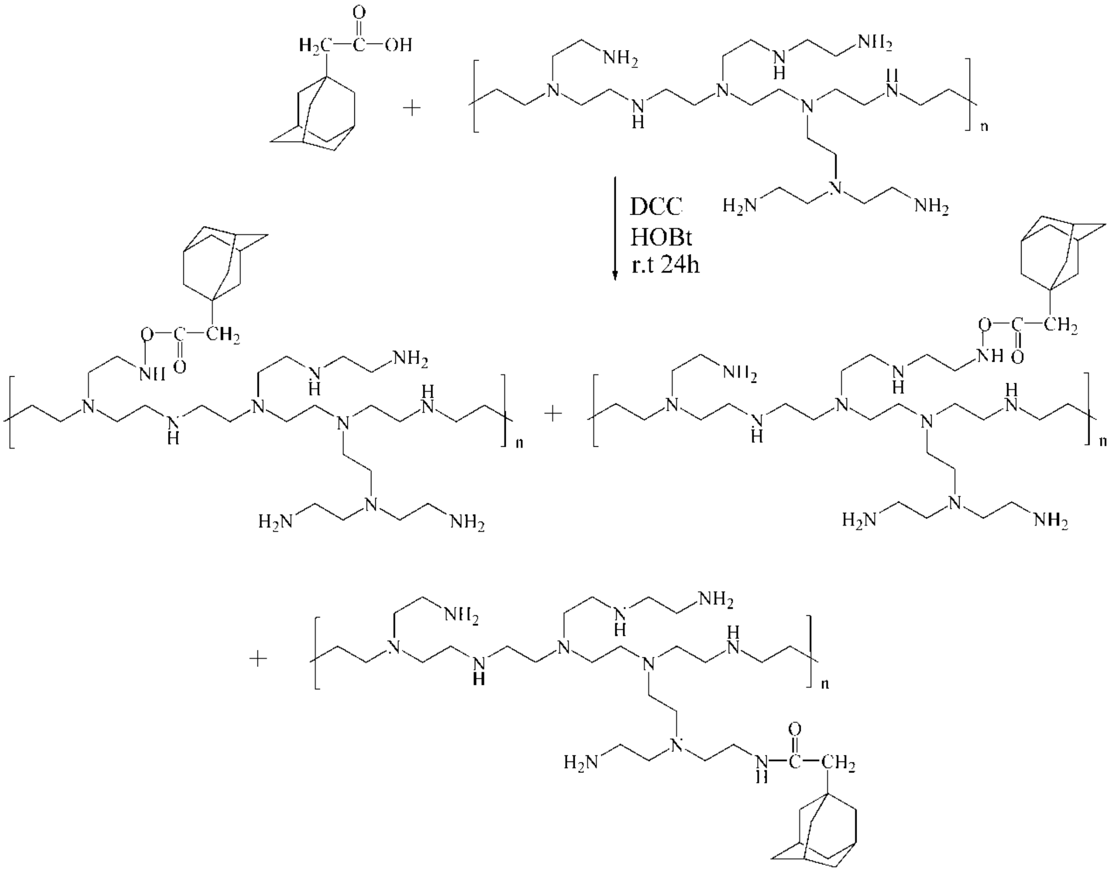
Immobilization of Py-β-CD onto SWNTs.

According to the literature previously reported.[3] Py-β-CD (1533 mg, 1.09 mmol) was dissolved in 0.1M NaOH. To the mixture, SWNTs (500 mg) was added and sonicated in ultrasonic bath (KQ-300DE) for 4 h, followed by centrifugation. The supernatant was dialyzed against 0.1M NaOH for a week to remove excess free Py-β-CD from the solution. And dialyzed against deionized water for three days to remove Na^+, followed by centrifugation. The precipitate was lyophilization by Freeze Drying Equipment.

Synthesis of polyethylenimine (PEI) oligomer grafted adamantane (PEI-Ad).

PEI-Ad were synthesized through esterification (Scheme S3). The dried dichloromethane solution (30 mL) including Ad-CH_2-COOH (1166.9 mg, 6 mmol) and PEI (M=1800, 2700.3 mg, 1.5 mmol), DCC (2472.5 mg, 12 mmol) and HOBt (810.8 mg, 6 mmol) were added at 0 °C under argon atmosphere. The temperature of the mixture was allowed to rise at room temperature and the reaction mixture was stirred overnight. After concentrated by Rotary evaporator, the concentrated solution was dissolved in solution of H_2O/diethyl ether (v/v=1:10) aiming to extraction and separation. We got aqueous solution of product. This operation was repeated several times to remove the unreacted Ad-CH_2-COOH and DCU. The aqueous solution of product was lyophilization by Freeze Drying Equipment. ^{1}HNMR (600MHz, $CDCL_3$) δ1.58 (m, 12H, C(1) and C(3) of AD), 1.92 (m, 5H, C(2) and C(4) of AD), 2.60–4.09

(m, 169H, PEI). FT-IR (KBr): ν =3261.10 (ν_s, NH_2–, –NH–), 2924.76, 2848.74 (s, –CH_2–), 1641.66 (C=O bending vibration of –CONH-), 1097.15 (C–N stretching vibration of BPEI), 660.02, 1097.15, 1451.84cm^{-1}(stretching vibration and bending vibration of Ad ring).



Scheme S3. The synthetic route of PEI-Ad.

FTIR and ^{1}HNMR(600 GHZ) were used to characterize the structure and composition of PEI-Ad. By ^{1}HNMR calculating, it can be seen that the integrated peak area (S1) of 169 hydrogen of PEI and the integrated peak area (S2) of 5 hydrogen of Ad, The degree of substitution (DS) of the primary amine on the PEI was accounted by this formula: $DS=(S_2/5)/[(S_1/5) \cdot 0.35]$ (primary amine: secondary amine : tertiary amine=35:35:30) the grafting rate (GR)could be estimated by the following relationship: GR = ((5S2/169S1) = 3.56(meaning one PEI graft 3.56 Ad).

Preparation of SWNTs-β-CD/PEI-Ad complex.

