

Electrospun UV-responsive Supramolecular Nanofibers from Cyclodextrin-Azobenzene Inclusion Complex

Menglin Chen,^{*a} Søren Rosegaard Nielsen,^a Tamer Uyar,^b Shuai Zhang,^a Ashar Zafar,^c Mingdong Dong^a and Flemming Basenbacher^{*a}

Supporting Information

Experimental Section

Materials:

HP β CD was obtained from Wacker Chemie AG (Germany) and 4-aminoazobenzene (AAB) was purchased from Sigma-Aldrich (Germany). The water used was purified by a Millipore Milli-Q Ultrapure water system.

Preparation of HP β CD/AAB Inclusion Complex:

AAB was dispersed in water and stirred at 50°C for 0.5 h. HP β CD was then slowly added to the dispersion under vigorous stirring at 50°C in 1 to 2 h. All the AAB was dissolved and clear orange solutions were obtained.

Electrospinning:

The clear ICs solutions were placed in a 1 ml syringe fitted with a metallic needle of 0.6 mm inner diameter. The syringe was fixed horizontally on the syringe pump (Model: KDS101, KD Scientific), and an electrode of high voltage power supply (Spellman High Voltage Electronics Corporation, MP Series) was clamped to the metal needle tip. The flow rate of polymer solution was 1 ml/h, and the applied voltage was 18 kV. The tip-to-collector distance was set to 12 cm, and a grounded stationary rectangular metal collector (15 cm \times 20 cm) covered by a piece of clean aluminum foil was used for the fiber collection.

UV irradiated during electrospinning was supplied by a Spectroline Optimax 365 LED UV lamp.

Measurements and Characterization:

The fiber morphology was examined by high resolution scanning electron microscopy (SEM) (FEI, Nova 600 NanoSEM) at 5 kV. The mats were placed directly into the SEM chamber without any metal sputtering or coating.

Time-of-flight secondary ion mass spectroscopy (ToF-SIMS) analysis was performed using an ION-TOF TOF SIMS 5 instrument equipped with a Bi primary ion cluster source operating at 25 kV. In most cases, Bi³⁺ primary ions were used with a target current of 0.3 pA. High-resolution mass spectra ($M/\Delta M > 4000$ at $m/z = 27$) were acquired using the high current bunched mode.

High mass resolution spectra were obtained by the use of bunched primary ions. The analysis area was 500 μm by 500 μm . Only positive secondary ion spectra were acquired, and mass calibration of the spectra was based on CH₃⁺, C₂H₃⁺, and C₃H₅⁺ ions. Chemical imaging was performed with the burst alignment mode, which offers a high spatial resolution but low mass resolution. Due to the low mass resolution, chemical imaging was based only on peaks unambiguously identified from high mass resolution spectra over a specified area. In all cases, an electron flood gun was for charge compensation and the primary ions dose was kept below 10¹² ions/cm² to stay within the static SIMS regime. PCA of the ToF-SIMS spectra was performed using the PLS Toolbox v.5.2.1 (Eigenvector Research Inc.) for Matlab (the MathWorks Inc). Before applying PCA, a dataset was created by selecting all the peaks above 50 counts over the mass range of 0 to 300 u. Before the analysis, the peaks were normalized to the total intensity of all the peaks and the data set was mean centered.

The infrared spectra of the samples were obtained by using a Fourier transform infrared spectrometer (FTIR) (Bruker-VERTEX 70, Germany). The samples were mixed with potassium bromide (KBr) and pressed as pellets. The scans (64 scans) were recorded between 4000 and 400 cm⁻¹ at a resolution of 4 cm⁻¹.

The X-ray diffraction (XRD) (PANalytical X'Pert Powder Diffractometer, Netherlands) data of the AAB, HP β CD and HP β CD/AAB-IC nanofibers were recorded by using Cu K α radiation in a range of $2\theta = 5^\circ - 30^\circ$.

Differential scanning calorimetry (DSC) (TA Q2000, USA) and thermogravimetric analyzer (TGA) (TA Q500, USA) were used for the investigation of the thermal properties of the samples. DSC analyses was carried out under N₂; initially, samples were equilibrated at 0 °C and then heated to 200 °C at a heating rate of 10 °C/min. TGA of the samples was carried out from 25 °C to 450 °C at 20 °C/min heating rate and N₂ was used as a purge gas.

AFM based Quantitative Nanomechanical Mapping:

UV response experiments were carried out using Spectroline Optimax 365 LED UV lamp (365 nm, $I_{UV} = 15 \text{ mWcm}^{-2}$) for 4 hr.

All of the AFM images were recorded with Peakforce Tapping mode in a commercial Nanoscope VIII MultiMode SPM system (Bruker, Santa Barbara, CA) under ambient conditions (Temperature 24 °C; humidity 44%). Ultrasharp silicon tips (triangular, TESP-SS, Bruker) were used with a typical resonance frequency between 320-400 kHz in air, a spring constant of 20-40 nN/nm and a normal tip radius of 2-5 nm. All AFM images were recorded with 1-2 nm/pixel resolution, and they were flattened and analysed with offline software Scanning Probe Image Processor (SPIPTM, Image Metrology ApS, version 5.1.3, Lyngby, Denmark) and NanoScope Analysis (Bruker, Santa Barbara, CA).

