ADVANCED MATERIALS

Supporting Information

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Multifunctional Reversible Self-Assembled Structures of Cellulose-Derived Phase-Change Nanocrystals

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Following parts are included in Supporting Information.

1. Supporting methods, characterization and results.

2. Movie S1. Infrared thermal camera video recording the temperature variations of a glass slide coated by C18-UCNCs, a glass slide coated by stearic acid and a pure glass slide during the heating and cooling processes on a heating plate.

3. Movie S2. Infrared thermal camera video showing the leakage of stearic acid on the glass slide during heating process.

4 Movie S3. Infrared thermal camera video recording the temperature variations of a glass slide coated by C18-UCNCs, a glass slide coated by stearic acid and a pure glass slide during the simulated sunlight illumination process.

5. Movie S4. Microscopic video recording the disassociation process of the flaky self-assembled structures on C18-UCNCs film surface during heating treatment at 80 °C for 1 minute (normal play speed).

6. Movie S5. Microscopic video recording the regeneration process of the disassociated flaky structures on C18-UCNCs film surface after cooling down and aging at room temperature for 30 minutes (×24 play speed).

Experiential

Materials

Microcrystalline cellulose (MCC) with a granule size of 50 μm, 10-undecenoyl chloride, and 1-octadecanethiol were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Deionized water (DI water) was used in all experiments. All other chemicals were of analytical grade and were used as received.

Preparation of Cellulose nanocrystals (CNCs)

The CNCs were prepared through hydrochloric acid hydrolysis according to a slightly modified previously-reported procedure.[1] The detailed extraction process was as follows: 1g MCC were first added into 30 mL 6 mol L^{-1} HCl aqueous solutions, and the resultant suspension was subsequently treated under ultrasonic irradiation for 10 min in an ice-water bath, and soaked overnight at room temperature. Then the mixture with magnetic stirring was refluxed at 100 °C for 3 h. After the system was cooled down naturally to room temperature, the obtained suspensions were treated under ultrasonic irradiation for 30 min in an ice-water bath. After that, the obtained suspensions were diluted with deionized water and washed4 times by successive centrifugations with deionized water. Then the CNCs suspension was dialyzed 3 times to remove the remaining acids.

Synthesis of undecenoated CNCs (UCNCs)

UCNCs were prepared were prepared according to the synthesis reported before with a few modifications.[2] In a typical case, 1 g CNCs dispersing in water was separated from water by centrifugation, and was washed with methanol and pyridine to remove traces of moisture before it was suspended in 30 ml pyridine. The mixture was heated to 50 °C, and 10-undecenoyl chloride (2.72 ml, 2 mol 10-undecenoyl chloride per mole of anhydroglucose units of cellulose) was dropped to the CNCs suspension under stirring. After 30 min of stirring at 50 °C, the reaction mixture was poured into 200 ml ethanol, and the precipitate was separated by centrifugation. Thereafter, the product was repeatedly swollen in THF and precipitated in a 5-times excess of ethanol. Finally, the purified product was dried and dispersed in THF for further use. Yield of UCNCs: 91.2 ±2.7%. Degree of substitution (DS): 0.89±0.04 according to elemental analysis.

Synthesis of 1-octadecanethiolated UCNCs (C18-UCNCs) via the post-modification of UCNCs via thiol-ene reaction with 1-octadecanethiol

1-Octadecanethiol (1.5 mol per mol C=C) was added into the THF suspension of UCNCs (10 mg/ml). The mixture was exposed to UV light (320 – 400 nm with an intensity of 60 mW/cm^2) for 5 hours at room temperature with stirring. The obtained 1-octadecanethiolated UCNCs were referred to as C18-UCNCs. After 2 hours of stirring, the reaction mixture was poured into ethanol, and the precipitate was separated by centrifugation. Thereafter, the product was repeatedly swollen in THF and precipitated in a 5-times excess of ethanol. The final product was dispersed in THF and centrifuged for 15 min at 3,000 rpm at 20 °C to remove aggregates. Finally, the purified C18-UCNCs were dispersed in THF for further use.

For comparison, partially 1-octadecanethiolated UCNCs were also synthesized by adding lower amouts of 1-octadecanethiol (0.5 and 0.75 mol per mol C=C) for the thiol-ene reaction. The resulting products were referred to as C18$_{0.5}$-UCNCs and C18$_{0.75}$-UCNCs.