It is known that β-CD could interact with adamantane and its derivatives to form stable inclusion complex.[4] In this study, SWNTs-β-CD/BPEI-Ad complex was prepared by mixing SWNTs-β-CD and PEI-Ad aqueous solution (the molar ratio of β-CD and Ad was 1:5). After fully mixing, the mixture was moulded into a rectangle spline (long • wide • thick=2.5 cm • 0.5 cm • 0.1 cm) and dried 48 h in 40 ºC vacuum.

Preparation of physical mixture of SWNTs-β-CD and PEI-Ad.

Physical mixture of SWNTs-β-CD and PEI-Ad was prepared as a control sample using the similar method for preparation of SWNTs-β-CD/PEI-Ad complex, but using chloroform (without water) instead of water as solvent. It is known that the self-assembly between CD and guest moiety can't occur without water.[5] The resulting products are powders.

Mechanical measurement.

Mechanical tensile-stress experiments were performed using on a universal tensile tester (INSTRON 5567). We tested three samples. Tensile experiments were performed at room temperature (25 ºC) at a speed of 0.5 $\text{mm}\cdot\text{min}^{-1}$. Tensile-stress experiments of self-healing samples were performed at room temperature with three samples.

The water content and electrical conductivity measurement under different humidity.

The samples were tested using the constant temperature and humidity chamber (Noske-Kaeser KSP 252). Completely dried samples were placed in the chamber at different humidity values at 25 ºC for 24 h. The samples were weighed using an analytical balance before and after into the chamber, getting the weight of the difference, in order to calculate the water content of the sample. The sample was connected in a circuit with a commercially available light emitting diode (LED) bulb and calculated the resistance at different humidity.

Electromagnetic wave absorption properties of the SWNTs-β-CD/PEI-Ad complex.

Both the real and imaginary parts of the complex permittivity and permeability of the sample were measured by a vector network analyzer system (HP8722ES) in the frequency range of 2–18 GHz. The sample obtained by mixing SWNTs-β-CD/PEI-Ad complex with molten paraffin (4:1) was made into a ring of 7.00 mm×3.04 mm×3.00 mm (outer diameter×inner diameter×thickness) for electromagnetic parameters measurement. According to transmission line theory, the reflection loss (RL) curves were calculated from the relative permeability and permittivity at given frequency and absorber thickness with the following equations:[6]

$$Z_{in} = Zo\sqrt{\frac{\mu_r}{\varepsilon_r}}\tanh\left|j\left(\frac{2\pi fd}{c}\right)\sqrt{\mu_r\varepsilon_r}\right| \tag{1}$$

$$RL = 20Log\left|{Z_{in} - Zo}\middle/{Z_{in} + Zo}\right| \tag{2}$$

Where f is the frequency of the electromagnetic wave, d is the thickness of an absorber, c is the velocity of light, Z_0 is the impedance of air, and Z_{in} is the input impedance of absorber.

Characterization

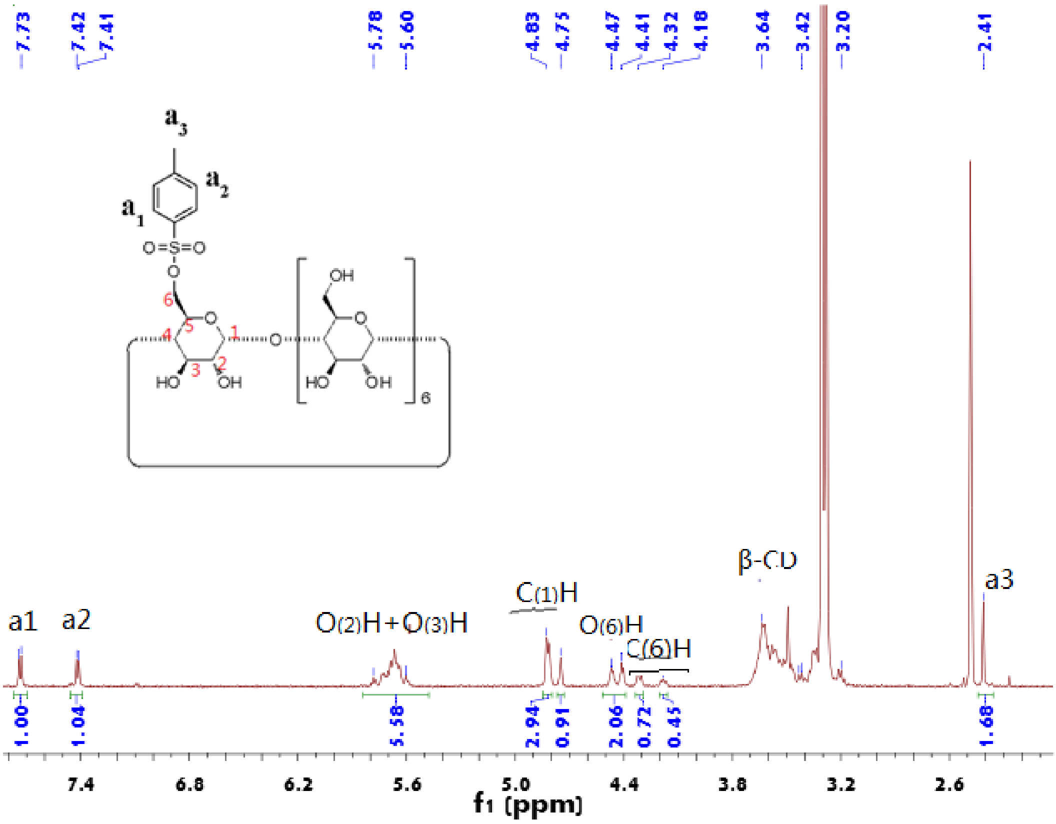


Fig. S1 ^{1}HNMR spectrum (600 MHz) of 6-OTs-β-CD in DMSO.

