

## **Supporting Information**

### **Triplet-triplet annihilation upconversion combined with afterglow phosphors for multi-dimensional anti-counterfeiting and encoding**

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## Experimental section

**Materials.** All reagents and chemicals were purchased from commercial sources and used without further purification. Platinum octaethylporphyrin (PtOEP) was purchased from Frontier Scientific, Inc. 9,10-diphenylanthracene (DPA) and tetrahydrofuran (THF) were purchased from J&K Scientific Ltd. Poly- $\alpha$ -pinene (P $\alpha$ P) ( $M_w = 2500$  Da) was purchased from Ganzhou Taipu Chemical Co., Ltd. Polyisobutylene (PIB) ( $M_w = 55000$  Da) was purchased from Aladdin Reagent (Shanghai) Co., Ltd. All afterglow phosphors were purchased from Dalian Luminglight Science & Technology Co., Ltd. The paper used for printing substrates were purchased from Deli Group Co., Ltd.

**Preparation of multi-mode luminescent inks.** 0.9 g P $\alpha$ P was weighed, ground into powder and then dissolved in 30 mL THF. 6 g PIB was added, and the solution was vibrated by a homogenizer until the mixture was homogeneous. Then the solution was mixed with 1 g afterglow phosphors and put aside for later use. PtOEP and DPA were dissolved in THF as a mother solution with concentrations of  $1 \times 10^{-4}$  M and  $1 \times 10^{-2}$  M, respectively. At last, the mother solution of triplet-triplet annihilation upconversion (TTA-UC) system was mixed with the polymer solution. The excessive THF was removed by rotatory evaporation to make the total weight of the ink was 10 g. The other inks with different composition used in the applications were prepared according to the above method.

**Printing of multi-mode luminescent patterns.** Patterning preparation of the multi-mode luminescent materials was proceeded using a direct-writing equipment (Sonoplot, Microplotter II). The inks were deposited on substrates by a capillary tube fixed on a X-Y-Z three-dimensional moving platform. The patterns were designed and drawn on the instrument software.

**Characterization.** Absorption and transmitted spectra were measured by a UV-vis-NIR absorption spectrophotometer (Shimadzu, UV-2600). Emission spectra, excitation spectra and phosphorescence decays were measured by fluorescence spectrophotometer (Edinburgh, FLS-920). The phosphorescence decays measurement was excited by a pulsed light source (Edinburgh, uF920H). Photoluminescence spectra were also measured by a fiber optical spectrometer (ideaoptics, NOVA). UC emission spectra were measured under the excitation of a 532nm CW laser (Lasever Inc., LSR532H-3W-FC, 3 W, 2 mm light spot diameter). The laser power intensity was measured by a power meter (Beijing Yanbang Technology Co., Ltd., VLP-2000). The laser power intensity was controlled by a double polarizer attenuator. The film samples was also excited by a 532 nm laser pointer (Whist Inc., A16). Photographs were taken by a smart phone. Viscosity was measured by a viscometer (Shanghai JingKe Scientific Instrument Co., Ltd.). The size and morphology of the phosphor powders were measured by a scanning electron microscope (Phenom, Pro).

**Quantum Yield Measurement.** The normalized upconversion efficiency of PtOEP/DPA dispersed in P $\alpha$ P/PIB polymer matrix was measured by using rhodamine 6G in ethanol ( $\Phi_{\text{std}} = 0.95$ )<sup>1</sup> as the standard sample. The concentrations of sensitizer and emitter were  $1 \times 10^{-5}$  M and  $2 \times 10^{-3}$  M respectively. The calculation equation<sup>2,3</sup> was as follows:

$$\xi_{\text{UC}} = 2\Phi_{\text{UC}} = 2\Phi_{\text{std}} \left( \frac{A_{\text{std}}}{A_{\text{UC}}} \right) \left( \frac{I_{\text{UC}}}{I_{\text{std}}} \right) \left( \frac{\eta_{\text{UC}}}{\eta_{\text{std}}} \right)^2$$

where  $\xi$ ,  $\Phi$ ,  $A$ ,  $I$ , and  $\eta$  represents the normalized upconversion efficiency, raw quantum yield (photons out/photons in), absorbance at excitation wavelength (532 nm), PL integrated intensity, and refractive index of the medium (1.36 for ethanol, 1.53 for P $\alpha$ P/PIB), respectively. The equation is multiplied by a

factor of 2 accounting for the fact that two absorbed photons are required to produce one upconverted photon.

**TTET efficiency.** The TTET efficiency from the sensitizer PtOEP to the annihilator DPA was calculated through the following equation:<sup>4</sup>

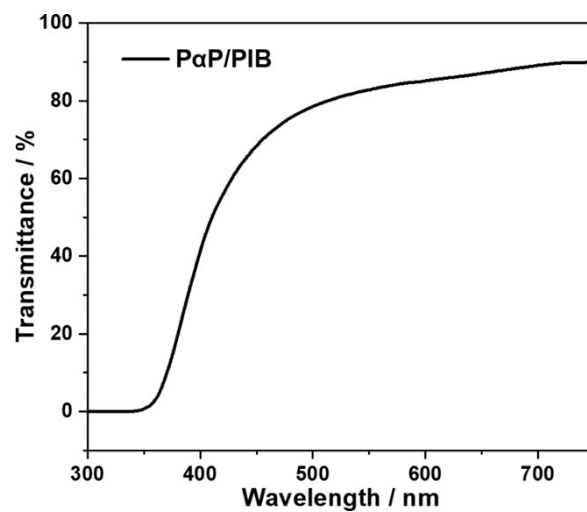
$$\Phi_{\text{TTET}} = 1 - \frac{\tau_{S/A}}{\tau_S}$$

where  $\tau_{S/A}$  and  $\tau_S$  represent the phosphorescence lifetime of sensitizer PtOEP with and without the annihilator DPA in the dual polymer matrix, respectively.

