

Electronic Supplementary Information(ESI)

In-situ Growth of Luminescent Perovskite Fibers in Natural Hollow Templates

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Experimental details

Chemicals

Calotropis gigantea fibers were provided by Tropical Crop Genetic Resources Institute, Chinese Academy of Tropical Agricultural Sciences (CATAS). CsCl, CsBr, CsI, PbBr₂ were purchased from Aladdin Chemistry Co. Ltd. PbCl₂ was from Tianjin Guangfu Chemical Institute, PbI₂ was from Beijing Chaoyang Zhonglian Chemical Reagent Factory. Oleic acid (OA) was from Yantai Shuangshuang Chemical Factory Co. Ltd. Oleylamine (OAm) was from Energy Chemical. Methanol, N, N-Dimethylformamide (DMF) was from RianlonBohua (Tianjin) Pharmaceutical & Chemical Co. Ltd. Eosin Y water soluble (EY) was from Aladdin Chemistry Co. Ltd. Toluene was from Guangdong Fine Chemicals Engineering Technology Research Center Co. Ltd. Silicone (HY—E625#) was from Shenzhen Hongyejie Technology Co., Ltd. All solvents and chemicals were used without any further purification. Deionized water with resistivity of 18.3 MΩ•cm was used to prepare aqueous solution throughout the experiment.

Preparation of precursor solution

PbBr₂ (0.6 mmol) and CsBr (0.6 mmol) were dissolved in DMF (10.0 ml) in a flask at 30 °C. OA (0.6 mL) and OAm (0.3 mL) were added to stabilize the precursor solution. Other samples of different emission were made with corresponding mixture of PbX₂ and CsX (X = Cl, Br, I) with the same stoichiometric ratio.

Preparation of luminescent fibers

At room temperature, a bundle of natural fibers (1.6 mg) was immersed in 4.0 ml of precursor solution in a vial, which was degassed to 13 Pa within ~4 h to remove the gas and solution in the fiber. Then the vacuum was released to let the precursor solution fill the fibers by atmosphere pressure. The fibers full of precursor solution were subsequently taken out and heated at 60 °C for 11 hours. Thereafter, the outer wall of the fibers was washed successively with toluene and methanol to obtain smooth surface. Finally, Silicone was used to encapsulate the fibers. 0.2 g of silicone was dissolved in 2 mL of dichloromethane (DCM). Then the fibers were dipped into the solution repeatedly for 10 times.

Preparation of artificial human sweat

According to previous reports,¹ the artificial sweat was prepared by dissolved 0.5 g of nicotinic acid ($C_6H_5NO_2$), 0.16 g of NaCl, and 0.06 g of urea (CH_4N_2O) in 100 mL of deionized water (36 °C) under stirring, and the pH value was adjusted to 5.4.

Characterization methods

Spectroscopic measurement

The fluorescence decay measurements (detected at 514 nm) were performed on a FluoTime 200 (PicoQuant GmbH, Germany) fluorescence lifetime spectrometer by means of Time-Correlated Single Photon Counting (TCSPC) technique, with a 5 nanosecond pulsed LED at 375 nm (Pulse width <750 ps) as the excitation source. Optical and fluorescent images were captured using a Leica DMI4000 B microscope with excitation from 340 nm to 380 nm. The diffuse reflectance spectra (DRS) were obtained on a Shimadzu UV Probe 2600 with $BaSO_4$ as reference. The fluorescence spectra were collected on an AvaSpec-2048TEC-FT (Avantes, Netherlands) fluorescence spectrometer, with a LED at 375 nm as the excitation source.

Other characterizations

The SEM images were collected on a field-emission scanning electron microscopy (FE-SEM, Hitachi S4800). Fluorescent images were captured using a Nikon ECLIPSE-80i microscope equipped with a Thorlabs DCU224C CCD with excitation from 330 nm to 380 nm. The height and amplitude features of the products were characterized on an Atomic Force Microscope of Agilent 5500. The TEM micrographs were obtained using Talos F200S Field Emission Transmission Electron Microscopes (FEI, USA) at an operating voltage of 200 kV, respectively. Powder X-ray diffraction (XRD) patterns of the products were recorded on a Panalytical X'Pert PRO diffractometer using $Cu K \alpha$ X-rays between 5 ° and 60 °.

