Supplementary Information

Controlled disassembly of azobenzene cellulose-based thin films using visible light

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1. Experimental methods

1.1. Materials

NaCS was purchased from Scientific Polymer (CAT#023) and BBY was procured from Sigma (LOT 34H3729, C18H18N8.2HCl, FW=419.3 g/mol), and was recrystallized before use. Spectroscopic grade THF was purchased from Sigma (CAS #109-99-9). Sodium chloride salt (CAS#7647-14-5) was purchased from ACP. NaOH pellets (CAS#1310-73-2) were purchased from Sigma and 36% HCl from ACP (LOT # H-6100).   The dipping solutions were prepared by dissolving the chemicals in deionized water (MiliQ system). A 10 mM solution of NaCS (molar in terms of a one monomer repeat unit) was prepared (pH = 6.4) and a 3 mM solution of BBY was prepared (pH = 3). The structures of the polymer and dye used are shown in (Fig. 1).

1.2. LbL assembly of thin films

Multi-layered films of sodium cellulose sulfate-Bismarck Brown Y (NaCS/BBY) were deposited on glass, quartz, and aluminium substrates. All slide surfaces, excluding the aluminium, which was cleaned with water and acetone, were cleaned using a 'piranha solution' (mixture of sulfuric acid/ hydrogen peroxide). The multilayer deposition process was as follows: The treated substrates were immersed in the polymer solution for t = 10 min, followed by three rounds of rinsing with deionized (DI) water (pH = 7) for 1 min each. The films were then immersed in the azo solution for t = 10 min, followed by 3 rounds of rinsing with DI water. This dipping process was repeated to form a film with 50 bilayers. The process of LbL assembly is shown in (Fig. 1).

1.3. Characterization of LbL NaCS/BBY thin films

UV-Vis spectroscopy: The UV-Vis spectra of BBY in water and NaCS in water were recorded on a Cary 300 Bio UV-Vis spectrophotometer, using a Hellma quartz cuvette (Catalog #117-100-10-40) with a pathlength of 1 cm, over the range 200–800 nm. The absorption of BBY in the LbL films was then monitored by UV-Vis spectroscopy of the dye's $\pi \rightarrow \pi^*$ transition peak. This was taken directly from films deposited on glass and quartz slides.

FTIR spectroscopy: The Infrared (IR) spectra of a solvent cast BBY film and multi-layered NaCS/BBY films on an aluminium substrate were acquired on a Bruker Hyperion 1000 microscope coupled with the Bruker Vertex 70 FTIR spectrometer (Catalog #: BOPT Hyperion 1000, BOPT Vertex 70). The IR spectra were recorded in reflectance mode over the range 600 to 4000 cm⁻¹, with a resolution of 2 cm⁻¹ averaged from 64 scans. The Infrared (IR) spectra of powdered BBY and powdered NaCS were recorded on an FTIR spectrometer (Spectrum II, PerkinElmer, USA) with a single bounce diamond attenuated total reflectance (ATR) accessory employed. The IR spectra was recorded in transmittance mode over the range 400 to 4000 cm⁻¹ with a resolution of 1 cm⁻¹ averaged over 32 scans.

Confocal Raman spectroscopy: Raman spectra and optical microscopy images of a solvent cast BBY film, a solvent cast NaCS film and multi-layered NaCS/BBY films on quartz substrates were recorded using a confocal Raman microscope (Alpha 300R, WITEC). Measurements were performed using a 532 nm laser at varying power, 100x objective (Zeiss, numerical aperture [NA] = 0.9) with a thermoelectrically cooled CCD detector behind a 600-g /mm grating, with integration time: 1 s, scan speed: 1 s/μm, and resolution: 1 spectra /μm. Kinetic measurements were performed by monitoring the change in the intensity of the Raman signal near the 1285 cm⁻¹ peak for 50 s, at constant laser power of 0.1 mW, focusing on the same spot.