FTIR:

The FTIR spectra of pure AAB, HP β CD and HP β CD/AAB-IC nanofibers are depicted in Figure S1. In the FTIR spectrum of the HP β CD, the salient absorption bands at around 1020 cm⁻¹ and 1070 cm⁻¹ correspond to the coupled C–C and C–O stretching vibrations and the absorption band at around 1150 cm⁻¹ attributed to the anti-symmetric stretching vibration of the C–O–C glycosidic bridge. The FTIR spectrum of AAB indicates the characteristic peaks

at 1618, 1597, 1504, 1415, 1306 and 1140 cm^{-1} .^[20] While 1618 and 1504 cm^{-1} correspond to the tangential C–C stretching in benzene ring, the in-plane N–H deformation occurs at 1597 cm^{-1} . The N=N vibrations are observed near 1415 cm^{-1} and the absorption around 1306 cm^{-1} is assigned to C–N stretching vibrations. Finally, the peak absorbed at 1140 cm^{-1} belongs to NH_2 rocking vibration mode. The HP β CD/AAB-IC nanofibers exhibit the characteristic peaks of AAB which shifted from 1597 to 1602 cm^{-1} and from 1504 to 1508 cm^{-1} . This results from the host-guest interaction between HP β CD and AAB molecules in IC fibers. The other characteristic peaks of AAB are diminished or could not be observed because the IC formation suppresses the molecular vibration of dye molecules in CD cavity, in addition, some of the characteristic AAB peaks overlapped with the HP β CD peaks.

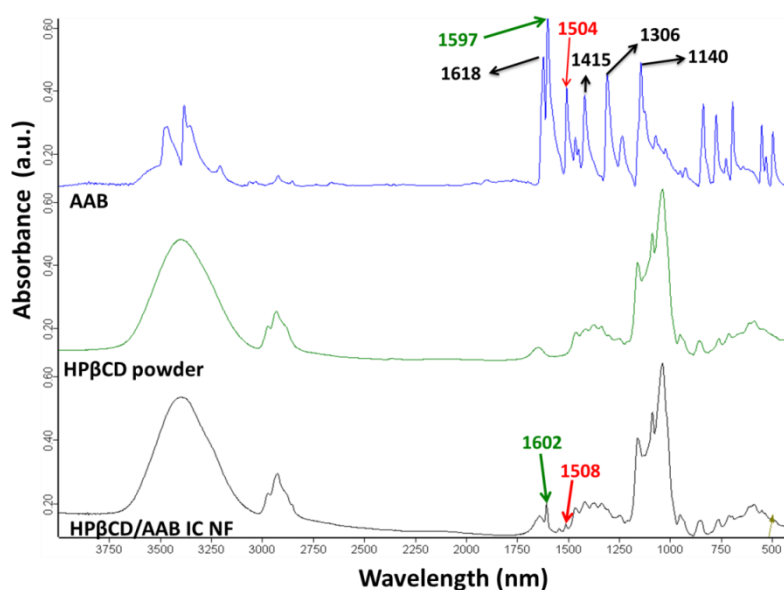


Figure S1. FT-IR spectra of the electrospun HP β CD/AAB-IC mat III and the components AAB and HP β CD.

XRD:

XRD spectra of pure AAB, pure HP β CD and HP β CD/AAB-IC nanofibers are shown in Figure S2. The AAB is a crystalline material having salient diffraction peaks at $2\theta = 16.9^\circ$, 17.9° , 19.5° , 20.4° , 22.1° , 25° , 27.1° and 27.5° , while the XRD patterns of the HP β CD/AAB-

IC mat III are very similar to those of pure HP β CD nanofibers having amorphous structures, consistent with the ToF-SIMS imaging (Figure 3). The XRD results of the HP β CD/AAB-IC fibers show no diffraction pattern for AAB, suggesting that the AAB molecules were included inside the amorphous HP β CD cavities.