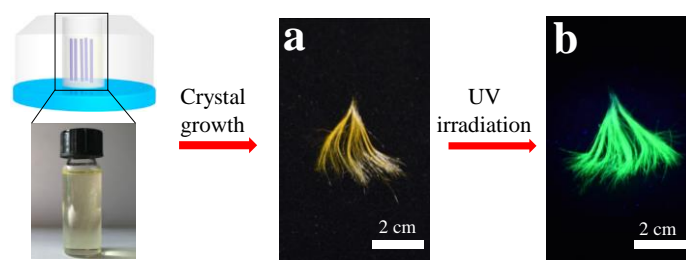


Figure S1. (a) Prepared luminescent *Calotropis gigantea* fibers without and (b) with UV lamp (375 nm, 3 W) irradiation.

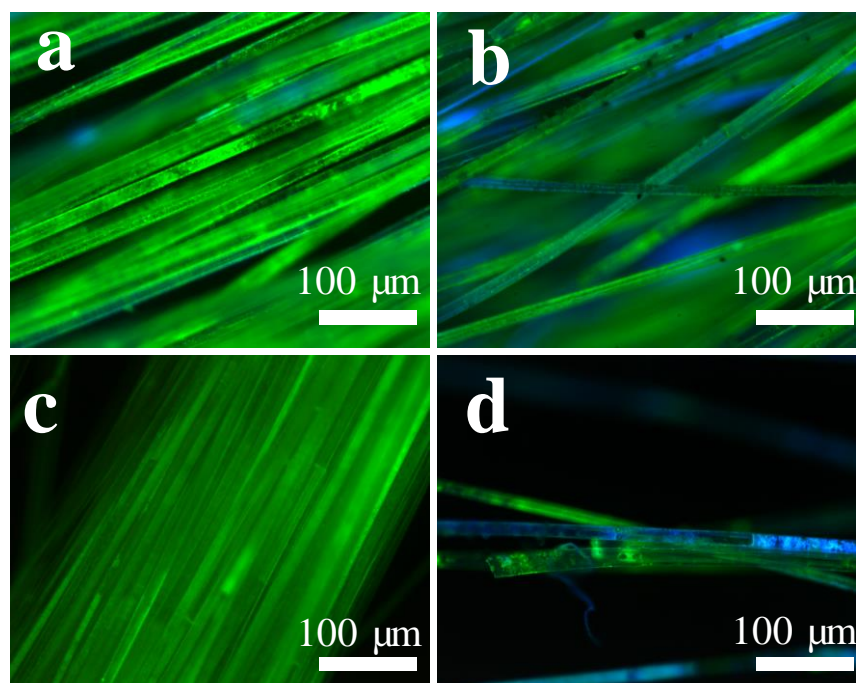


Figure S2. (a) and (c): Fluorescent images of perovskite NCs@*Calotropis gigantea* fibers with vacuum-assisted synthesis under UV light irradiation. (b) and (d): Fluorescence images of perovskite NCs@*Calotropis gigantea* fibers with single siphon synthesis. Single siphon is not strong enough to pull the solution inside the inner wall and results in the aggregation of the NCs mainly at the orifice of the fibers.