SEM-EDS: The surface (planar view) of the NaCS/BBY thin films deposited on a glass substrate was imaged by high resolution Field Emission Scanning Electron Microscopy (FE-SEM) using a FEI Quanta 450 Environmental Scanning Electron Microscope with EDAX Octane Super 60mm SDD. Elemental mapping was done using the TEAM EDS analysis system. The accelerating voltage used was

10 kV after sputter coating with platinum with a thicnkess of about 7 nm. Other paramters: resolution: 128.9 eV, mag: 6387 and amplitude time: 7.68 μs.

XPS analysis: the degree of substitution (DS) of NaCS polymer was determined by XPS analysis, performed on a Thermo Scientific K-Alpha, with X-ray source: Aluminium-kα, spot size of 400 μm. Survey scan: pass energy of 200 eV, step size of 1 eV and high-resolution scan (C1s, O1s, S2p, N1s, Na1s): pass energy of 50 eV, step size of 0.1 eV. The software used for data processing was Thermo Avatage (version 5.9914).

Contact angle experiments: the contact angles of the surface of the LbL NaCS/BBY thin films, films of solvent cast NaCS and films of solvent cast BBY on quartz substrates were determined using an optical contact angle goniometer (Model OCA 20, Dataphysics, USA). The sessile drop method was employed, whereby a droplet of water was placed on the sample mounted on a stage, and the image of the drop taken by a high-resolution camera. Images were recorded instantaneously (t = 0 s) and overtime (t = 1 min, 2 min and 4 min) to allow the drop to equilibrate. The contact angle was then determined using the SCA20 software.

1.4. Film stability: ionic strength, temperature, and pH

To evaluate the effect of ionic strength of the 'wash solution' on the stability of the LbL films, films were soaked in 60mL DI water (pH = 7), tap water (pH = 8) and 2M NaCl$_{(aq)}$ at RT for 7 days. To analyze the effect of pH, films were left in 60 mL DI water of varying pH values (= 2, 4, 7, 8, 9,10,11 and 12) to soak for 7 days at RT. The pH of DI water was adjusted using concentrated NaOH and HCl stock solutions. To analyze the effect of heat, films were soaked in 60 mL DI water at RT = 21 °C, 70 °C and 100 °C for 1 hr. The UV-Vis spectra were acquired before and after treatments for all films.

1.5. Pump-probe isomerization experiments

A solution of BBY in THF in a quartz cuvette (pathlength 1 mm) was probed using a tuneable Ar$^+$ laser at λ= 488 nm at low laser power (1 mW/cm^2) and irradiated for 1 s using a 532 nm laser at high laser power (100 mW/cm^2). The signal was recorded before, during and after irradiation. Measurements were performed in triplicate.

1.6. Simulated sunlight & rainfall experiments

'Sunlight and rainfall' conditions were simulated to examine the environmental disassembly of the films by light, as shown in (Fig. 1). The films deposited on glass and quartz substrates were clamped under DI water (pH = 7) or (Montreal) tap water (pH = 8), flow rate = 1 L/min, T = 21–25°C and the bottom section of the films were covered with a black mask. The films were irradiated with visible 460 nm (229 mA, 12.50 V) light. The UV-Vis absorption spectra were recorded from 200–600 nm for quartz slides and 330–600 nm for glass slides. UV-Vis measurements were taken at various intervals. The films were dried under a stream of air for 20 s before each measurement. The simulated sunlight & rainfall experiments were performed in triplicate, and the disassembly rate was calculated according to the equation below:

$$\text{Ln}\left[A_{450\,nm}\right] = -\,kt + \text{Ln}\left[A_{450\,nm}\right]_0$$