Thermal transport performance

The thermal transport performance of samples was characterized using an infrared thermal imaging camera (Fotric 226s-L28, China). The glass slide coated by C18-UCNCs (referred to as G+C18-UCNCs) was placed on a heating/cooling apparatus for heating to 80 °C (the set temperature) and cooling to 20 °C. A glass slide coated by stearic acid (referred to as G+stearic acid) and a pure glass slide (referred to as glass) were simultaneously measured as controls.

Light-to-thermal conversion test

A light-to-thermal conversion experiment was performed under simulated sunlight using a CEL-HXUV300 xenon lamp (CEAULIGHT, China) with an AM 1.5 filter. Samples were tested, and the irradiation distance was kept constant at 30 cm from the light source. The environmental temperature was ca. 26 °C. The temperature variations in the samples were recorded by a thermal-imaging camera (Fotric 226s-L28, China).

Imaging tests of the patterned surfaces by C18-UCNCs

Various substrates including glass slide, steel strip and foil paper were patterned by C18-UCNCs suspension in THF and dried at RT. The imaging results of the patterned letters on the substrates were recorded by a thermal-imaging camera during heating on a heating apparatus or under simulated sunlight illumination.

Preparation of multifunctional C18-UCNCs films

Films were obtained after the deposition of homogeneous THF suspensions of C18-UCNCs with a concentration of 10 mg/ml on Teflon substrates using solvent-casting. After 24 hours of drying at room temperature, the films were removed from the Teflon substrates for further characterization. For comparison, the THF suspensions of UCNCs, $C18_{0.5}$-UCNCs and $C18_{0.75}$-UCNCs were also solvent-casted and formed self-standing films.

Mechanical stability and self-healing property of the self-assembled flaky structures

Sandpaper abrasion test was adopted to assess the mechanical stability of the superhydrophobic flaky structures. The C18-UCNCs films were placed on sandpaper with 800 meshes and moved 20 cm as measured by a ruler under an item with the weight of 50 g by an external force, which is defined as one abrasion cycle. For the self-healing test, the surface layer of C18-UCNCs films containing flaky structures was damaged by aforementioned sandpaper abrasion treatment. Then, the damaged film was heated at 80 °C for 30 min, and further went through the treatments containing the cooling down and the aging at RT for 24 h. Static water contact angles were measured before and after every abrasion cycle. The surface morphologies were recorded using SEM before and after every abrasion cycle.

Surface superhydrophobization by C18-UCNCs

For the superhydrophobization, the surfaces of two kinds of substrates including glass slide and filter paper, were coated by dropping THF suspensions of C18-UCNCs. After drying, the surfaces with superhydrophobicity can be obtained.

Characterization

A solid-state ^{13}C NMR spectrometer (AVANCE III 400 MHz WB, Bruker, Switzerland) and an FTIR spectrometer (ZN-04, KINGSLH, China) were used to analyze the chemical structures of the UCNCs and C18-UCNCs. Dynamic light scattering (DLS) measurements were performed on a Zetasizer Nano ZS (Malvern Instruments Ltd., UK). The carbon, hydrogen, and sulfur contents were determined with an Elemental Analyser 4.1 vario EL III (Elementar, Germany). The total degree of substitution (DS) of the 10-undecenyl groups was calculated according to ref.[3] AFM measurements were performed on a Multimode 8 AFM (Bruker, Germany)with a NanoScope V controller using PeakForce Tapping Mode witha ScanAsyst-Air Cantilever. TEM observations were performed on a CM 12 transmission electron microscope (Philips, Netherland). SEM images were obtained on a LEO Supra-35 high-resolution field emission scanning electron microscope (Carl Zeiss AG, Germany). Polarized images of samples were observed using via OPM (CX40P, Ningbo, China). Transmittance spectra of the samples at wavelengths ranging from 200 to 800 nm were measured using an ultraviolet-visible spectrophotometer (TU-1950, Beijing Purkinje General Instrument Co., Ltd., Beijing, China). An electromechanical universal testing machine (CMT5504, MTS, China) was used to measure the tensile properties of C18-UCNCs film. A digital microscope with a large depth of field (VHX-6000, Keyence, Japan) was used to observe the regeneration of the flaky structures. Small-angle X-ray scattering (SAXS) experiments were carried out on a Nano-InXider vertical SAXS/WAXS system (Xenocs SA, France). The thermal conductivity was measured via a laser flash thermal analyzer (LAF-457, Netzsch, Germany). Phase-change properties were characterized by differential scanning calorimetry (DSC, TA Instruments Inc., USA) from 0 to 100 °C at a scanning rate of 10 °C/min. Static water contact angles were measured using a contact angle meter (Attension Theta, Biolin Scientific, Sweden) at RT.