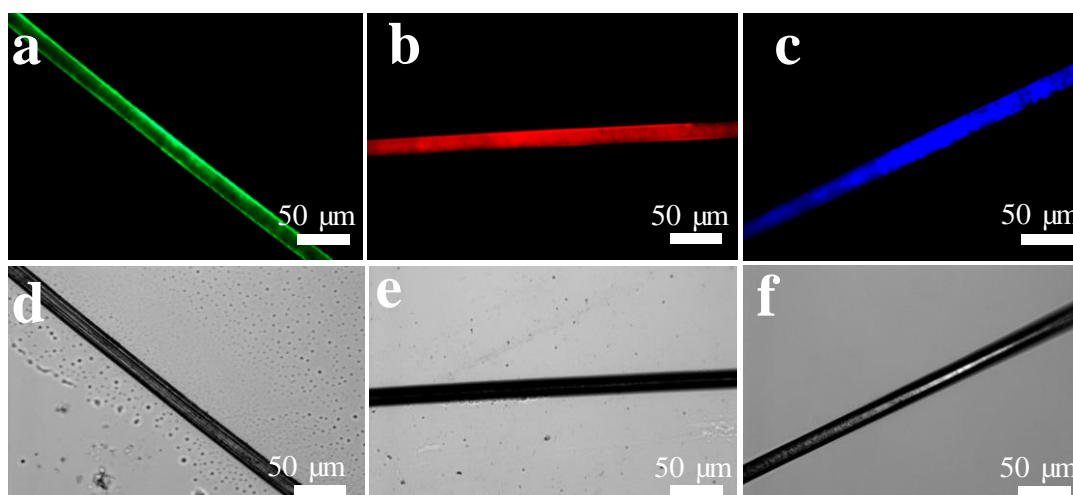


Figure S3. (a) ~ (c) Florescent images of perovskite NCs@*Calotropis gigantea* fibers showing green (CsBr and PbBr₂ as the precursor), red (CsBr and PbI₂ as the precursor), blue (CsBr and PbCl₂ as the precursor) with at 380 nm-excitation; and corresponding optical microscopic images (d) ~ (f).

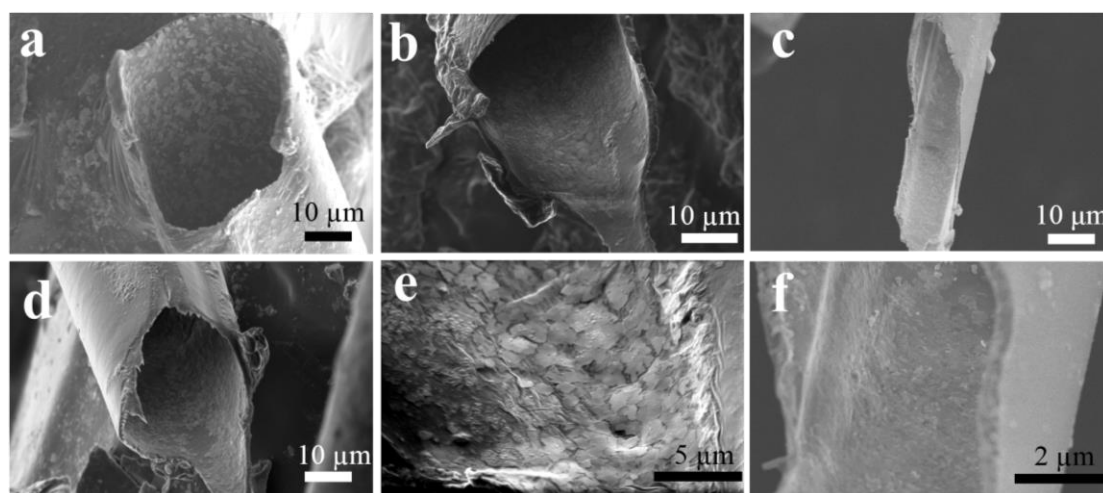


Figure S4. SEM images of perovskite NCs@*Calotropis gigantea* fibers with varied facets and resolution.

Note during growth the NCs were also sparsely spread on the orifice and outer surface of the fiber besides the main interior products, which were however easily removed through washing and hence not used for the luminescence purpose.

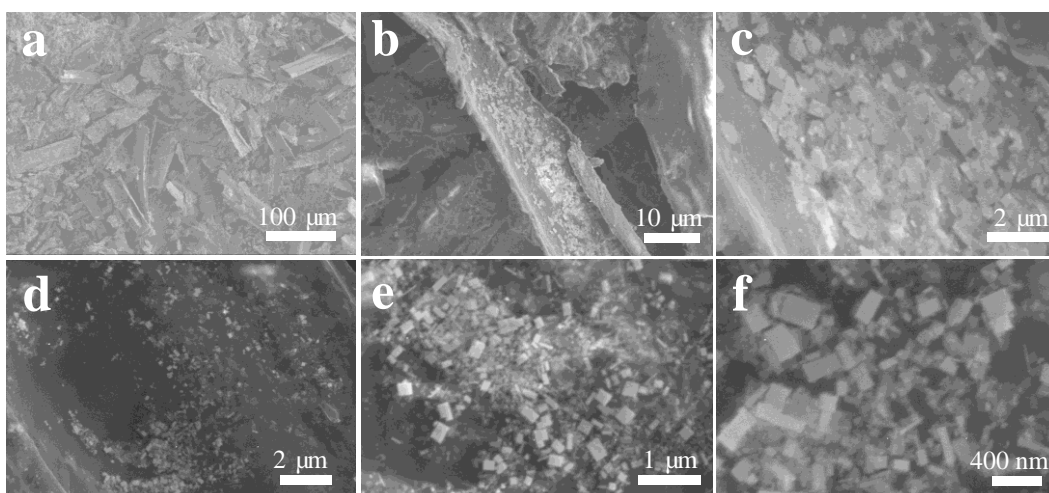


Figure S5. (a) ~ (f) More SEM images ground perovskite NCs@*Calotropis gigantea* fibers.