1.7. AFM

Atomic Force Microscopy (AFM) was used to determine the thickness of the films. Films were prepared by applying a parafilm mask to the middle of the glass substrate during the dipping process. The mask was removed following film deposition and the masked area cleaned using ethanol to remove any residue. The thickness of the films was measured as the change in height at the boundary of the films. Measurements were performed at 6 different areas along the film's boundary. Surface topology of the bare glass and NaCS/BBY film deposited on glass were also acquired by AFM. AFM measurements were performed on a MFP3D AFM equipped with molecular force probe controller (Asylum Research – Oxford Instruments) in AC mode in air using ACTA (AppNano) probes. Data processed using MountainsSPIP v. 9.1.9837 (digital Surf). Scan specs: resolution (512 x 512), Scan rate (0.5 Hz and 1.0 Hz), scan size 5-50 μm.
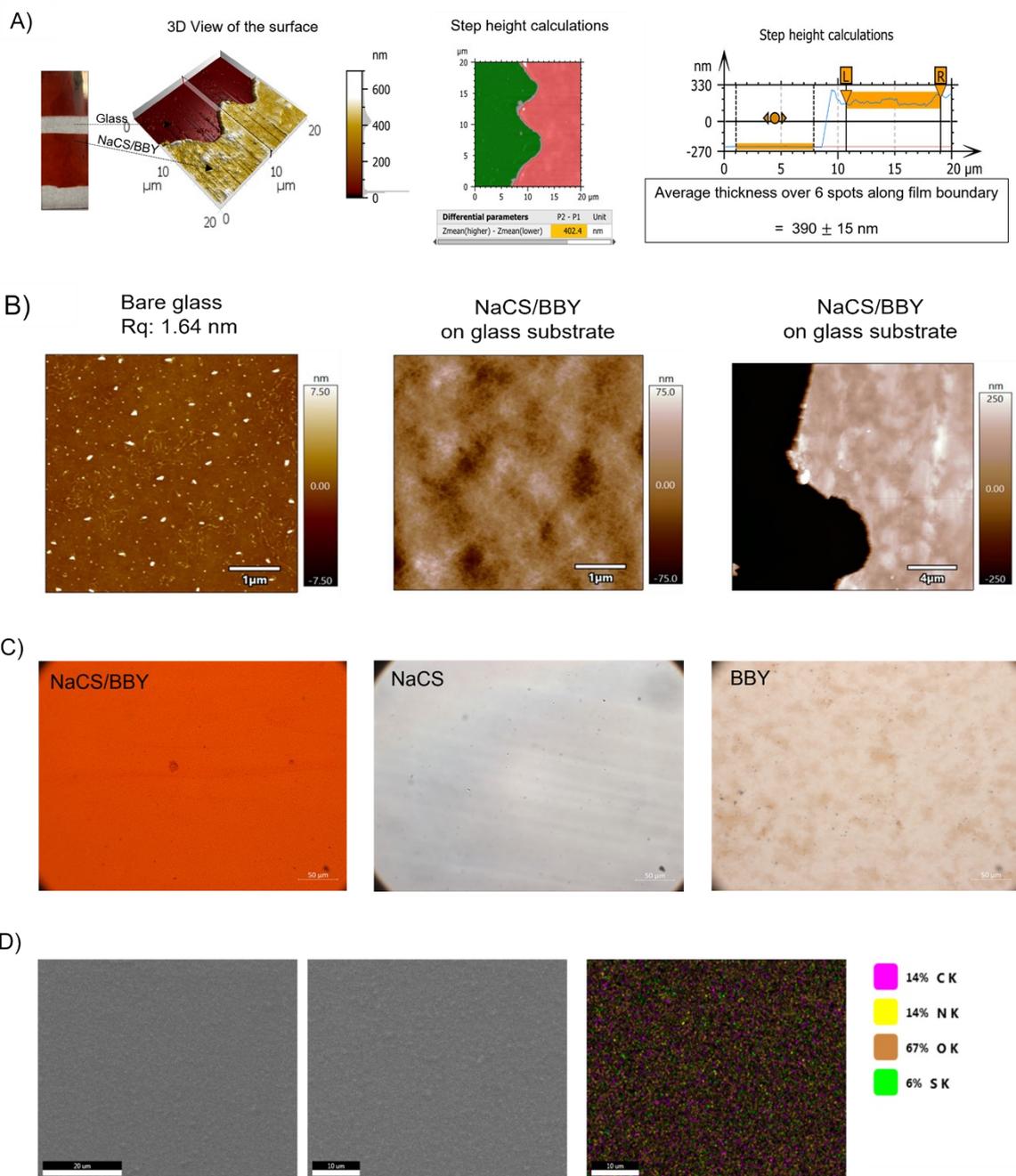
Fig. S1. (A) AFM used to determine the thickness of NaCS/BBY films deposited on glass substrate (Rq: 1.97 nm). (Right) Image of NaCS/BBY thin film (red) deposited on glass substrate (grey) and 3D view of the surface of the thin film (yellow) onto on glass substrate (red). (Middle) Step height