**Energy transfer efficiency from TTA-UC to phosphor.** The energy transfer efficiency ( $\phi_{\text{ET}}$ ) from TTA-UC to phosphors was calculated using equation<sup>5,6</sup> as follows:

$$\phi_{\text{ET}} = \frac{n_{\text{abs}}^{\text{P}}}{n_{\text{em}}^{\text{UC}}} = \frac{I_0^{\text{UC}} - I_{\text{P}}^{\text{UC}}}{I_0^{\text{UC}}}$$

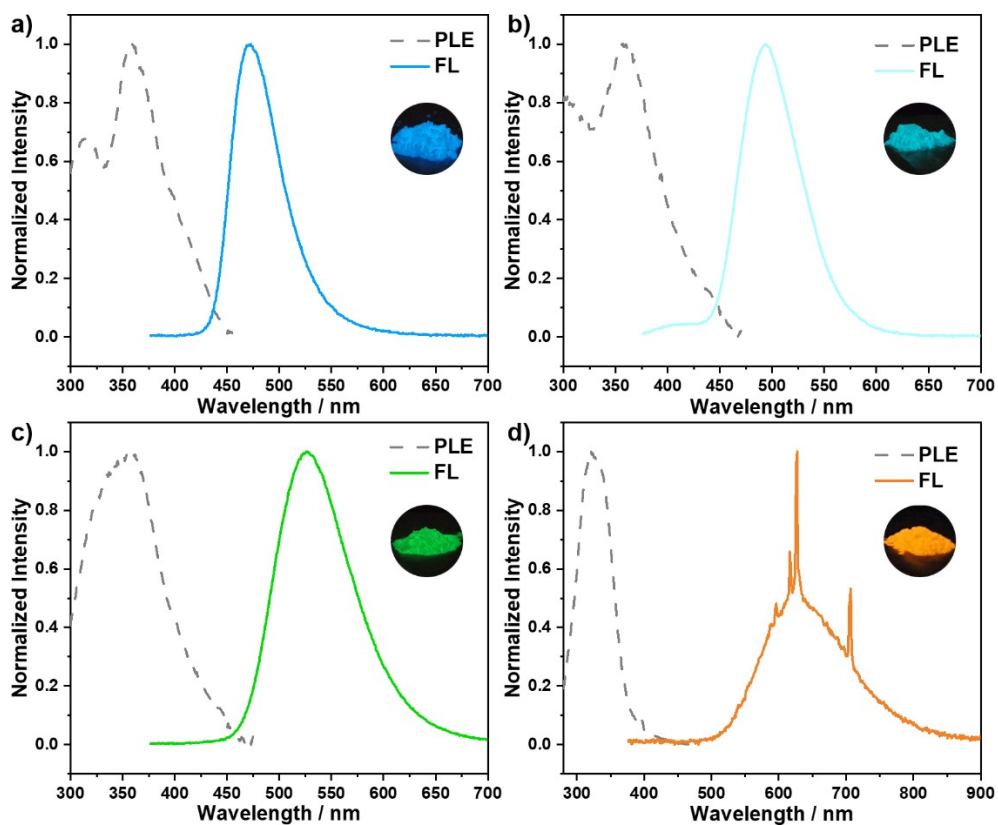
where  $n_{\text{abs}}^{\text{P}}$  and  $n_{\text{em}}^{\text{UC}}$  represent the number of photons absorbed by the phosphors and the number of photons emitted by TTA-UC.  $I_0^{\text{UC}}$  and  $I_{\text{P}}^{\text{UC}}$  is the UC integrated intensity of PtOEP/DPA and PtOEP/DPA/phosphor, respectively.



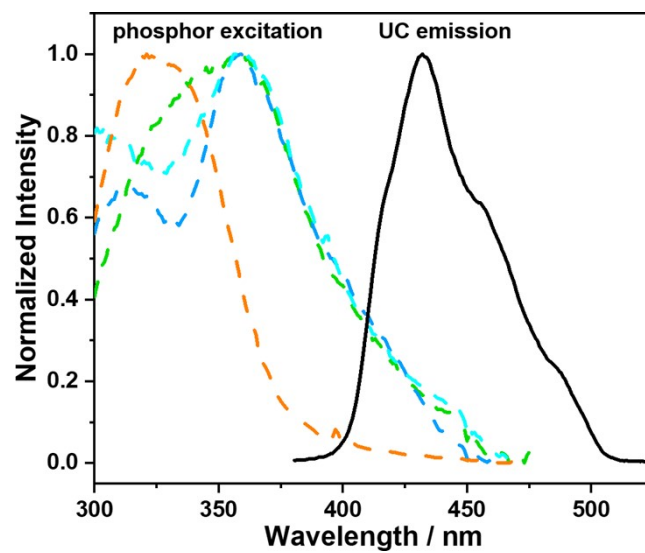
**Fig. S1** The transmittance of the blank dual polymer matrix. The weight ratio of PαP/PIB was 3:20.