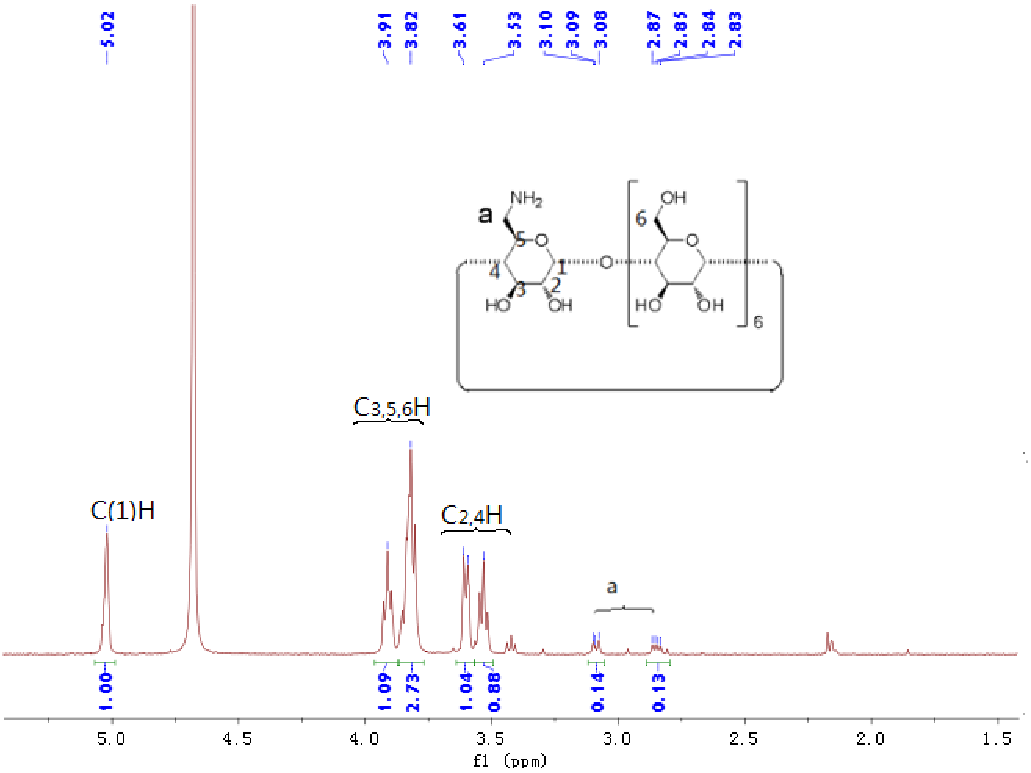


Fig. S2 ^{1}HNMR spectrum (600 MHz) of 6-NH$_2$-β-CD in D$_2$O.

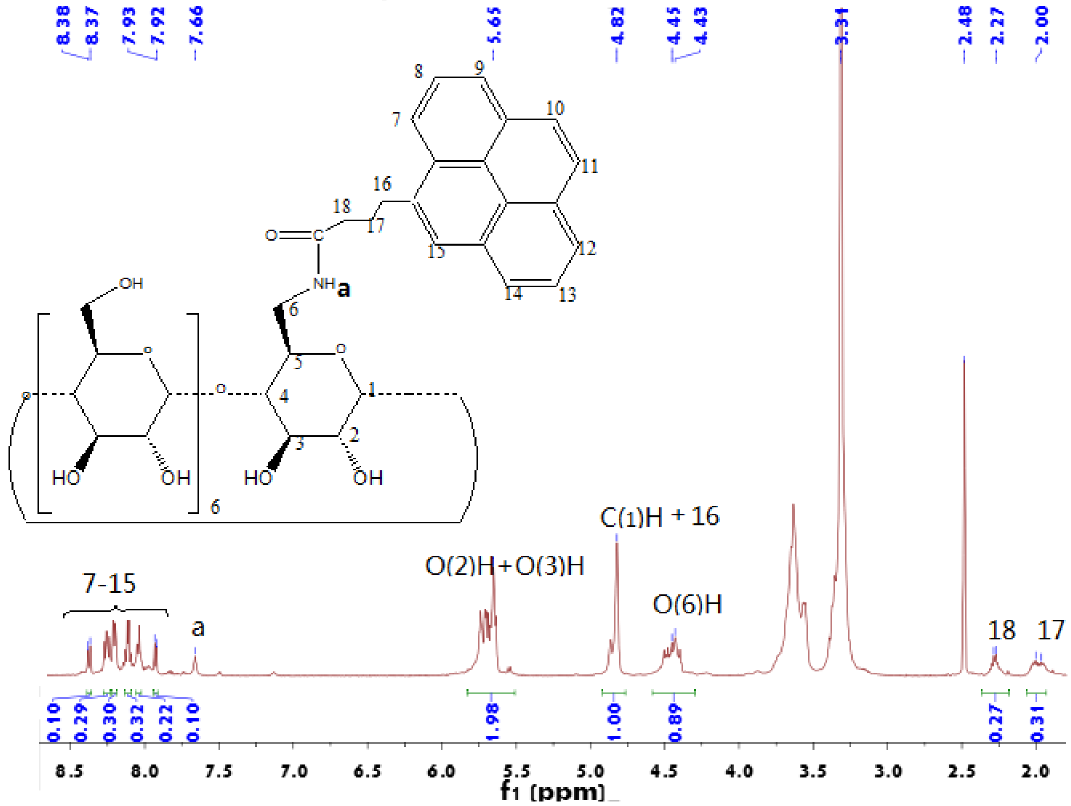


Fig. S3 ^{1}HNMR spectrum (600 MHz) of Py-β-CD in DMSO.