calculations between the glass substrate (green) and thin film (red). (Left) Step height calculations along one line of the thin film shown in the top, right figure. Measurement parameters: 20 μm, FAA 1.0 V, SP: 568 mV, IG 5, 0.5 Hz, 512 x 512. (B) AFM of the surface topology of (Left) bare glass substrate (Rq: 1.97 nm) and (Middle) NaCS/BBY deposited on glass substrate showing a fairly uniform surface. (Right) 3D image of surface and edge of NaCS/BBY film deposited on glass substrate. (C) Confocal Raman optical Images of (Left) NaCS/BBY LbL thin film (Middle) NaCS polymer and (Right) BBY azo dye deposited on quartz substrate. Images were obtained using confocal Raman microscope (Alpha 300R, WITEC), 100x objective. Scale bar = 50 μm. (D) (Right & Middle) SEM images of NaCS/BBY thin film deposited on glass substrate at 2 different areas of interest (scale bars are 20 μm and 10 μm, respectively). (Left) Elemental mapping of NaCS/BBY thin film showing presence of polymer NaCS (S=6%) and BBY (N= 14%) uniformly across film surface.
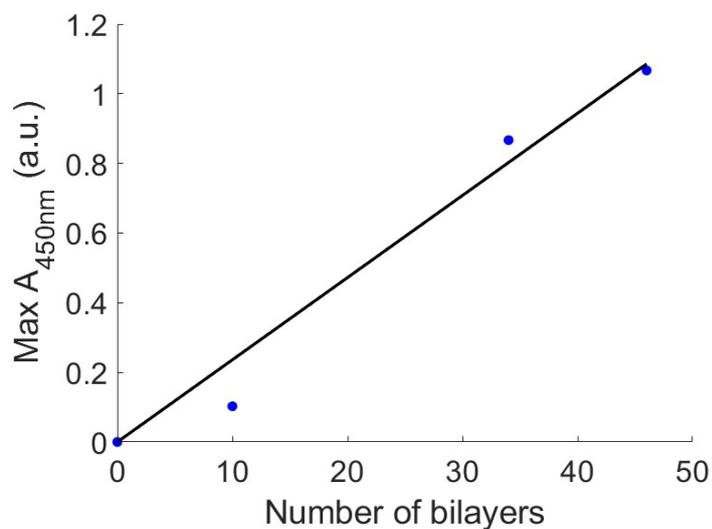
Fig. S2. Plot of max absorbance at 450 nm of BBY with increase in the number of bilayers of NaCS/BBY LbL thin films.
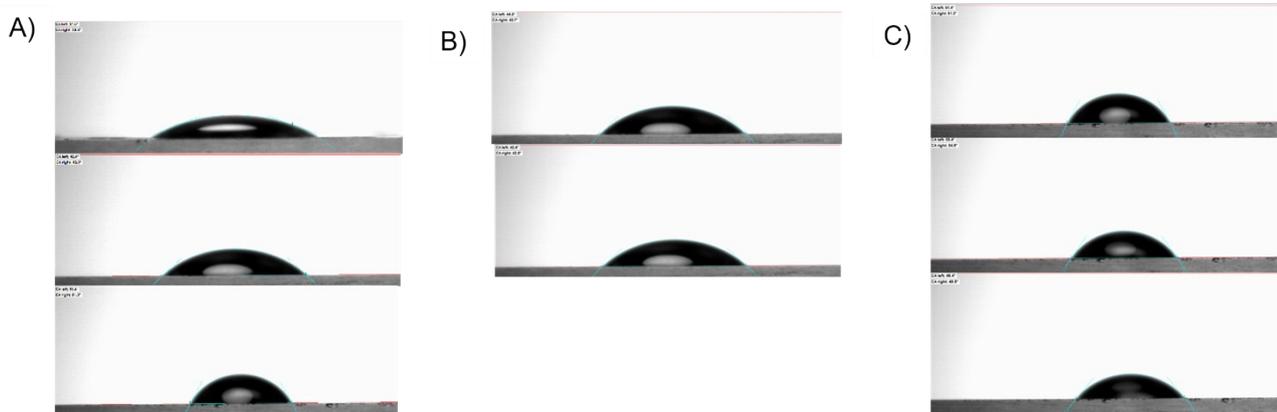