**Table S1** Information of the commercial afterglow phosphors.

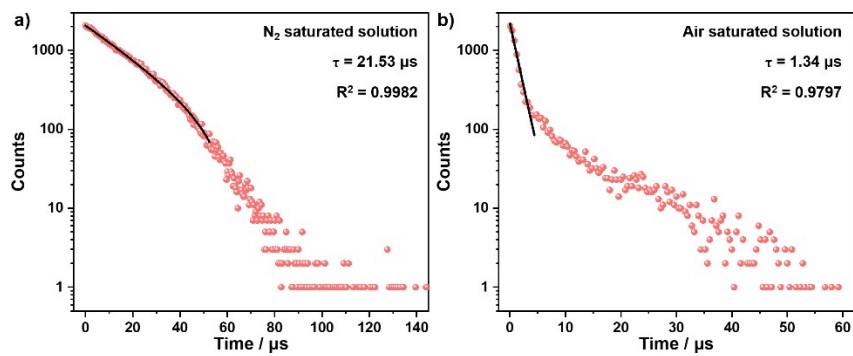
<b>Product Number</b>	<b>Apparent Color</b>	<b>Luminescent Color</b>	<b>Main Composition</b>	<b>Excitation Range (nm)</b>	<b>Emission Peak (nm)</b>
SB-8	white	<b>blue</b>	MeO·0.5SiO <sub>2</sub> :Eu (Me: Mg & Sr)	300-450	472
PLB	light green	<b>cyan</b>	SrO·2Al <sub>2</sub> O <sub>3</sub> :Eu	300-470	493
PLO	light yellow	<b>green</b>	SrAl <sub>2</sub> O <sub>4</sub> :Eu	300-470	526
REO-1	white	<b>orange</b>	Y <sub>2</sub> O <sub>2</sub> S:Eu	300-450	627



**Fig. S2** Photoluminescence excitation (PLE) and PL spectra of europium-doped inorganic phosphors with different luminescent colors: (a) blue (Emission: 472 nm for PLE spectrum), (b) cyan (Emission: 493 nm for PLE spectrum), (c) green (Emission: 526 nm for PLE spectrum) and (d) orange (Emission: 627 nm for PLE spectrum). Excitation: 365 nm for PL spectrum.

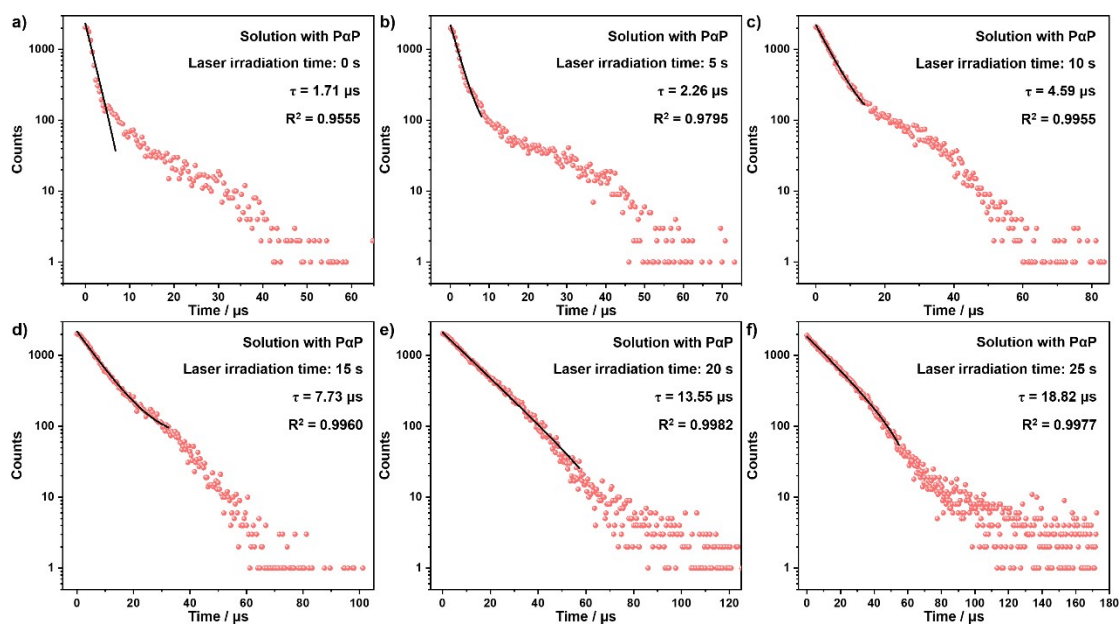


**Fig. S3** PLE spectra of the phosphors (dashed lines) (the same results in Fig. S2) and the UC emission spectrum of PtOEP/DPA in THF solution (solid line). Excitation: CW 532 nm laser, 50mW.



**Fig. S4** The fitting results of the phosphorescence decay curves in Fig. 2b. The phosphorescence lifetimes of PtOEP in N<sub>2</sub> saturated THF solution and air saturated THF solution were 21.53  $\mu\text{s}$  and 1.34  $\mu\text{s}$ , respectively. Measurement excitation: 532 nm pulsed light source; emission: 645 nm.