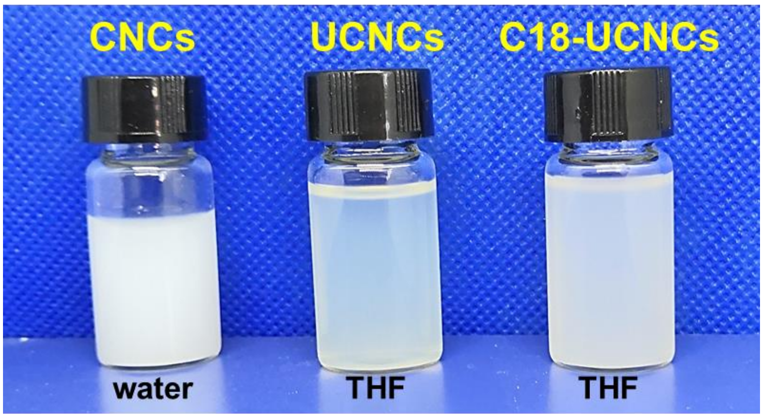

Figure S1. Photos of suspensions of CNCs dispersed in water, UCNCs dispersed in THF and C18-UCNCs dispersed in THF.

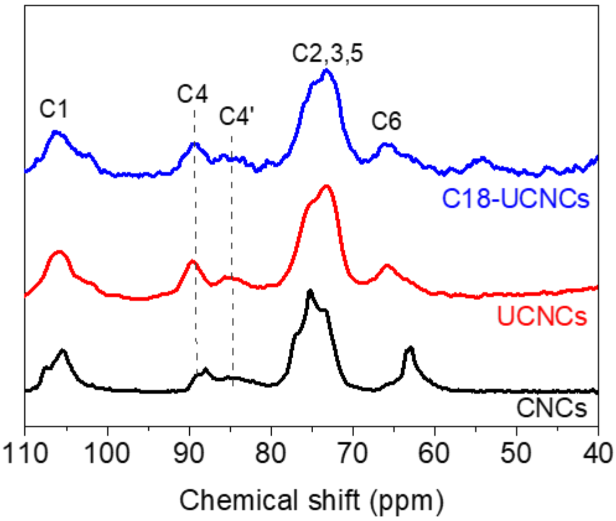

Figure S2. Solid-state ^{13}C NMR spectra of CNCs, UCNCs and C18-UCNCs (Only signal region of cellulose backbone is shown here).

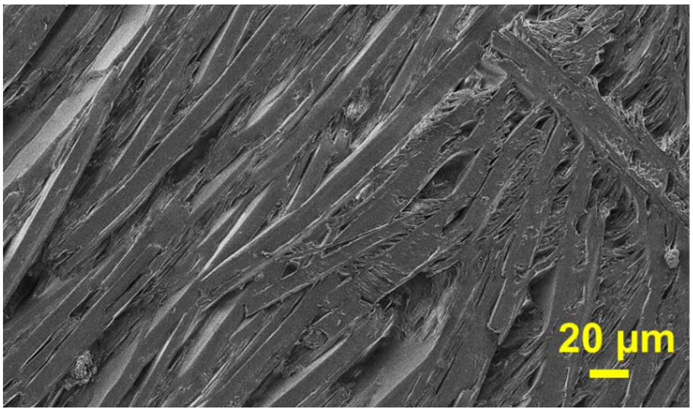

Figure S3.SEM image of the surface morphology of G+stearic acid.