Fig. S3. (A) Shows differences in the contact angle of films of the starting material vs LbL film. Initial measurements of contact angle are as follows; top: NACS (θ =21.0 °, 20.6 °), middle: BBY (θ =44.8 °, 43.7 °) and bottom: NaCS/BBY (θ =61.4 °, 61.3 °). (B) Changes in contact angle for BBY film over time. Top: t=0 min (θ =44.8 °, 43.7 °), bottom: t= 1 min (θ =42.4 °, 42.0 °). (C) Changes in contact angle for NaCS/BBY film over time. Top: t=0 min (θ =61.4 °, 61.3 °), middle: t=2 min (θ =55.4 °, 55.9 °) and bottom: t=4 min (θ =49.4 °, 49.5 °).

Atom	Atomic % 1	Atomic % 2	Atomic % 3	Avg Atomic %
C1s	23.70	22.22	20.91	22.28
S2p	11.52	12.09	10.89	11.5

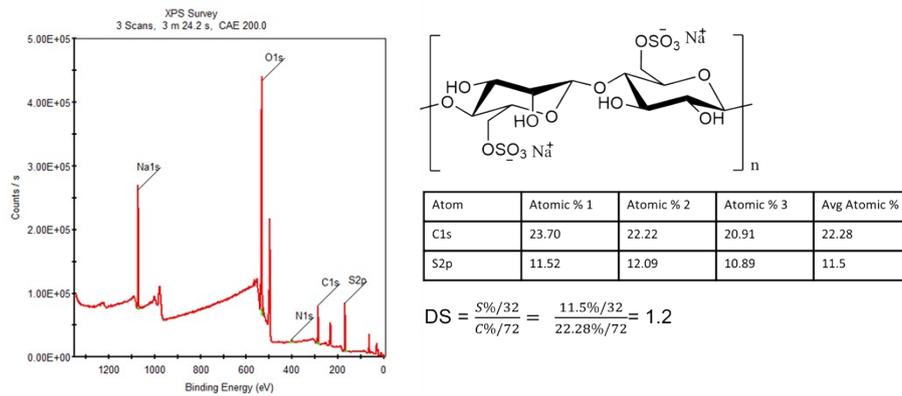$$DS = \frac{S\%/32}{C\%/72} = \frac{11.5\%/32}{22.28\%/72} = 1.2$$