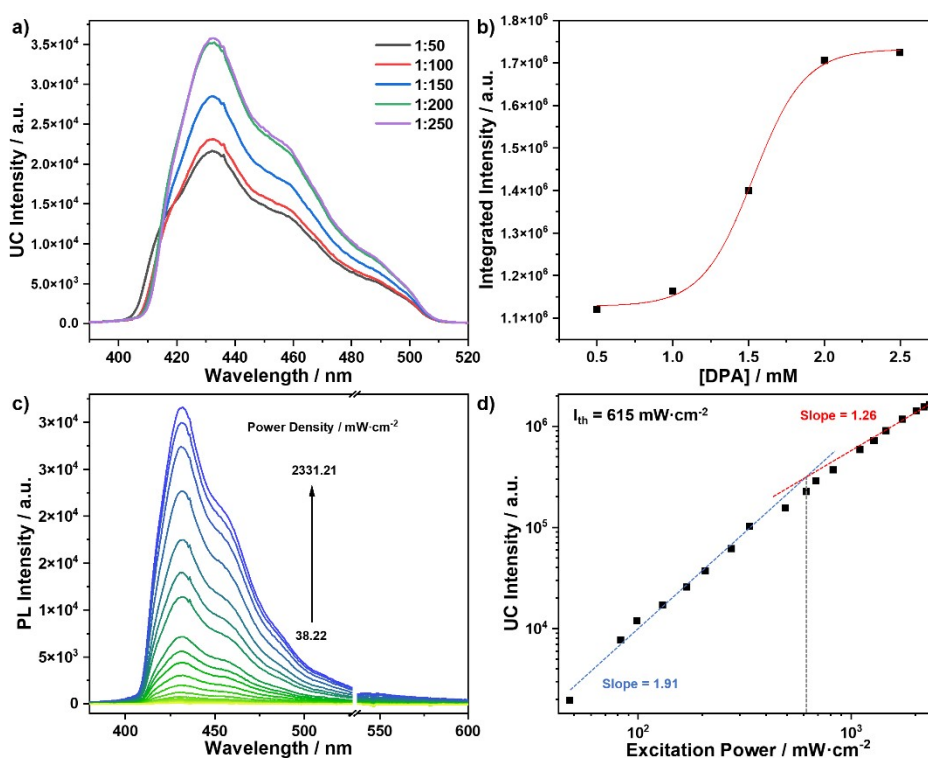




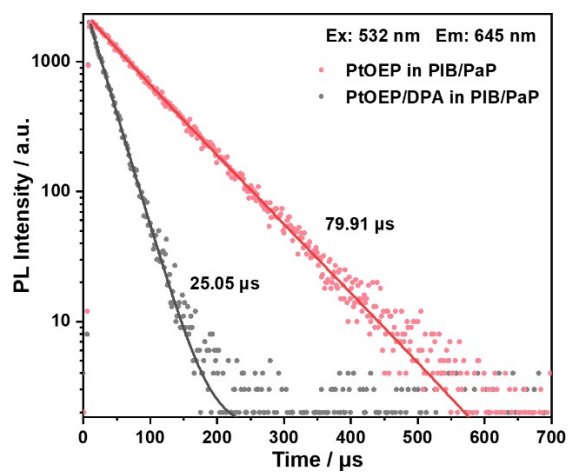
**Fig. S5** The fitting results of the phosphorescence decays in Fig. 2c. The phosphorescence lifetime of PtOEP in air saturated THF solution with PaP gradually increased from 1.71  $\mu\text{s}$  to 18.82  $\mu\text{s}$  under the irradiation of a 50 mW CW 532 nm laser. The irradiation time from 0 to 25 s. Phosphorescence decay measurement excitation: 532 nm pulsed light source; emission: 645 nm.

**Table S2** The fitting results of the phosphorescence decay curves in Fig. 2b and 2c.

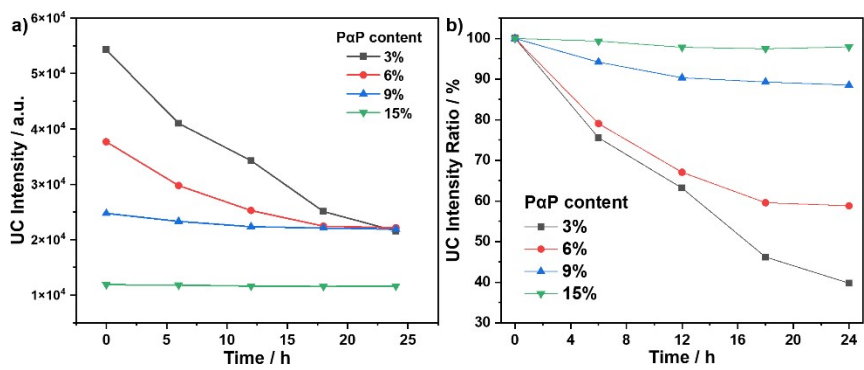
Fitting Equation	Results						
$y = Ae^{-\frac{x}{\tau}} + y_0$	THF solution						
	atmosphere condition	air saturated			N <sub>2</sub> saturated		
	$\tau / \mu\text{s}$	1.34			21.53		
	THF solution with P $\alpha$ P						
	laser irradiation time / s	0	5	10	15	20	25
	$\tau / \mu\text{s}$	1.71	2.26	4.59	7.73	13.55	18.82



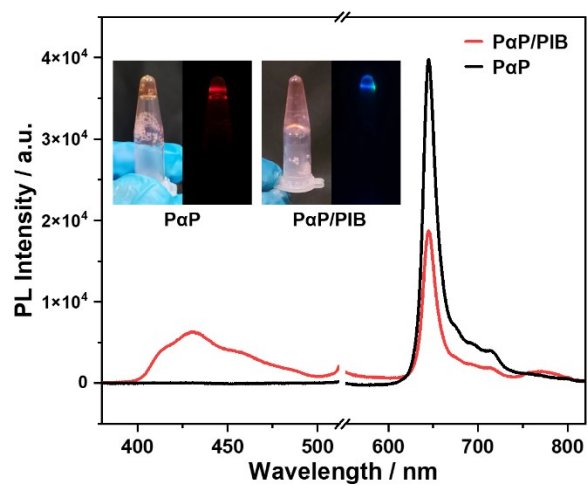
**Fig. S6** (a) UC spectra of the solid-state samples (PtOEP/DPA@PαP/PIB, weight ratio of PαP/PIB was 3:20) with constant sensitizer concentration ( $1 \times 10^{-5}$  M) and increasing annihilator concentration from  $5 \times 10^{-6}$  M to  $2.5 \times 10^{-5}$  M. Excitation: CW 532 nm laser, 50 mW. (b) The integrated UC emission intensity of samples in (a) dependent on DPA concentration. (c) UC spectra of the optimum sample in (a) excited by 532 nm laser with increasing power density. (d) Double logarithmic diagram of the integrated UC intensity in (c) depending on excitation power density.