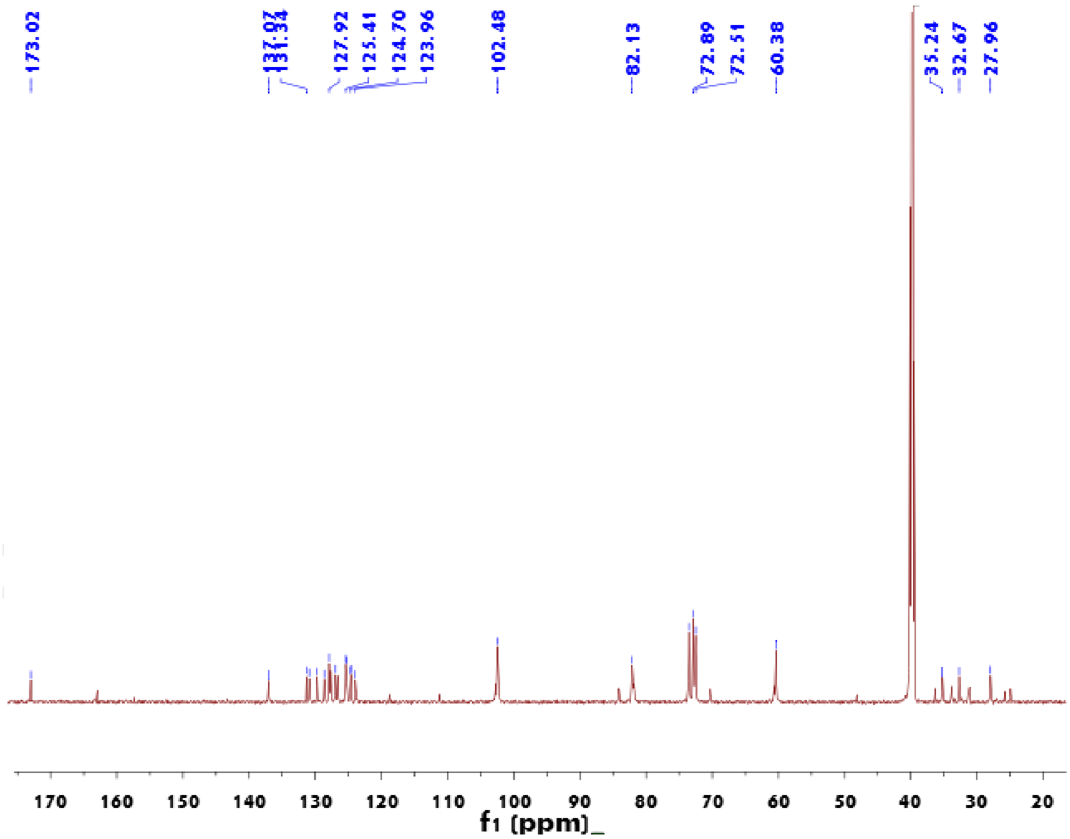


Fig. S4 ^{13}C NMR spectrum (100 MHz) of Py-β-CD in DMSO.

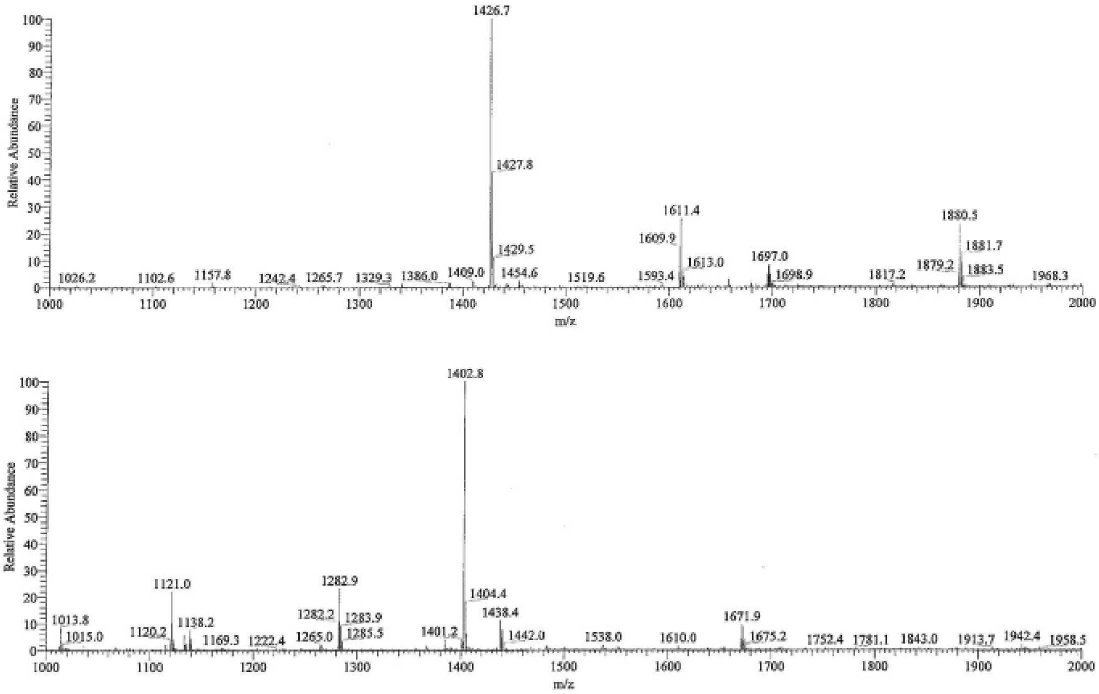


Fig. S5 Mass spectrum of Py-β-CD in DMSO.

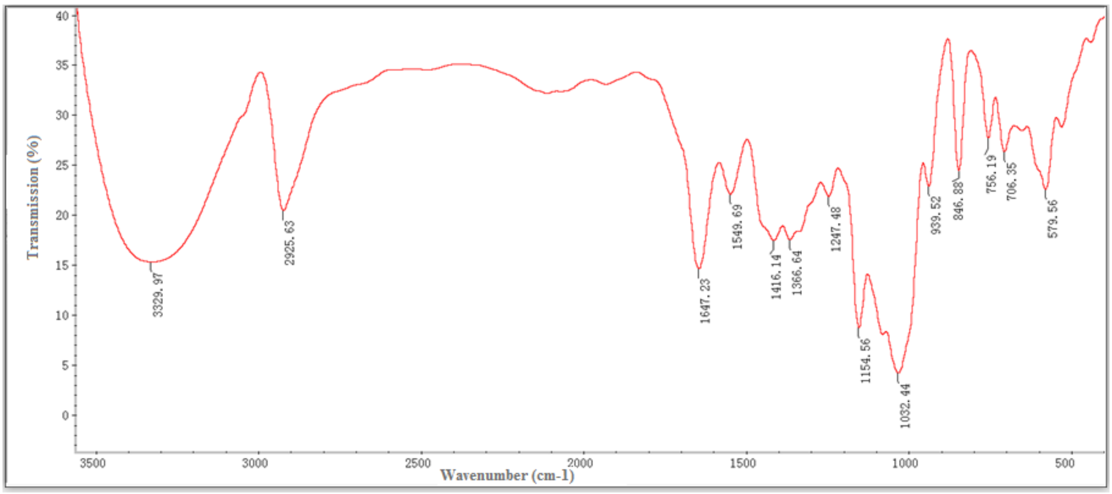


Fig. S6 FT–IR spectrum of Py-β-CD.