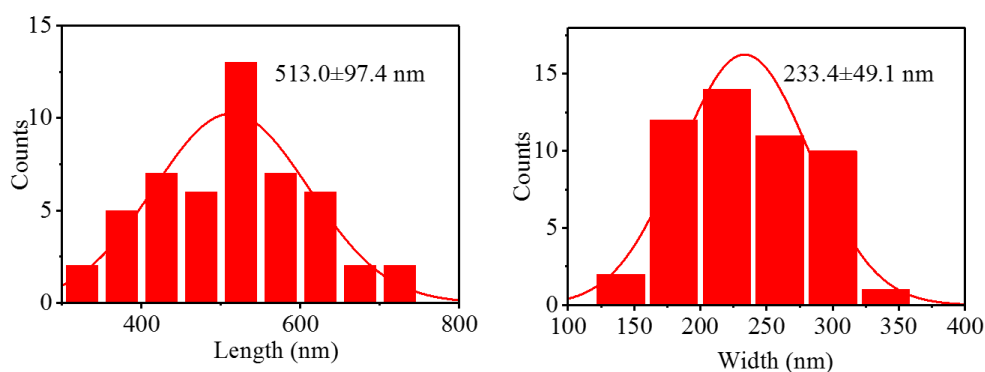


Figure S6. The size histograms of ~50 nanosheets verified they mainly demonstrated length of 513.0 ± 97.4 nm and width of 233.4 ± 49.1 nm.

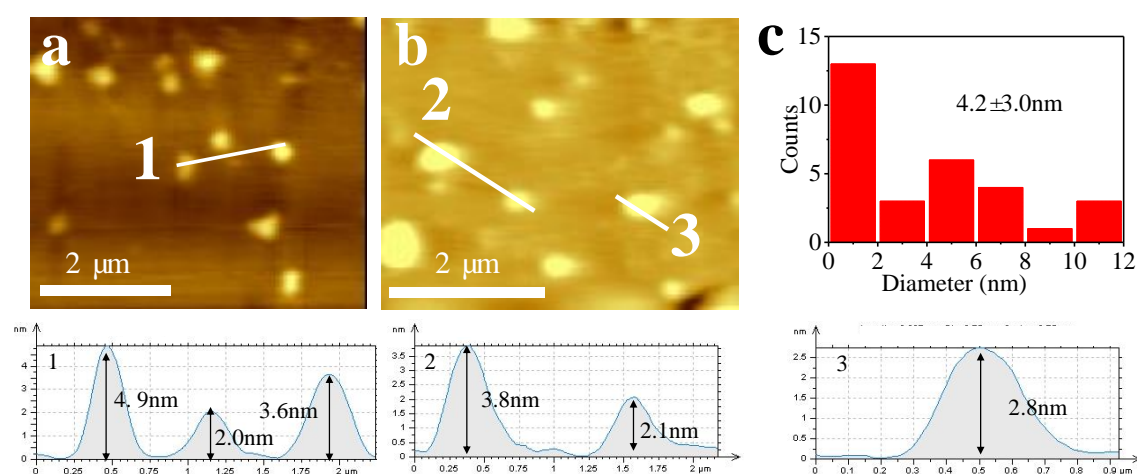


Figure S7. Representative AFM images verified the thickness of the nanosheets. Typical thickness was 4.2 ± 3.0 nm based on the statistical data of 30 flakes.