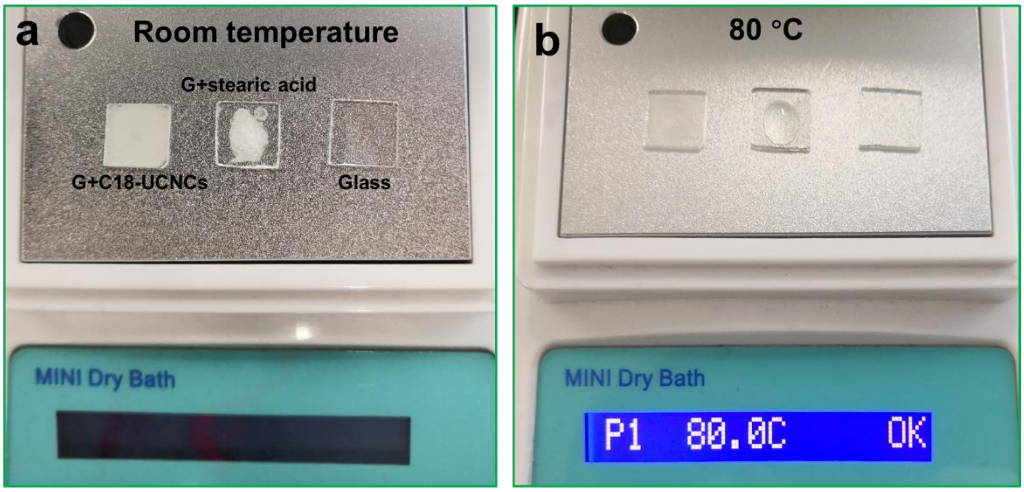

Figure S4. (a-b) Photos of G+C18-UCNCs, G+stearic acid and glass on a heating plate at (a) RT and (b) 80 °C.

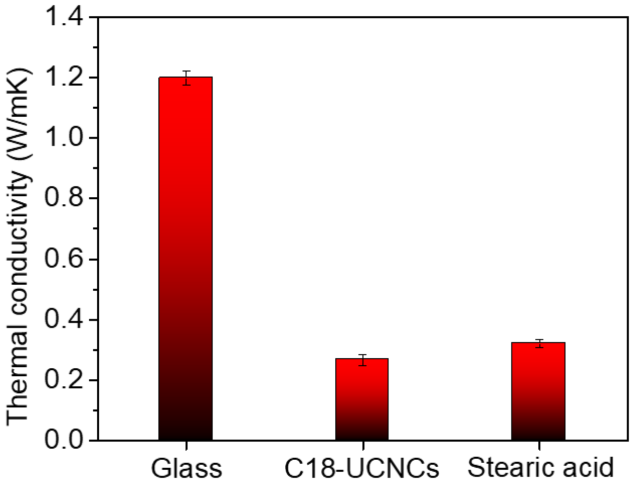

Figure S5. Thermal conductivity of C18-UCNCs, stearic acid and glass.