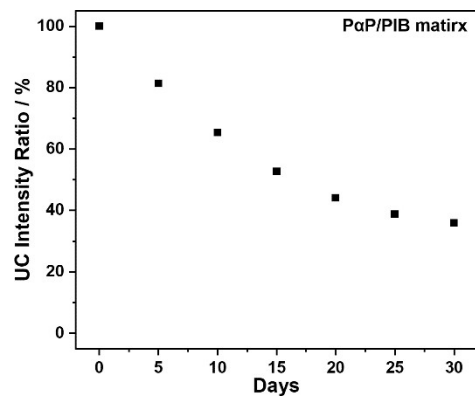
**Fig. S7** Phosphorescence decays of PtOEP in PaP/PIB dual polymer matrix (weight ratio of PaP/PIB was 3:20) with and without DPA. Excitation: 532 nm pulsed light source; emission: 645 nm.



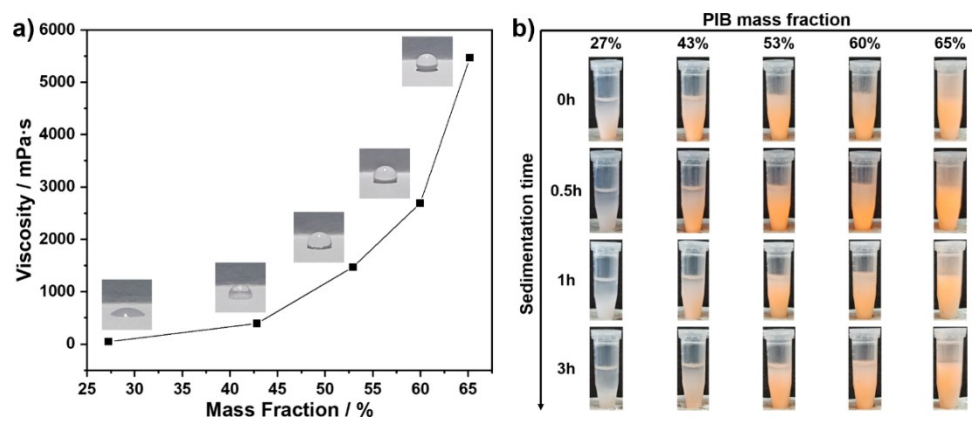
**Fig. S8** The UC emission stability measurement of the PtOEP/DPA/phosphor/PαP/PIB@THF ink samples with different PαP content exposed in air for 24h. (a) Time dependence of absolute UC intensity. (b) Time dependence of relative UC intensity. All samples were stored and measured at room temperature. Excitation: CW 532 nm laser, 50 mW.



**Fig. S9** PL spectra of multi-mode luminescent system dispersed in solid-state PαP and PαP/PIB (3:20). Inset: bright- and dark-field images of the two solid samples in a sample tube. Excitation: CW 532 nm laser, 50 mW.

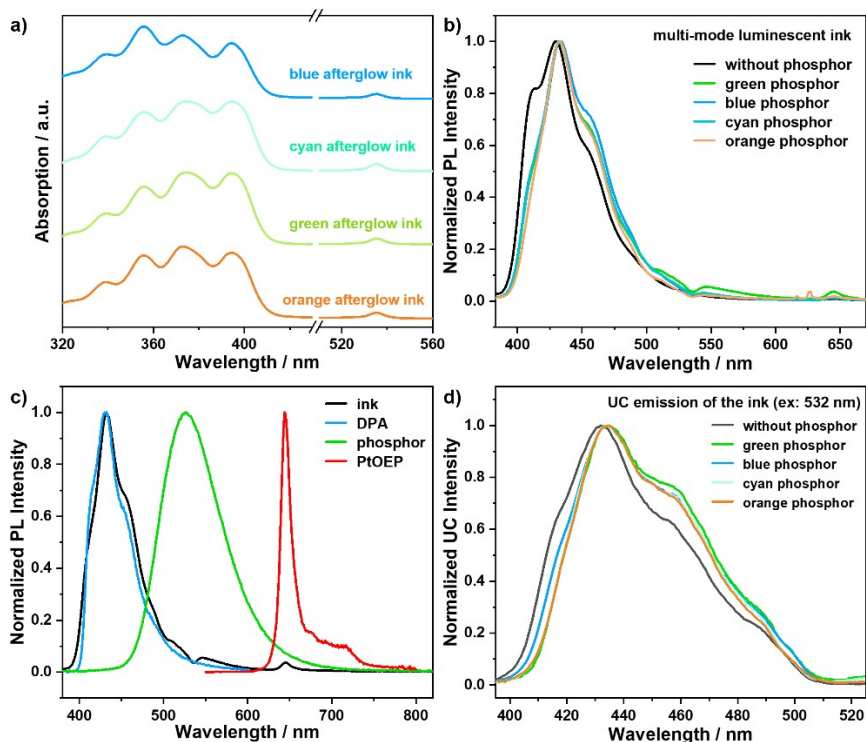


**Fig. S10** The UC emission stability measurement of the PtOEP/DPA/phosphor@PaP/PIB solid-state sample. The weight ratio of PaP/PIB was 3:20. The sample was stored at room temperature and in dark place. Excitation: CW 532 nm laser, 50 mW.