Fig. S4. XPS analysis of NaCS commercial sample showing the binding energy for different atoms.
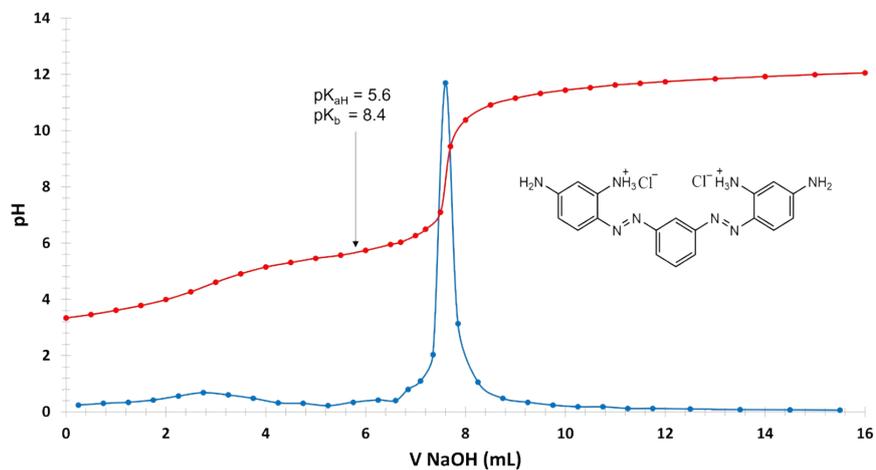
Fig. S5. Titration of NaOH (50.15 mM) against BBY (2.421 mM). Red line shows titration curve (pH vs V NaOH), and blue line shows the first derivative.
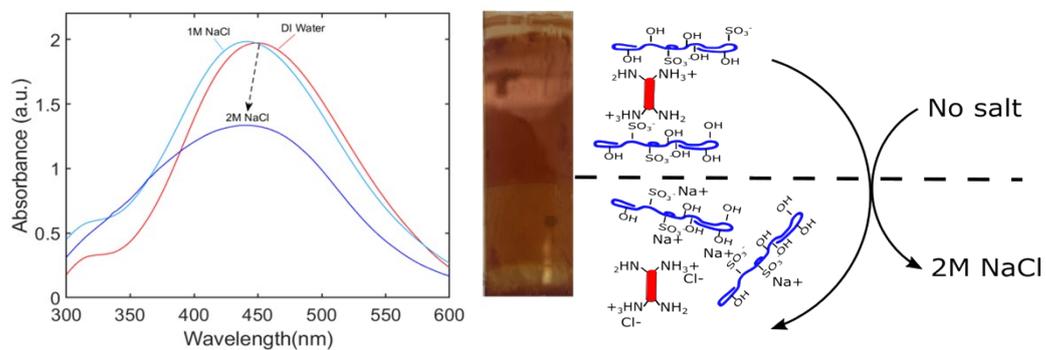
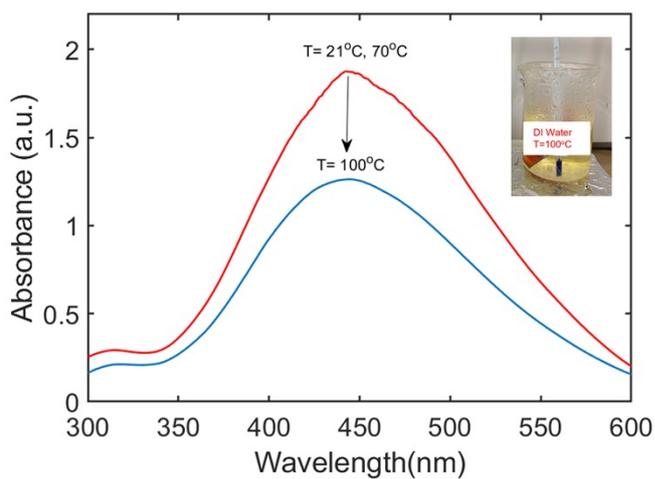Fig. S7. Effect of salt (2M solution) on the stability of NaCS/BBY thin films.

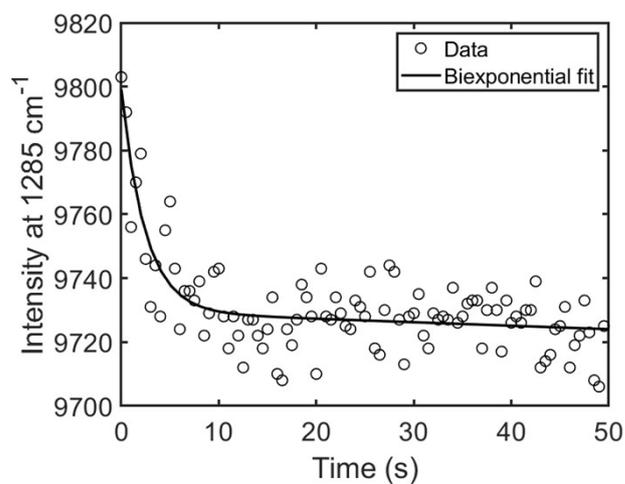Fig. S8. Effect of temperature on the stability of NaCS/BBY thin films.