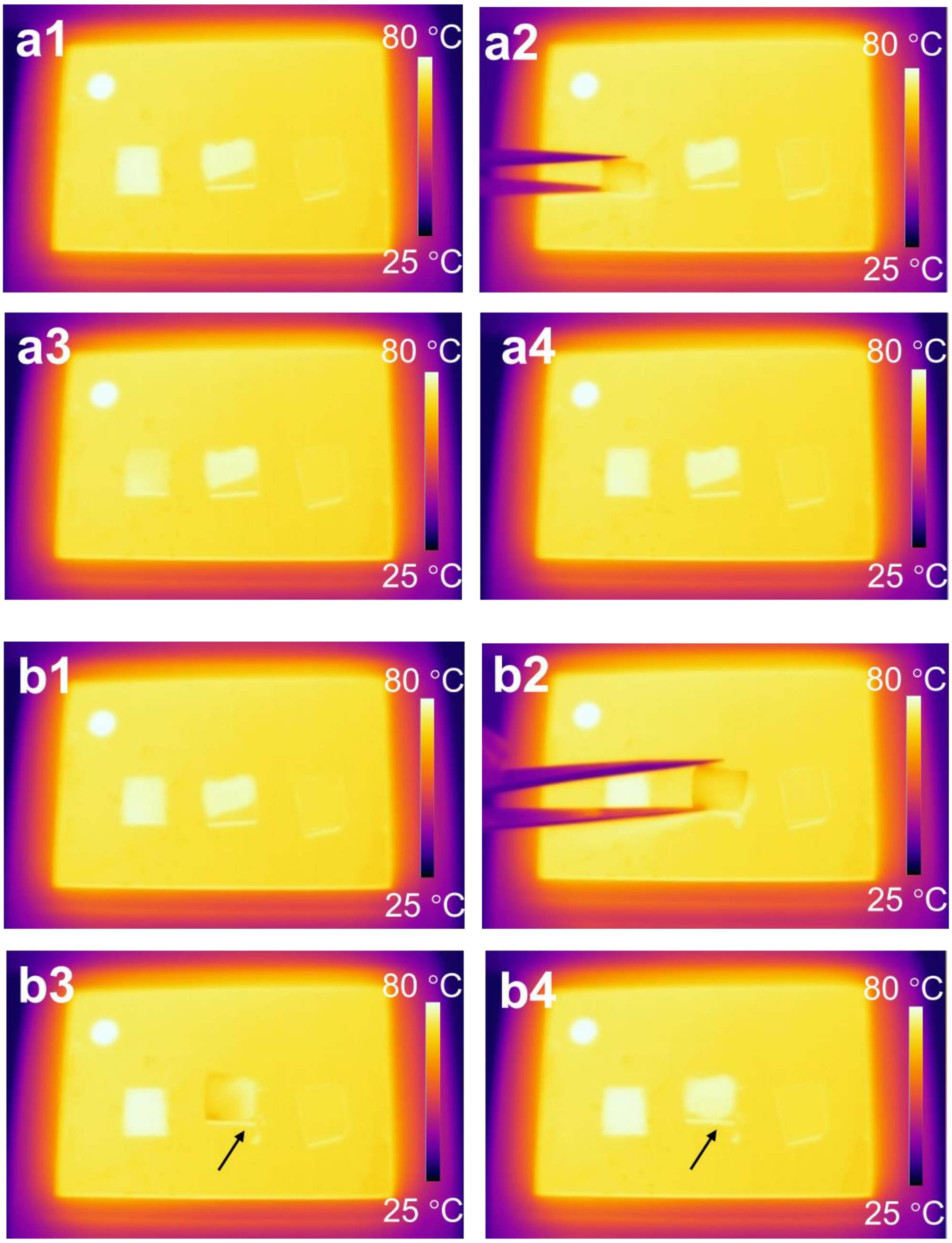

Figure S6. (a) Infrared images during tilting G+C18-UCNCs on a heating plate at 80 °C. (b) Infrared images during tilting G+stearic acid on a heating plate at 80 °C. The arrows in (b3 and b4) show the flowing and leakage of stearic acid due to melting.

Figure S7. Photos of the simulated sunlight setup for light-to-thermal imaging tests.

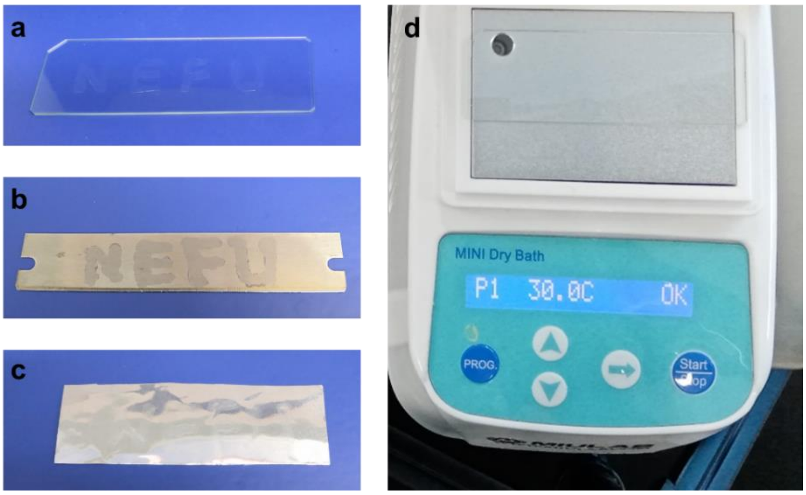

Figure S8. (a-c) Photos of (a) a glass slide, (b) a steel blade and (c) a sheet of foil paper having C18-UCNCs patterns of "NEFU" on the surfaces. (d) The photo of the patterned glass slide on a heating plate for the imaging test.

Figure S9. (a-e) Infrared images showing the temperature variations of the patterned glass slide on a heating plate at different set temperatures of (a) 30 °C, (b) 40 °C, (c) 60 °C, (d) 70 °C and (e) 80 °C.

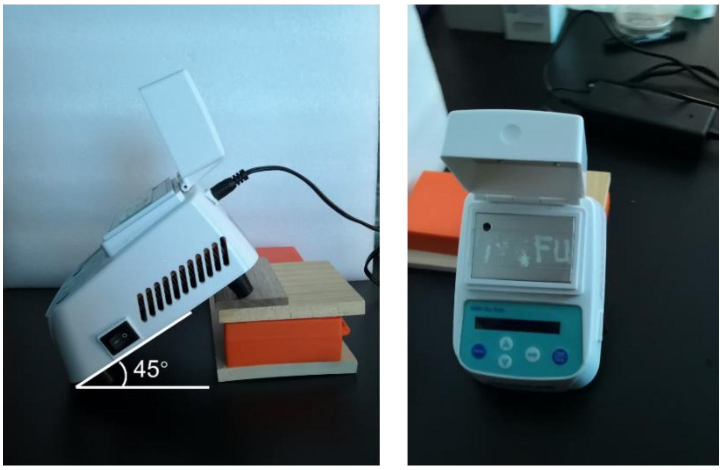

Figure S10. The photos of the patterned glass slide on a heating plate with a tilt angle of 45° for the imaging test. The patterned letters of “NE” are formed by stearic acid, and the letters of “FU” are formed by C18-UCNCs.