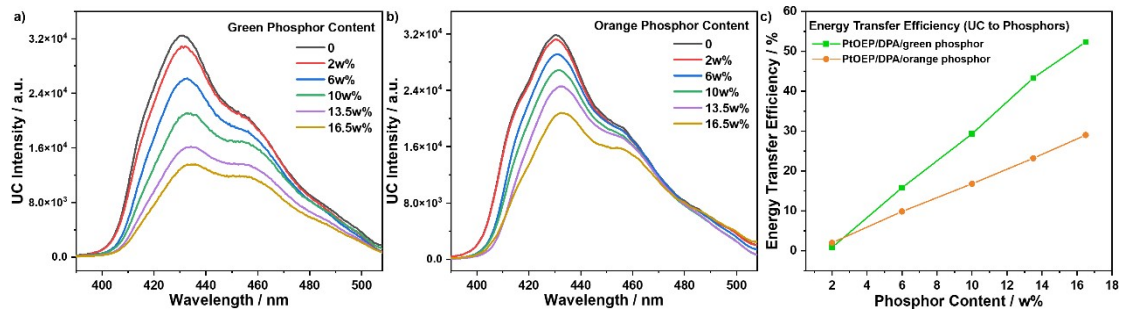


**Fig. S11** (a) Ink viscosity dependence on the mass fraction of PIB. Inset: photographs of the wetting behaviors of the corresponding ink droplets on a paper substrate. (b) Dispersivity behaviors of the same amount of phosphor powders (10 w%) in the inks with different PIB contents after different sedimentation time.

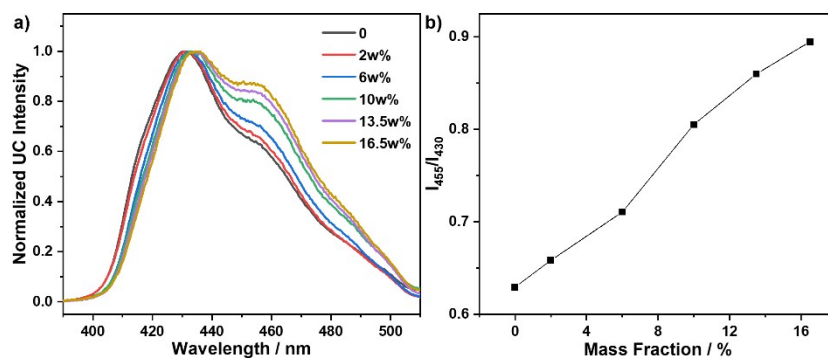




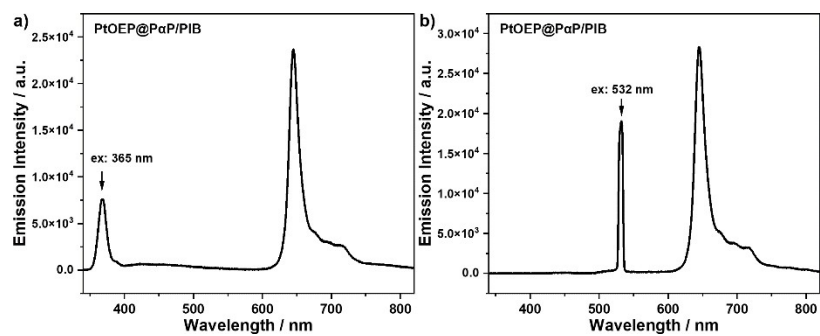
**Fig. S12** Optical properties of the multi-mode luminescent inks (DPA/PtOEP/phosphor/PαP/PIB@THF) with different afterglow colors. (a) Absorption spectra of ink samples. (b) Normalized PL spectra of the ink samples. Excitation: 365 nm. (c) Comparison of normalized PL spectra of the ink sample with the green phosphor, DPA, green phosphor and PtOEP. Excitation: 365 nm. (d) UC emission spectra of the ink samples. Excitation: CW 532 nm laser, 50 mW.



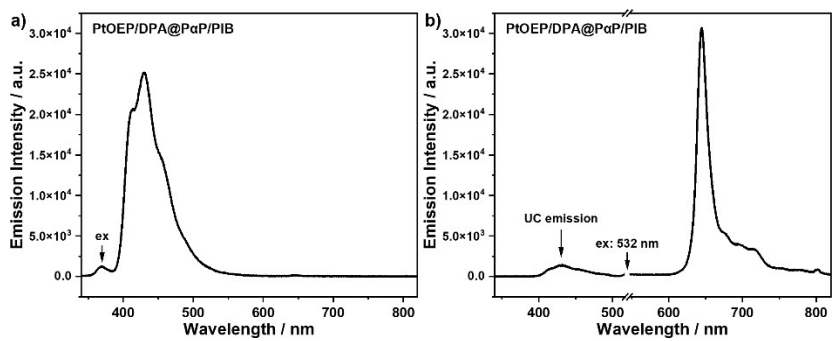
**Fig. S13** (a) UC spectra of PtOEP/DPA/phosphor@PαP/PIB with different content of the green phosphor. (b) UC spectra of PtOEP/DPA/phosphor@PαP/PIB with different content of the orange phosphor. (c) Calculated energy transfer efficiencies from TTA-UC to the phosphors based on the results in (a) and (b). Excitation: CW 532 nm laser, 50 mW.