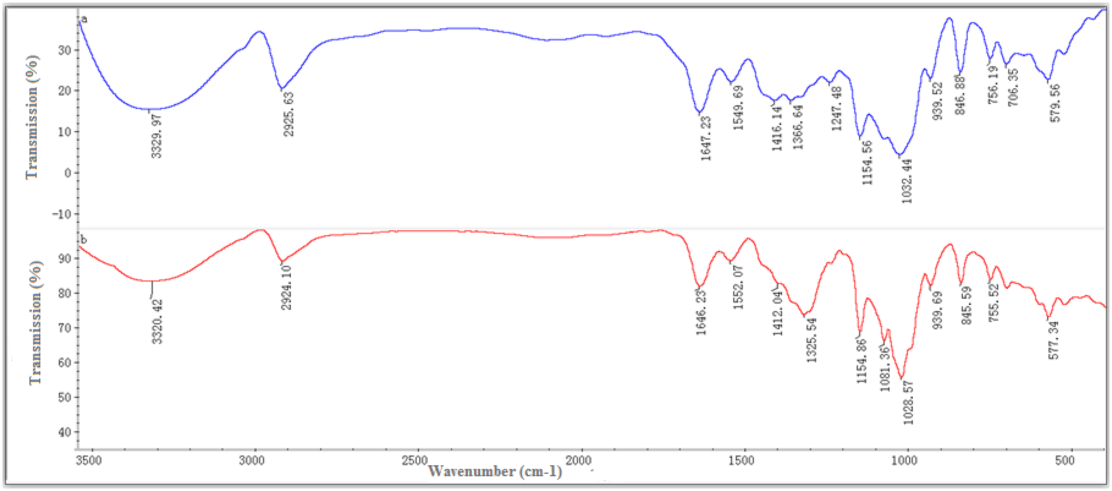


Fig. S7 FT-IR spectrum of (a) Py-β-CD, (b) Py-β-CD/SWNT.

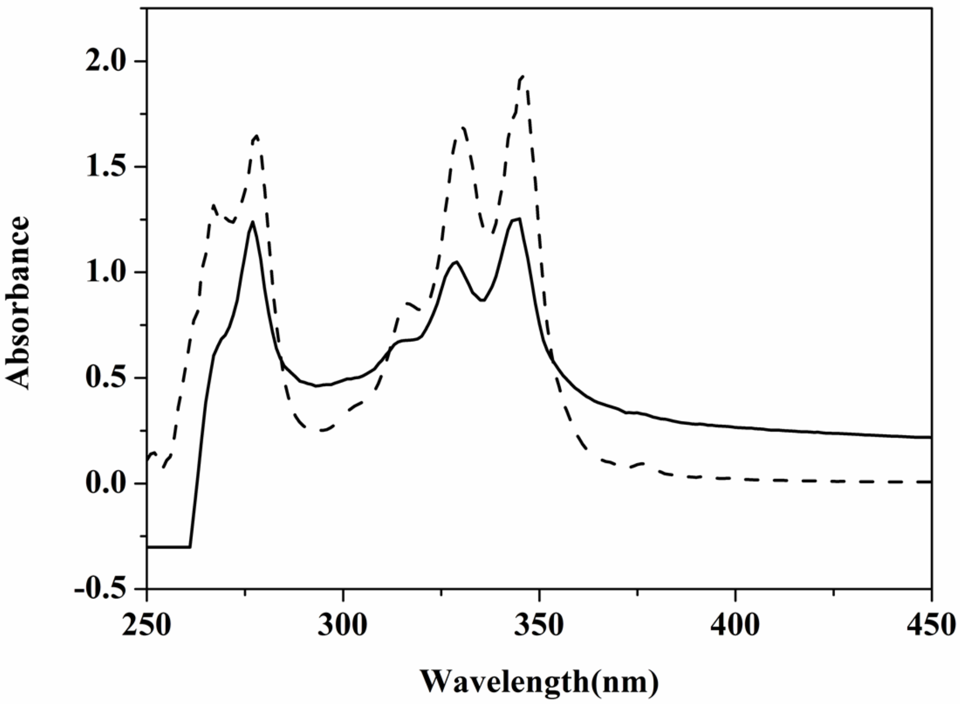


Fig. S8 UV-vis-NIR spectrum Py-β-CD (dash line) and SWNTs-Py-βCD (solid line).