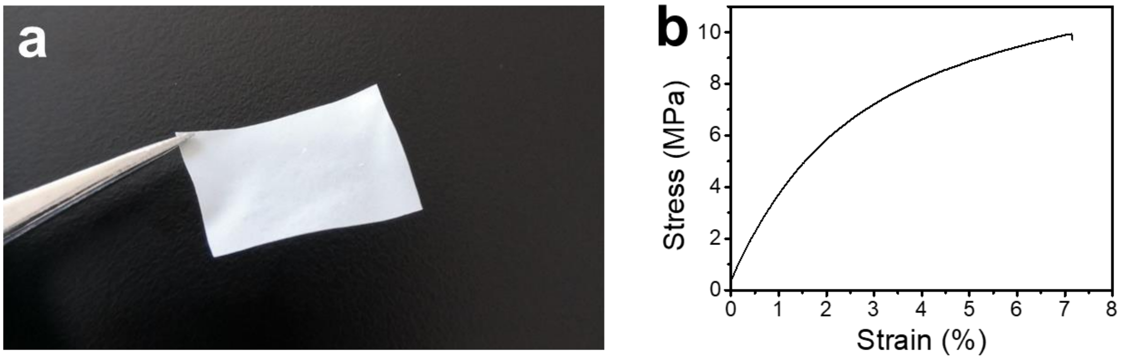

Figure S11. (a)The photo of C18-UCNCs film. (b) Stress-strain curve of the C18-UCNCs film.

Table S1 Characters of the self-assembled structures of the dried C18-UCNCs on silica wafer

Samples	as prepared	1st	50th	100th
Thickness (nm)	157±54	153±36	146±47	151±33

Note: One hundred flakes of each sample were measured to calculate the average thicknesses.

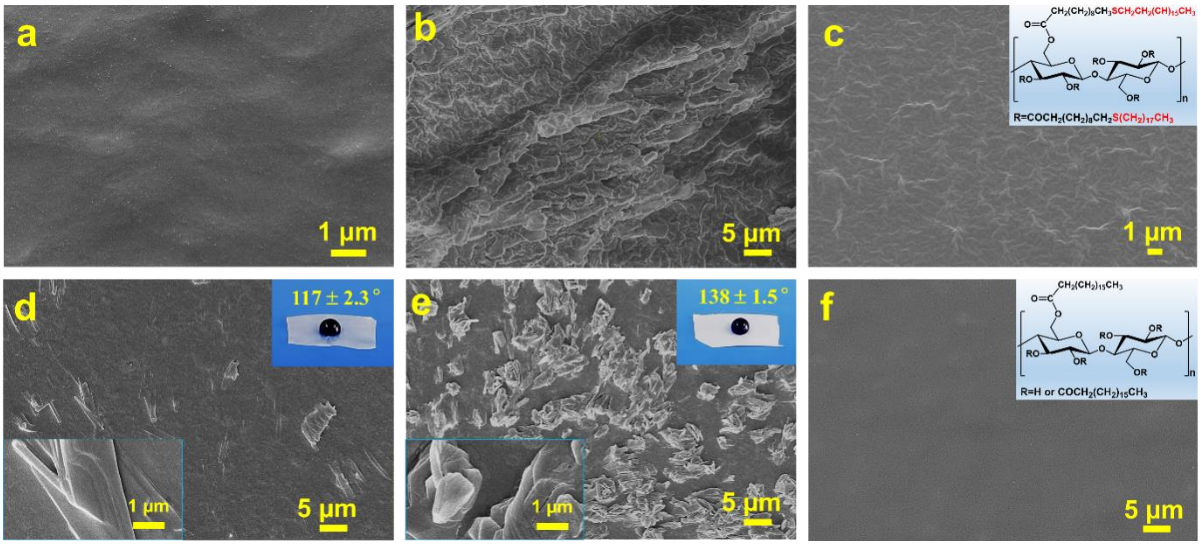

Figure S12. SEM images of the dried samples at 25 °C using their THF suspension or solution. (a) UCNCs; (b) 1-octadecanethiol; (c) Polymeric cellulose derivative obtained by the thiol-ene reaction of cellulose 10-undecenoyl ester with complete derivatization of hydroxyl groups (the DS is 3) and 1-octadecanethiol; (d) $C18_{0.5}$-UCNCs; (e) $C18_{0.75}$-UCNCs; (f) Stearoylated CNCs with the DS of 0.12. The insets in the top right in (c) and (f) show the chemical structures. The insets in the top right in (d) and (e) show the dyed water droplets on the films surface and corresponding static water contact angles. The insets in the bottom left in (d) and (e) show the enlarged SEM images.