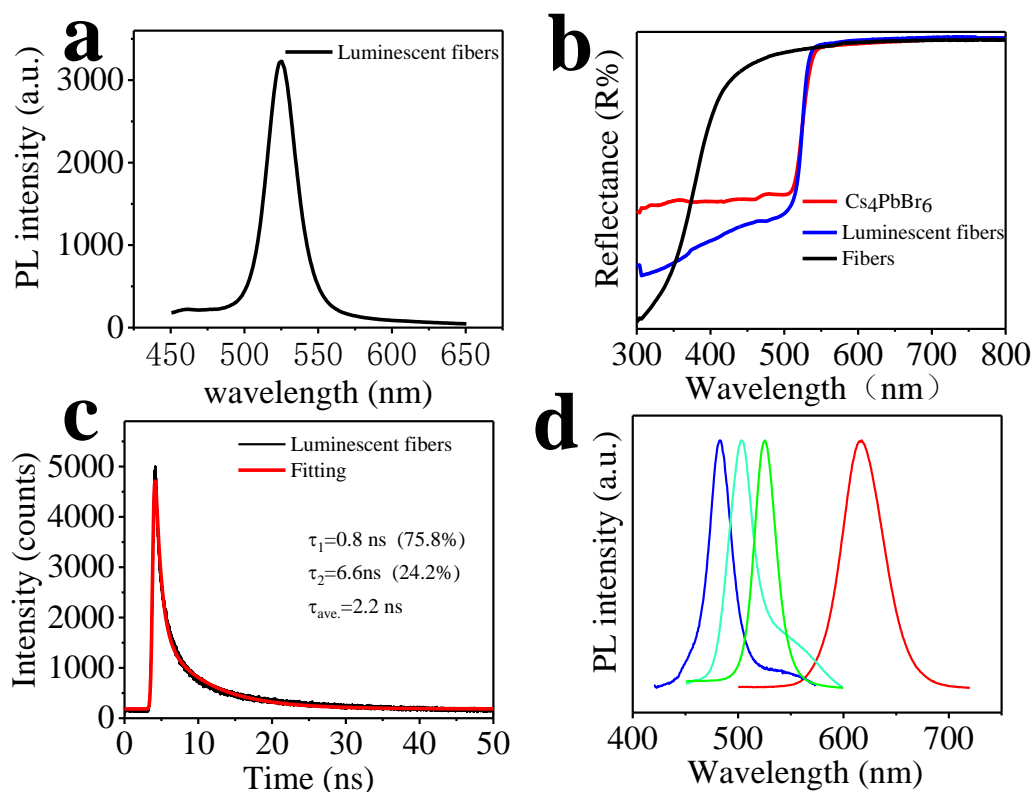


Figure S8. (a) The photoluminescence (PL) spectrum of $\text{Cs}_4\text{PbBr}_6@Calotropis\ gigantea$ fibers. (b) Diffuse reflection spectra of $\text{Cs}_4\text{PbBr}_6@Calotropis\ gigantea$ fibers, *Calotropis gigantea* fibers and Cs_4PbBr_6 NCs. (c) Time-resolved PL decay and fitting curve of $\text{Cs}_4\text{PbBr}_6@Calotropis\ gigantea$ fibers excited by the nanosecond pulsed LED at 375 nm (Pulse width <750 ps) and probed at 514 nm (d) Normalized fluorescence spectra showing samples emitting at varied wavelength by tuning precursor composition: 480 nm (PbCl_2 and CsBr as the precursor), 505 nm (PbBr_2 and CsCl as the precursor), 525 nm (PbBr_2 and CsBr as the precursor), 620 nm (PbI_2 and CsBr as the precursor).

Contents		Size	Shape	Quality	Emission peak	Fluorescence quantum yield/%	Fluorescence lifetime/ns
The optimizing of the experimental conditions	(1) Single siphon process	Irregular	Nano sheets	Single siphon is not strong enough to pull the solution inside the inner wall and results in the aggregation of the NCs mainly at the orifice of the fibers.			
	(2) The vacuum/devacuum process Controlling the amount of perovskites loaded in the fibers can be realized by controlling the degassing pressure; Reaction temperature;	Homogeneous nanosheets at optimized conditions.		<p>The use of vacuum/devacuum process effectively lets the precursor solution fill the fibers. As a result, perovskite crystals grew and spread along the inner walls of the fibers homogeneously. Eventually long and uniform luminescent fibers are obtained.</p> <p>Controlling the amount of perovskites loaded in the fibers can be realized by controlling the degassing pressure. Direct soaking of the fiber, only a small amount of perovskites formed in the fibers; with the increase of degassing pressure, the quantity of perovskites produced in the fibers increased.</p> <p>Reaction temperature: varied reaction temperatures of 40°C, 60°C, 80°C were applied. 60°C was the optimum condition and the produced fibers showed the highest fluorescence quantum yield.</p> <p>For instance, 13 Pa and 60°C were the optimized conditions, which gave formation of largely uniform Cs₄PbBr₆ nanosheets with length of 513.0 ± 97.4 nm and width of 233.4 nm ± 49.1 nm.</p>			
	(3) Synthesized by supersaturated	Non-uniform	Bulk	The amount of perovskite NCs formed in the fiber cavity was very small; weak luminescence			