Fig. S9. Change in intensity of Raman signal around 1285 cm^{-1} peak overtime of NaCS/BBY thin films using a 532 nm laser at 0.1 mW power.
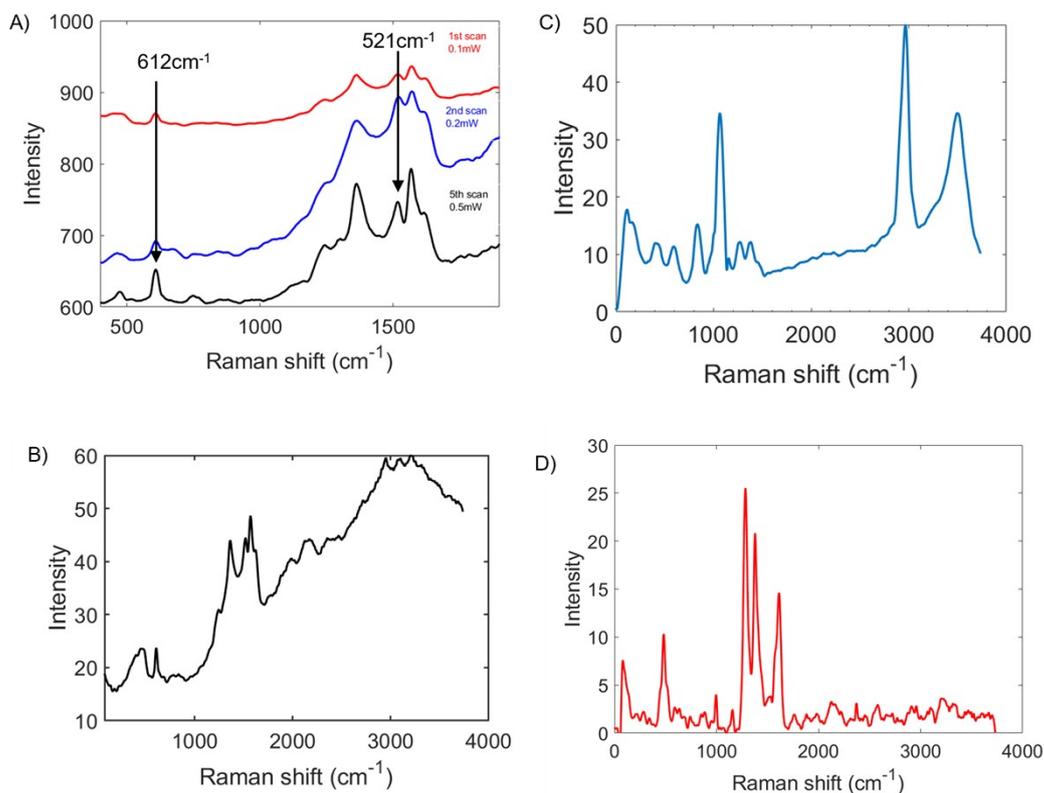
Fig. S10. (A) Raman spectra of BBY deposited on quartz substrate excited using a 532 nm laser at 0.1 mW (red), 0.2 mW (blue) and 0.5 mW (black) laser power. As laser power increases, the intensity of cis peaks at 1510 cm^{-1} and 612 cm^{-1} increases. (B) Full Raman spectrum of BBY only with 532 nm laser at 0.1 mW laser power. (C) Raman spectrum of NaCS only and (D) full Raman spectrum of NaCS/BBY thin films with 532 nm laser at 0.1 mW laser power.