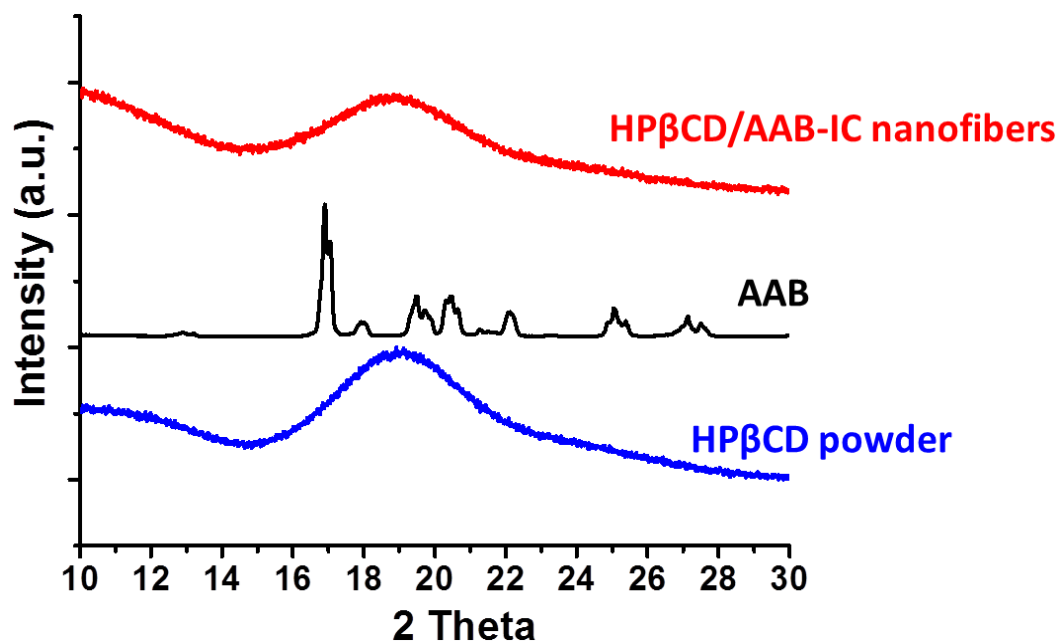


Figure S2. XRD spectra of the electrospun HP β CD/AAB-IC mat III and the components AAB and HP β CD.

UV irradiation prior to electrospinning:



Figure S3. A) UV irradiation prior to electrospinning caused precipitation of AAB from the aqueous IC solution. B) AAB suspension in water.

UV spinning:

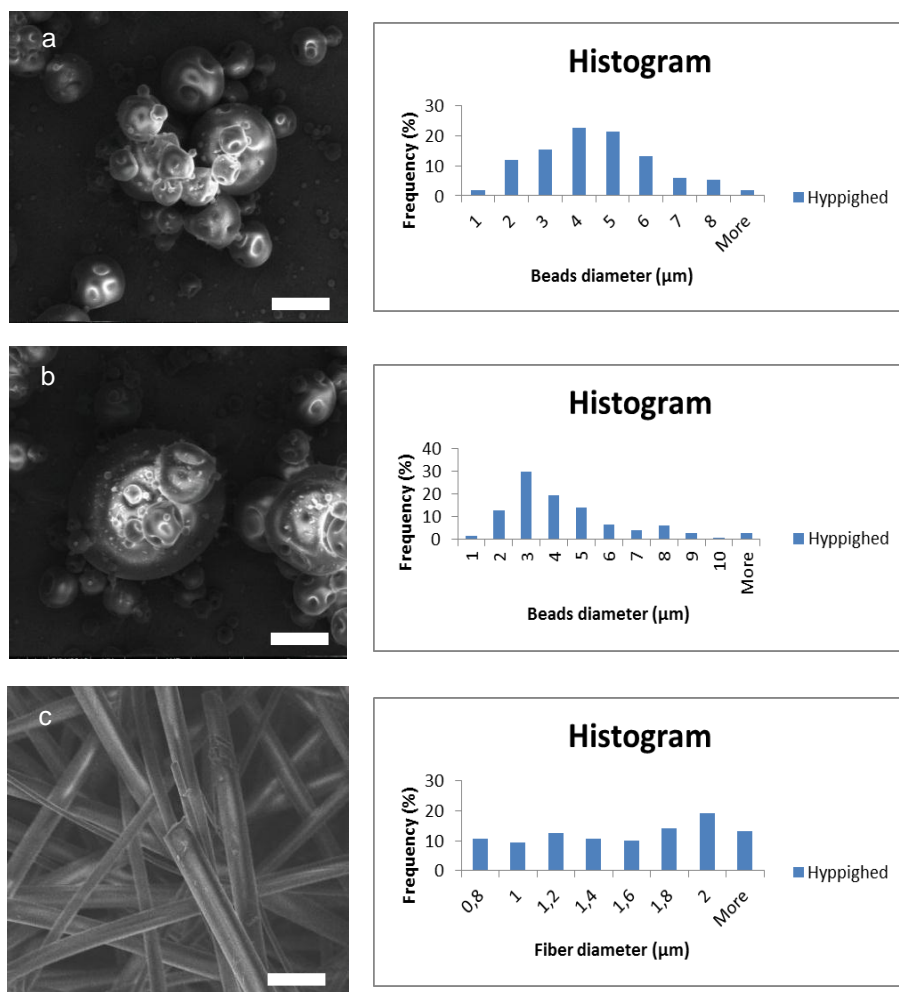


Figure S4. Electrospinning of HPβCD/AAB-IC upon UV irradiation: a) Mat UV-I, b) Mat UV-II and c) Mat UV-III