	recrystallization method and directly extracted with toluene.	cubes					
Material composition	The emission wavelength of luminescent fibers was mainly adjusted through changing the types of precursor components.	PbCl ₂ and CsBr	Homogeneous nanosheets at optimized conditions.	Good	480 nm	14.8	τ_1 : 0.4 (80.9%) τ_2 : 4.2 (19.1%) $\tau_{ave.}$: 1.2
		PbBr ₂ and CsCl		Good	500 nm	22.5	τ_1 : 0.6 (83.3%) τ_2 : 3.7 (16.7%) $\tau_{ave.}$: 1.3
		PbBr ₂ and CsBr		Good	525 nm	41.5	τ_1 : 0.8 (75.8%) τ_2 : 4.2 (24.2%) $\tau_{ave.}$: 2.2
		PbI ₂ and CsBr		Good	620 nm	10.4	τ_1 : 0.4 (74.8%) τ_2 : 3.0 (25.2%) $\tau_{ave.}$: 1.1

Table S1. A systematic study of the influence of synthesis parameter in the observed structures as well as their luminescence characteristics.

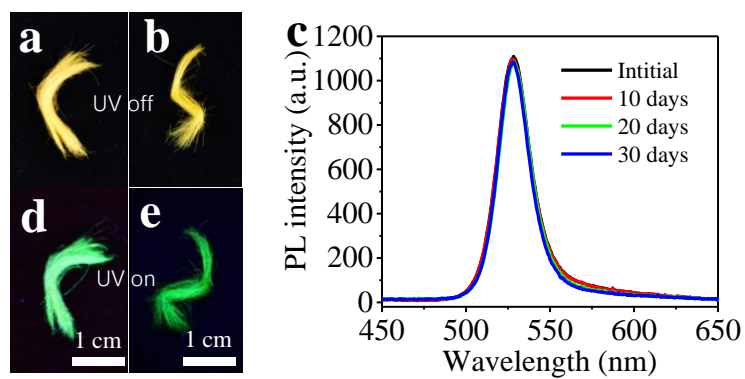


Figure S9. Photographs of Cs_4PbBr_6 @*Calotropis gigantea* fibers (a, d) before and (b, e) after 30 days under ambient atmosphere. (c) Corresponding fluorescence spectra of Cs_4PbBr_6 @*Calotropis gigantea* fibers before and after 30 days.