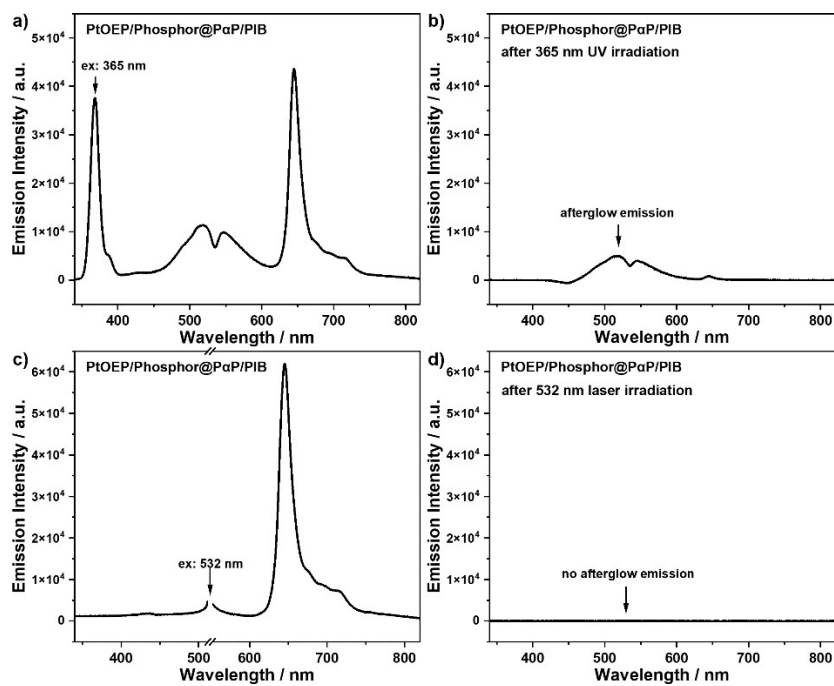
**Fig. S14** (a) Normalized UC spectra of PtOEP/DPA/phosphor@P $\alpha$ P/PIB with different content of the green phosphor. Excitation: CW 532 nm laser, 50 mW. (b) Ratio intensity ( $I_{455}/I_{430}$ ) of the samples in (a) dependent on the content of the green afterglow phosphor.



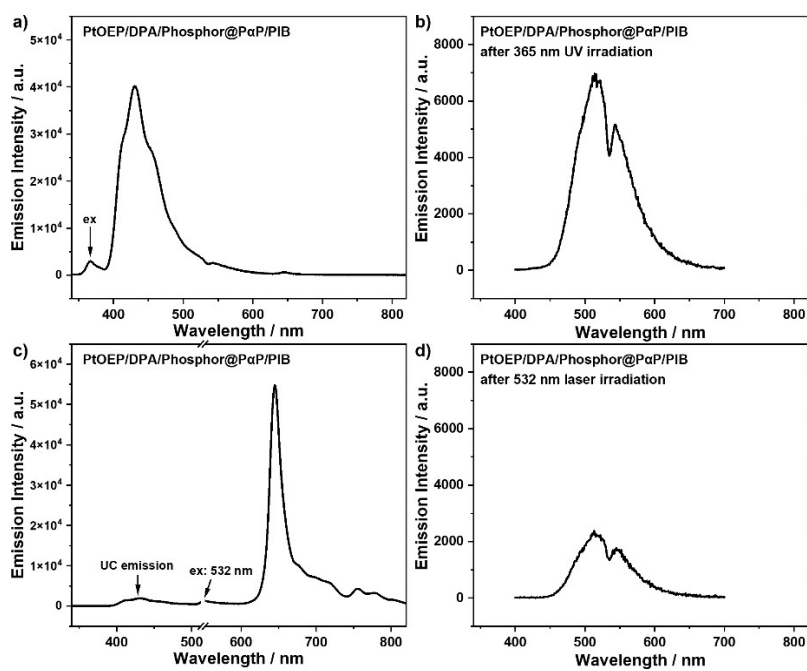
**Fig. S15** PL spectra of the solid-state sample PtOEP@PαP/PIB. Weight ratio of PαP/PIB was 3:20. (a) PL spectrum under the excitation of 365 nm UV light. (b) PL spectrum under the excitation of 532 nm laser (50 mW).



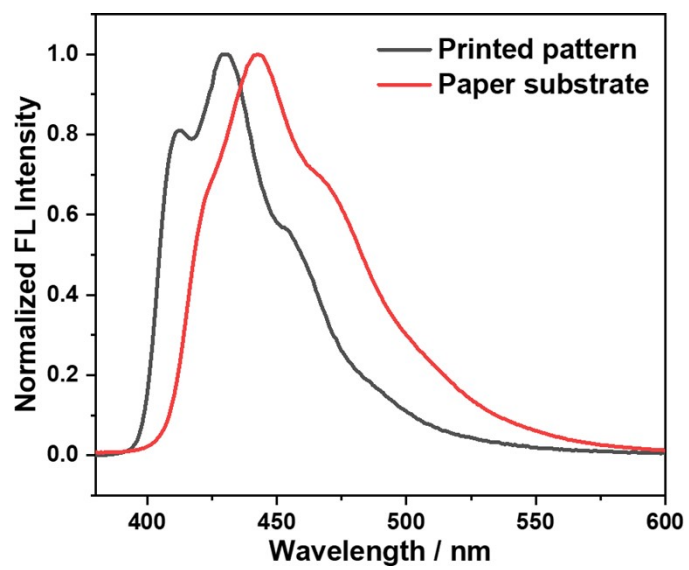
**Fig. S16** PL spectra of the solid-state sample PtOEPDPA@PαP/PIB. Weight ratio of PαP/PIB was 3:20. (a) PL spectrum under the excitation of 365 nm UV light. (b) PL spectrum under the excitation of 532 nm laser (50 mW).