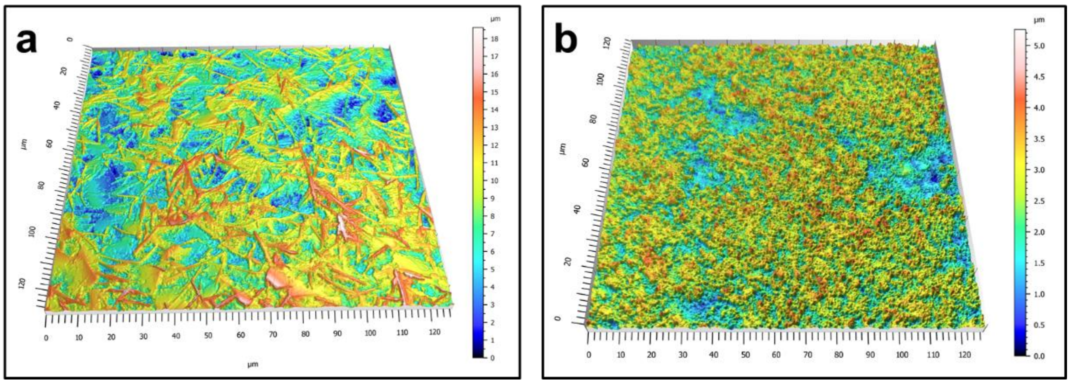

Figure S13. 3D LSM images of the surface morphology of C18-UCNCs film at (a) room temperature and (b) 80 °C.

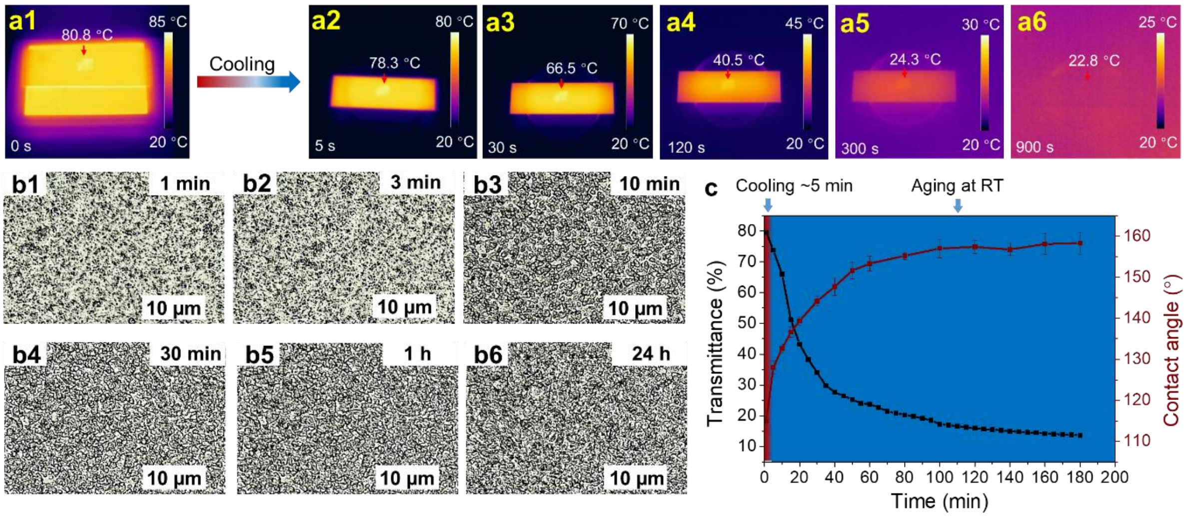

Figure S14. Time-dependent features of the self-assembled structures on the film of C18-UCNCs after cooling down to RT from 80°C. (a) Time-dependent infrared images showing the temperature change during cooling process (The cooling time from 80 °C to room temperature is around 5 min); (b) Time-dependent microscopic images of the self-assembled structure after cooling down from heating treatment at 80°C and aging at RT; (c) Time-dependent static water contact angles and transmittance of C18-UCNCs films.