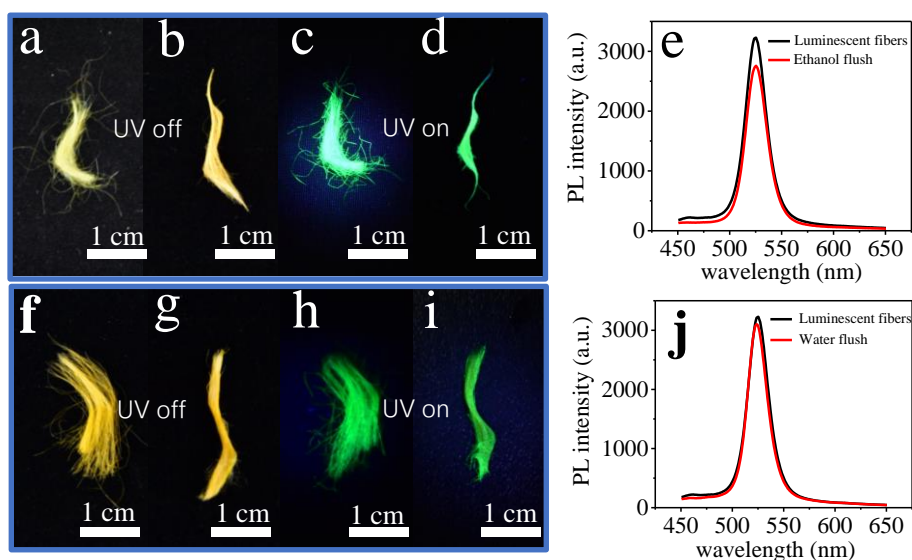


Figure S10. (a-d) Photographs and (e) corresponding fluorescence spectra of Cs_4PbBr_6 @*Calotropis gigantea* fibers (a, c) before and (b, d) after being washed by ethanol. (f-i) Photographs and (j) fluorescence spectra of Cs_4PbBr_6 @*Calotropis gigantea* fiber (f, h) before and (i, g) after being washed by water.

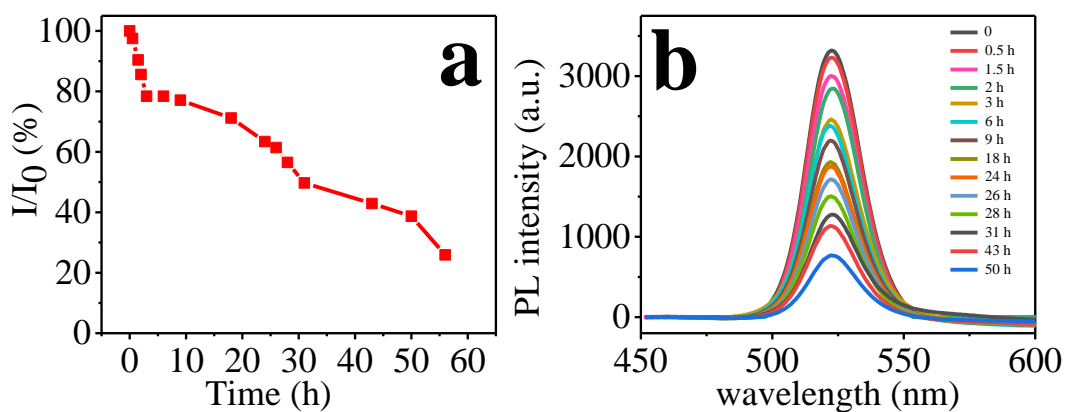


Figure S11. (a) Fluorescence intensity evolution of the luminescent fibers immersed in artificial human sweat as function of time. (b) Corresponding fluorescence spectra after 50 hours of immersion in artificial human sweat, the luminescence intensity of the fiber decreased to ~38.7% of initial intensity.

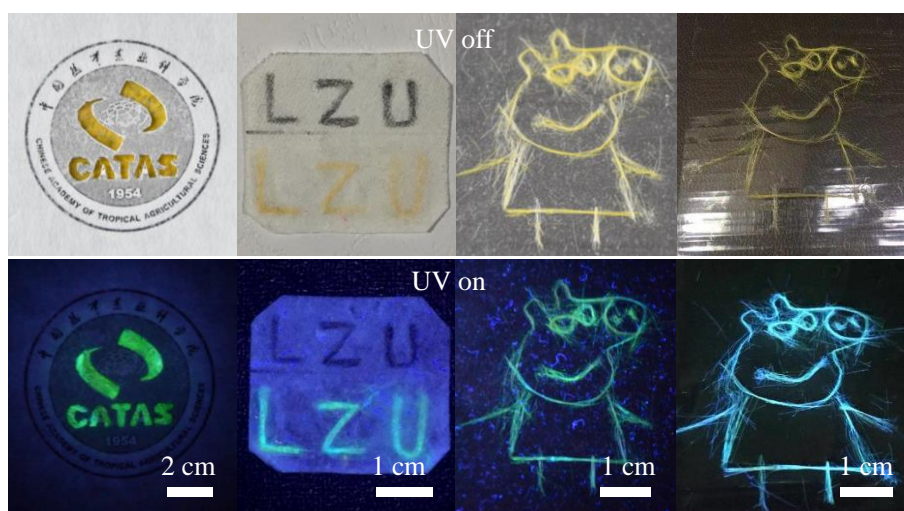


Figure S12. More demonstration of multicolor display using the luminescent fibers.

References

1. G. Liang, M. Yi, H. Hu, K. Ding, L. Wang, H. Zeng, J. Tang, L. Liao, C. Nan, Y. He and C. Ye, *Adv. Electron. Mater.*, 2017, 3, 1700401.