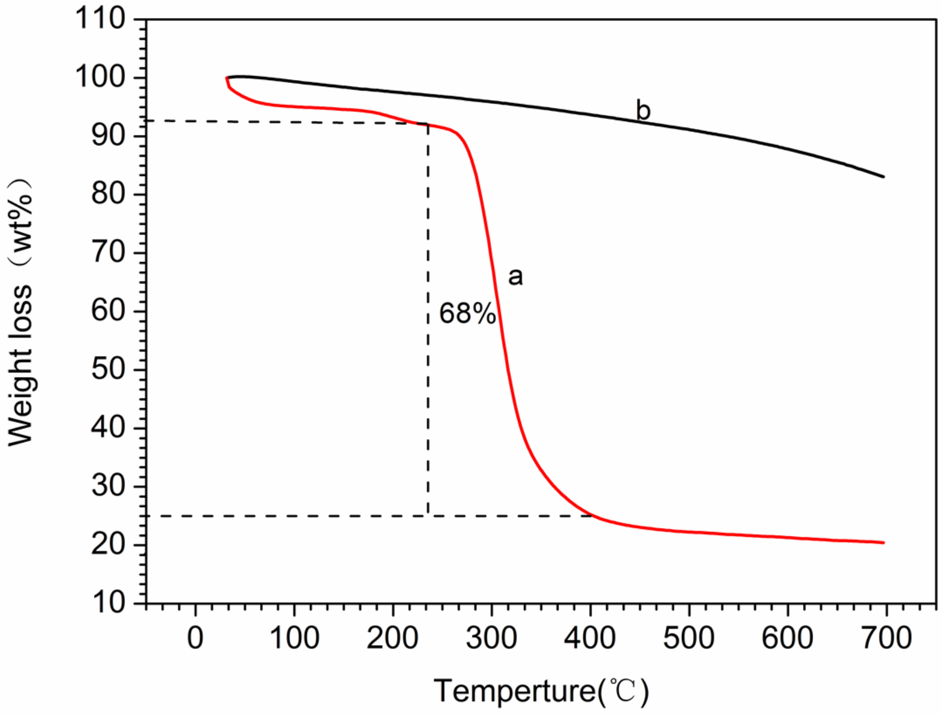


Fig. S9 TGA study of (a) SWNTs-Py-βCD Hybrids and (b) SWNT.

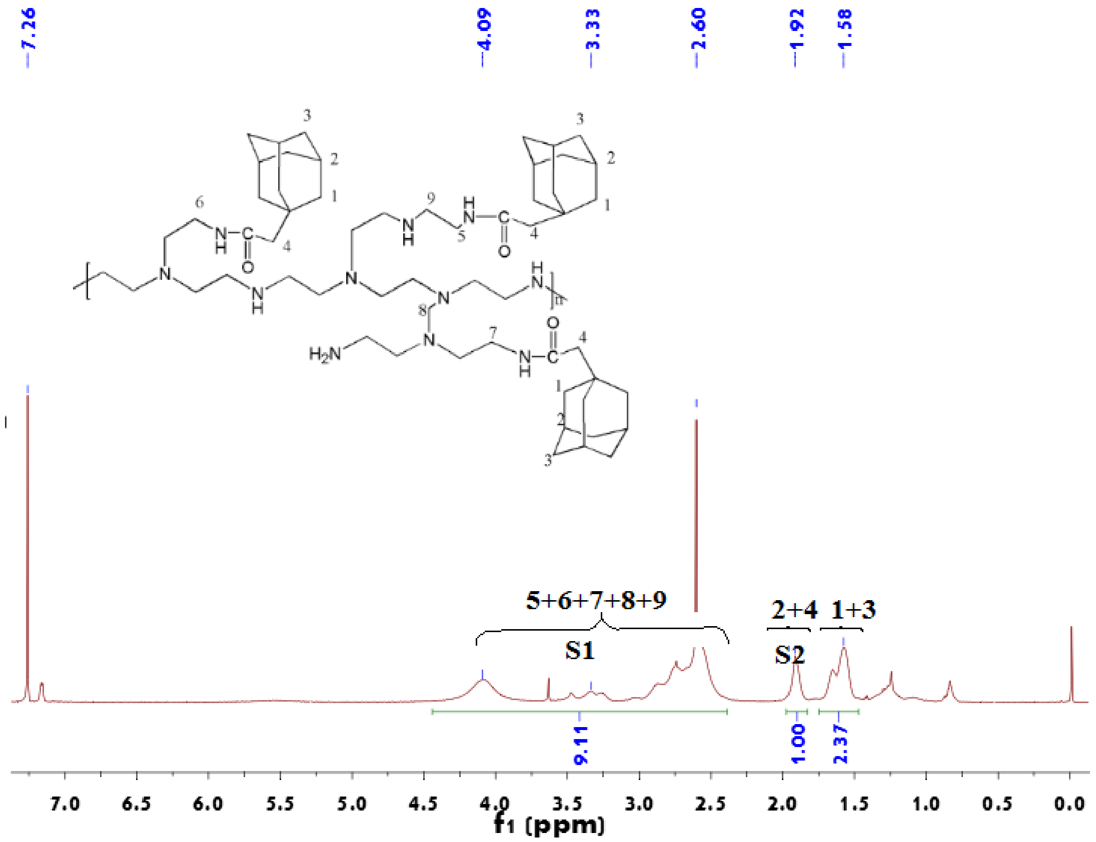


Fig. S10 ^{1}HNMR spectrum (600 MHz) of PEI-Ad in $CDCl_3$.

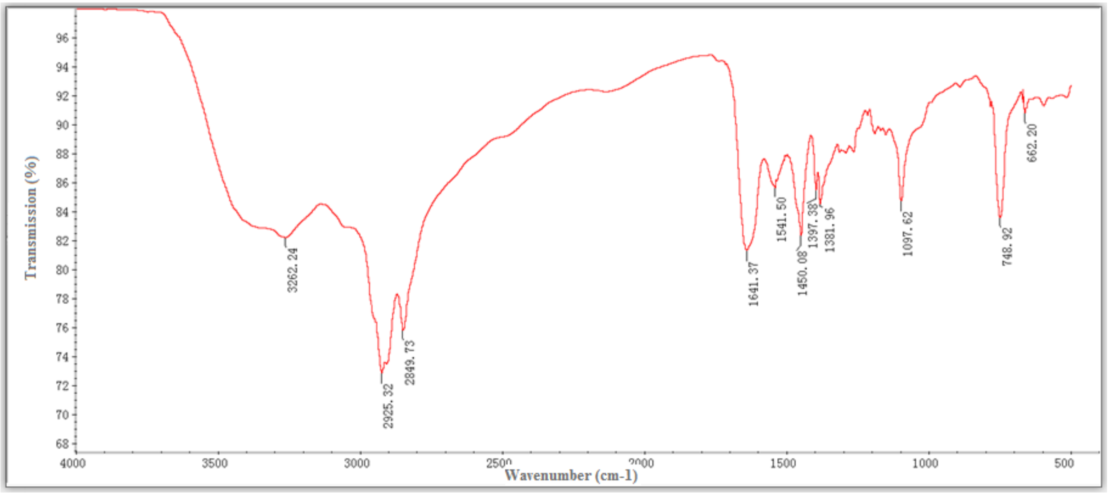


Fig. S11 FT–IR spectrum of PEI-Ad.