AFM t= 2weeks

❖ Initial thickness = 402 nm
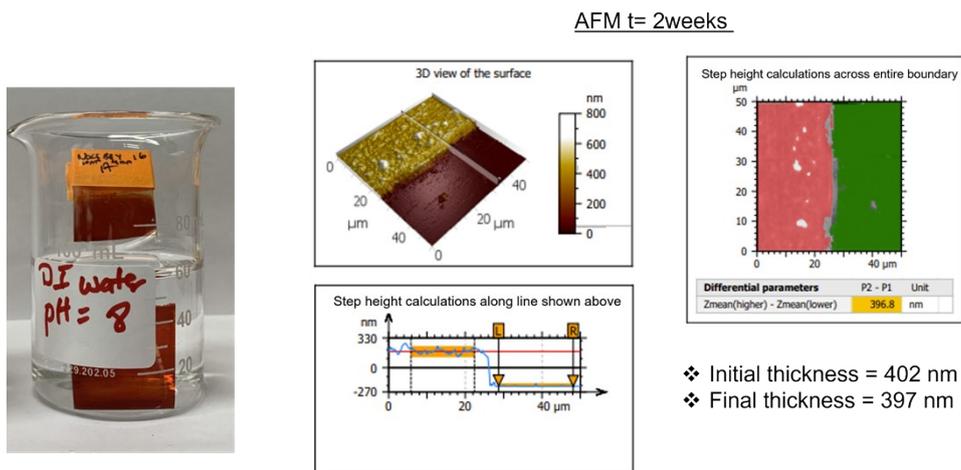❖ Final thickness = 397 nm

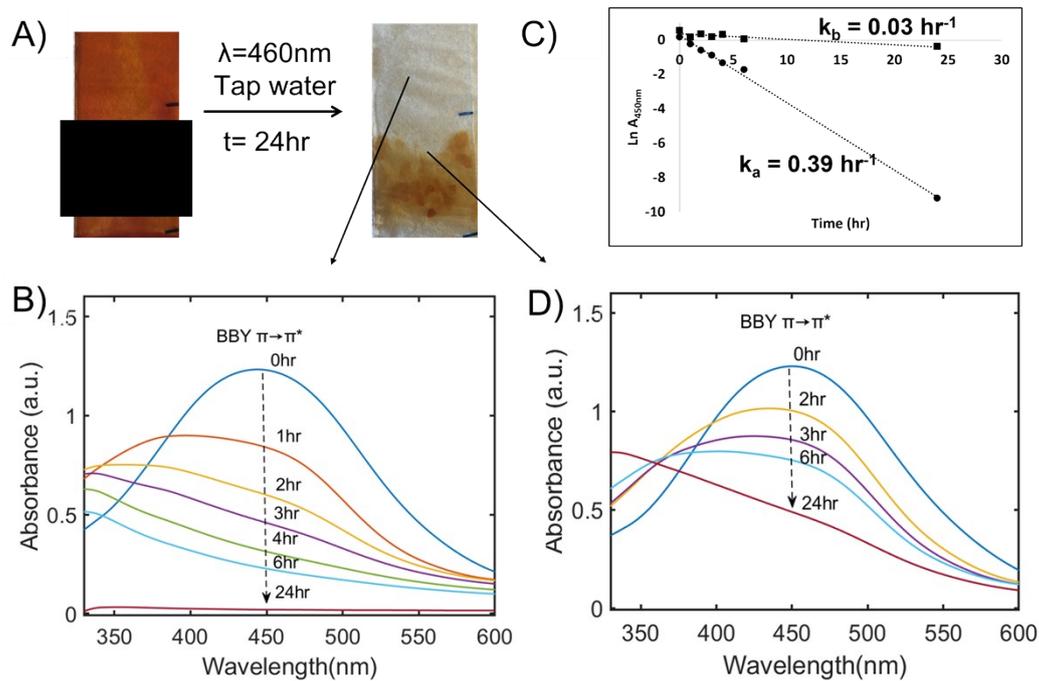Fig. S11. AFM disassembly after 2 weeks for film in DI water under ambient light.

Fig. S12. (A) Disassembly of NaCS/BBY films deposited on glass substrate triggered by blue light (460 nm LED, 299 mA, 12.50 V), washed with tap water. Upper section of films was left exposed (unmasked)while the lower section was masked. (B, D) Time resolved UV-Vis spectra of NaCS/BBY films following irradiation with blue light, washed using tap water for unmasked and masked sections, respectively (t=0–24hr). (C) Graph of ln A450 nm vs t during disassembly process for unmasked (circles) vs masked (squares) section of the films.