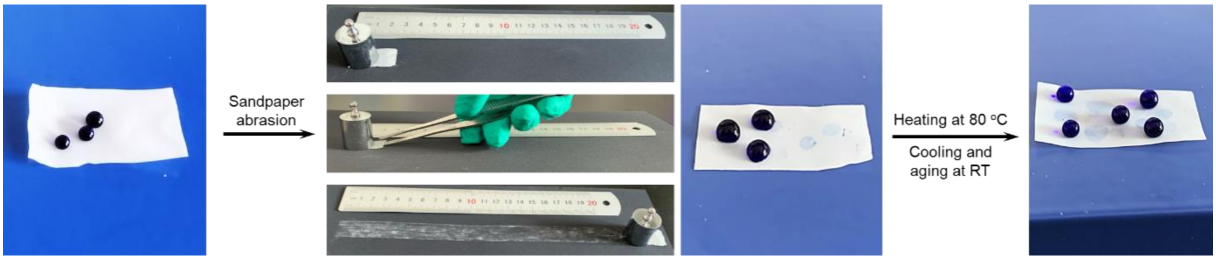

Figure S15. The photos showing sandpaper abrasion test and healing process of the flaky structures on C18-UCNCs film surface.

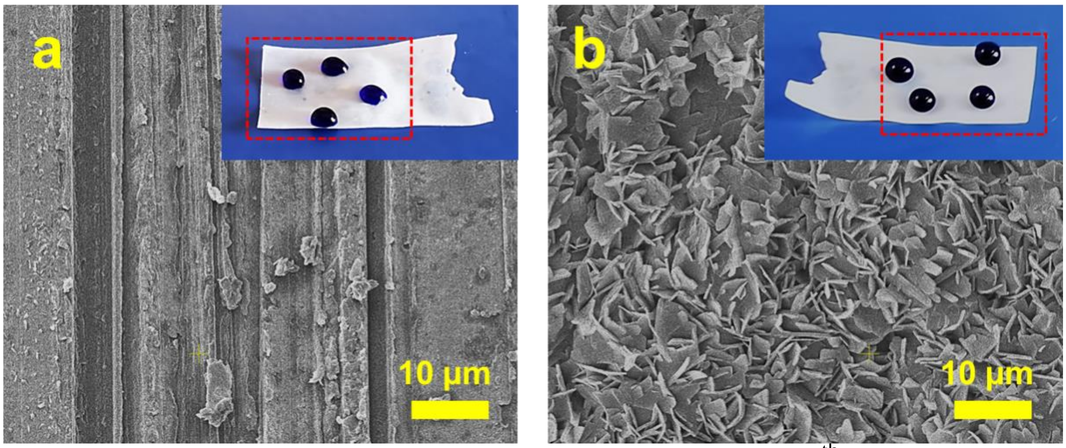

Figure S16. SEM images of the flaky structures as (a) after the 10th damage by sandpaper abrasion, and (b) after the 10th healing by heating at 80 °C for 30 min and aging at RT for 24 h. The insets in (a and b) show the dyed water droplets on the C18-UCNCs film surface, and the red areas show the damaged area and corresponding healed area.

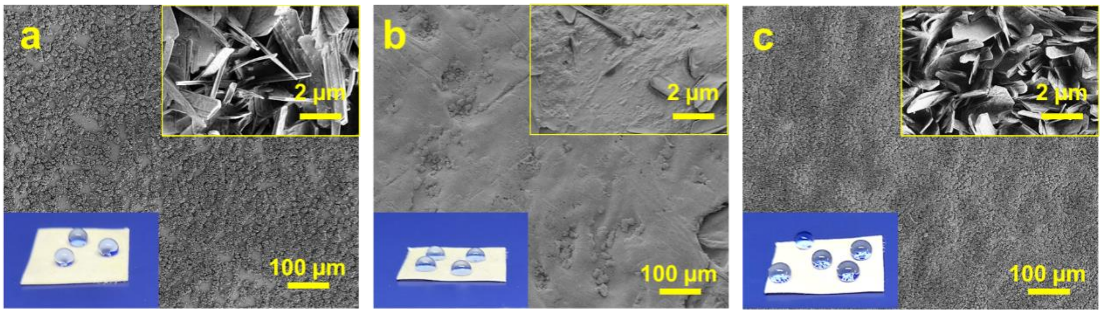

Figure S17.SEM images of the surface morphologies of the filter paper coated with C18-UCNCs under different conditions: (a) as-prepared sample, (b) damaged by scratching, (c) healed by heating at 80 °C for 30 min, cooling down and aging at RT for 24 h. The inset in (a-c) in top right show the enlarged SEM images, and in bottom left show photos of the water droplets on the corresponding surfaces.

References

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[3] C. Vaca-Garcia, M. E. Borredon, A. Gaseta, *Cellulose***2001**, *8*, 225.