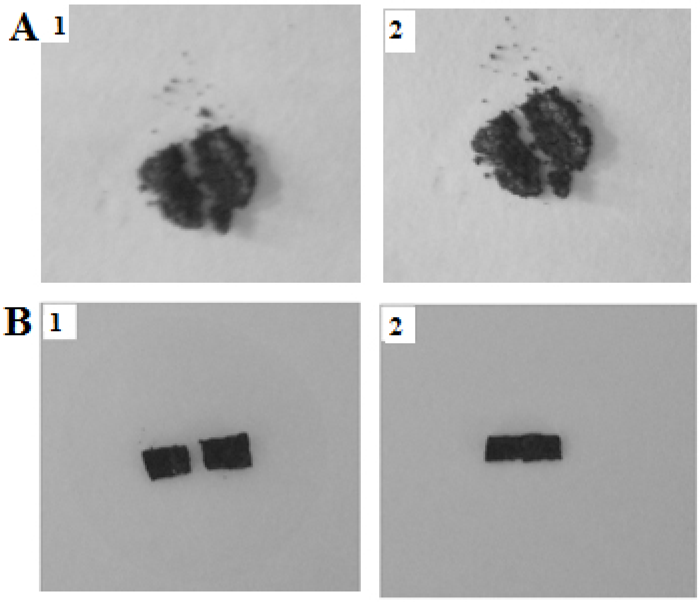


Fig. S12 (A) The sample was soaked in β-CD saturated solution for 48h. (1) Remove the solvent and drying in the vacuum drying oven; (2) Added β-CD saturated to the cut plane of the complex, the sample cannot self-healing; (B) The sample was soaked in water for 48h. (1) Remove the solvent and drying in the vacuum drying oven; (2) Added a little of water to the cut plane of the complex, the sample realize self-healing.

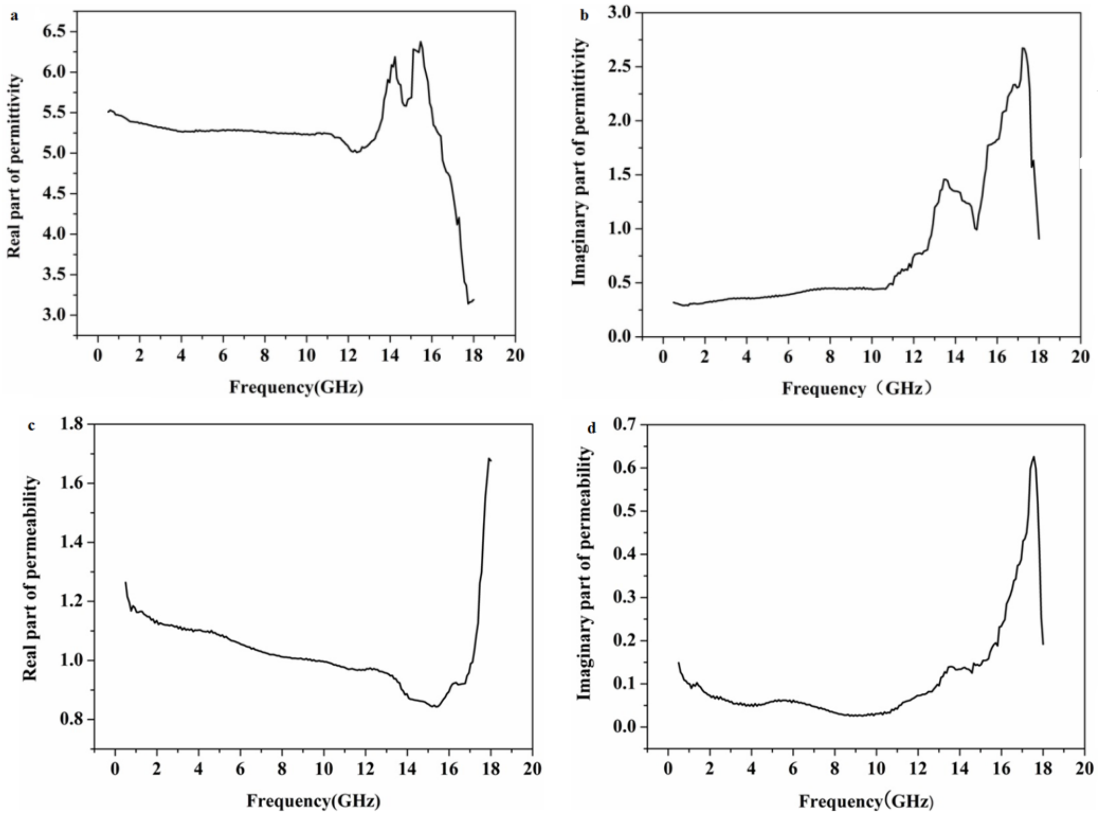


Fig. S13 The frequency dependence of complex permittivity and permeability: (a) the real part of permittivity; (b) the imaginary part of permittivity; (c) the real part of permeability; (d) the imaginary part of permeability.

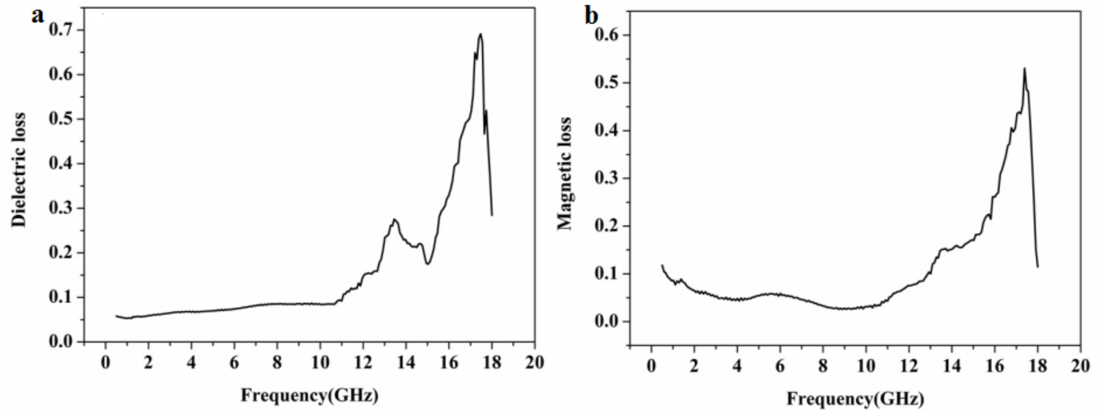


Fig. S14 (a) The dielectric loss of permittivity; (b) The magnetic loss of permeability.

Microwave absorption may result from dielectric loss and/or magnetic loss. They are characterized with the complex relative permittivity ε_r ($\varepsilon_r=\varepsilon'-\varepsilon''$, where ε' is the real part, ε'' is the imaginary part) and the complex relative permeability μ_r ($\mu_r=\mu'-\mu''$, where μ' is the real part, μ'' is the imaginary part).[7] The relation between them and frequency have been studied in Fig. S13. It can be seen that both the dielectric loss of permittivity and the magnetic loss of permeability at near 17 GHz has the largest values and an peak at 13 GHz (Fig. S14).

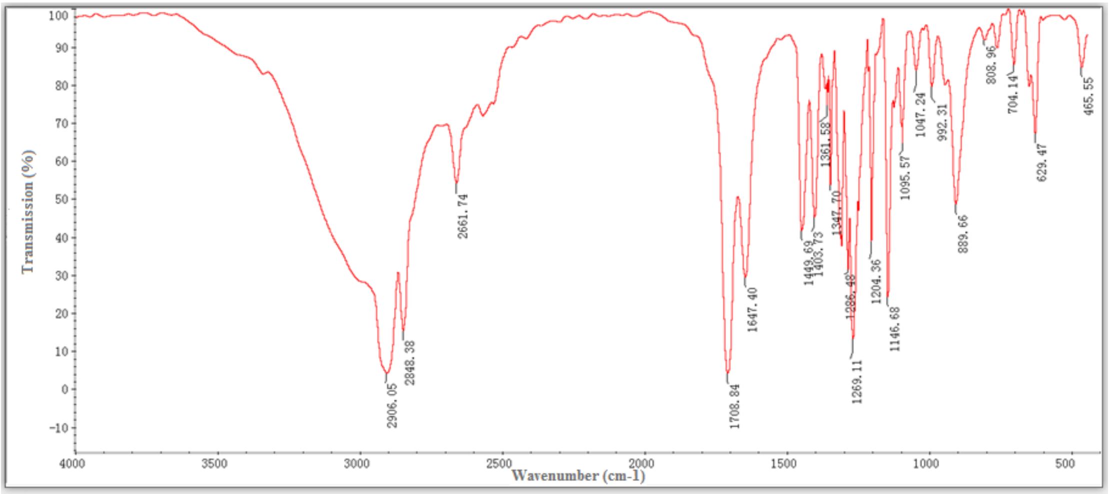


Fig. S15 FT–IR spectrum of Ad-CH_2-COOH.

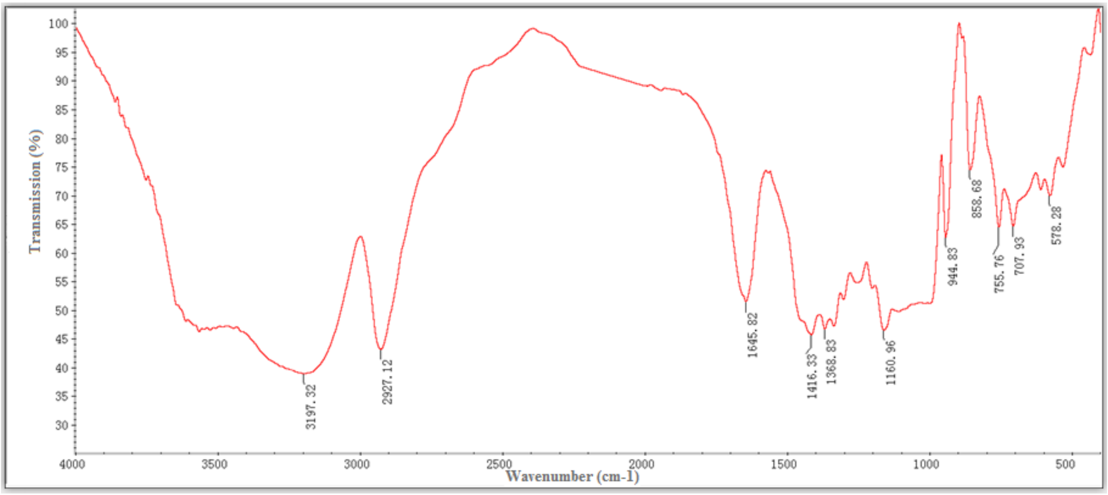


Fig. S16 FT –IR spectrum of β-CD.

"Glue" the other parts of material together

Water is also able to "glue" the other parts of material together, just like other water-healing materials. It was found that the conductive “healing efficiency” of other parts also near 100 %. However, the mechanical self-healing efficiencies of other parts of sample were not stable. Unlike the fractured surfaces, the surfaces of other parts did not match well. It seems that the matching degree affected the mechanical self-healing efficiency. And because the different parts having different matching degree, it is hard to get precise data. The Fig.S17 showed the “healing” results of other parts of SWNTs-β-CD/PEI-Ad composite. It can be seen that two parts were able to glue together partially by water indeed, however, there was a clear scar at the interface.

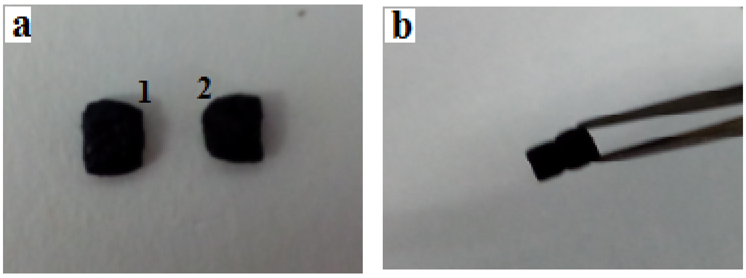


Fig. S17 (a) 1 and 2 are not fractured interfaces (1 interface is larger than that 2); (b) "glue"1 and 2 together.

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