**Fig. S17** PL spectra of the solid-state sample PtOEP/phosphor@PaP/PIB. Weight ratio of PaP/PIB was 3:20; afterglow color: green. (a) PL spectrum under the excitation of 365 nm UV light. (b) Afterglow emission spectrum after 10 s irradiation of the 365 nm UV light. (c) PL spectrum under the excitation of 532 nm laser (50 mW). (d) Emission spectrum after 10 s irradiation of the 532 nm laser.

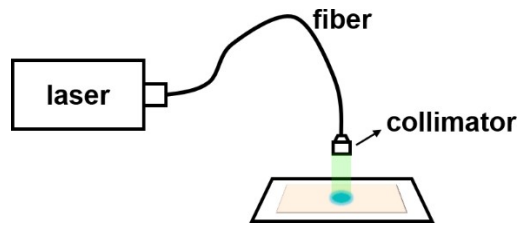


**Fig. S18** PL spectra of the solid-state sample PtOEP/DPA/phosphor@PaP/PIB. Weight ratio of PaP/PIB was 3:20; afterglow color: green. (a) PL spectrum under the excitation of 365 nm UV light. (b) Afterglow emission spectrum after 10 s irradiation of the 365 nm UV light. (c) PL spectrum under the excitation of 532 nm laser (50 mW). (d) Afterglow emission spectrum after 10 s irradiation of the 532 nm laser.

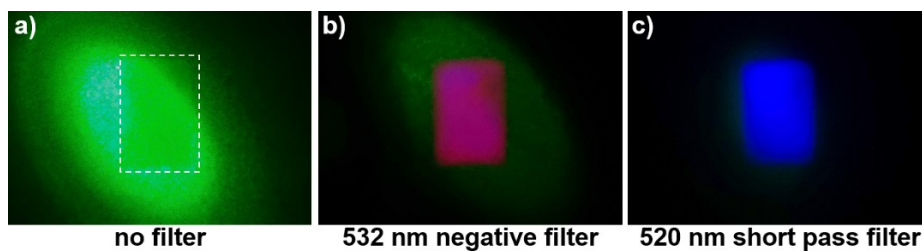


**Fig. S19** Normalized PL spectra of the commercial white printing paper (black line) and DPA (red line). Excitation: 365 nm.

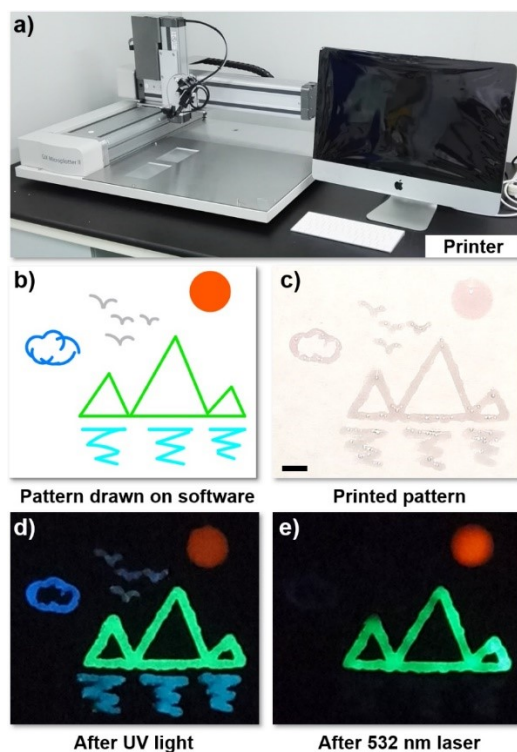




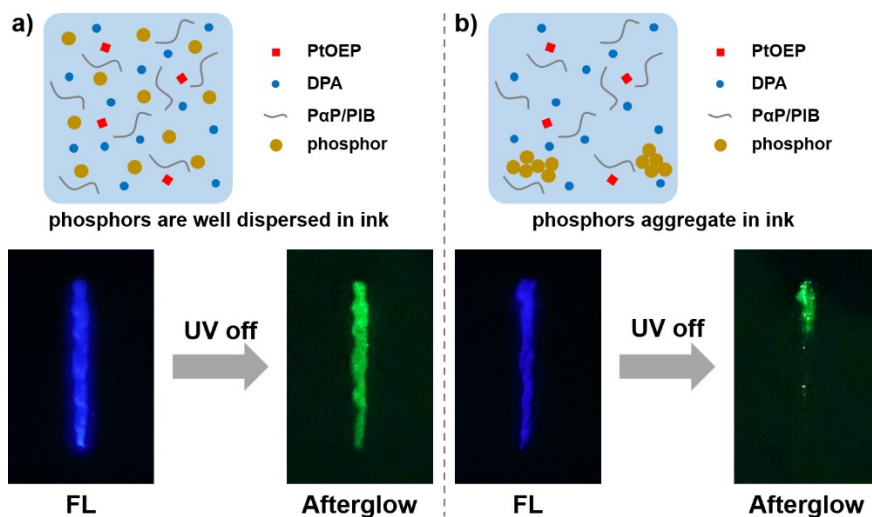
**Fig. S20** The setup of the 532 nm area light source based on a “laser-fiber-collimator” system.



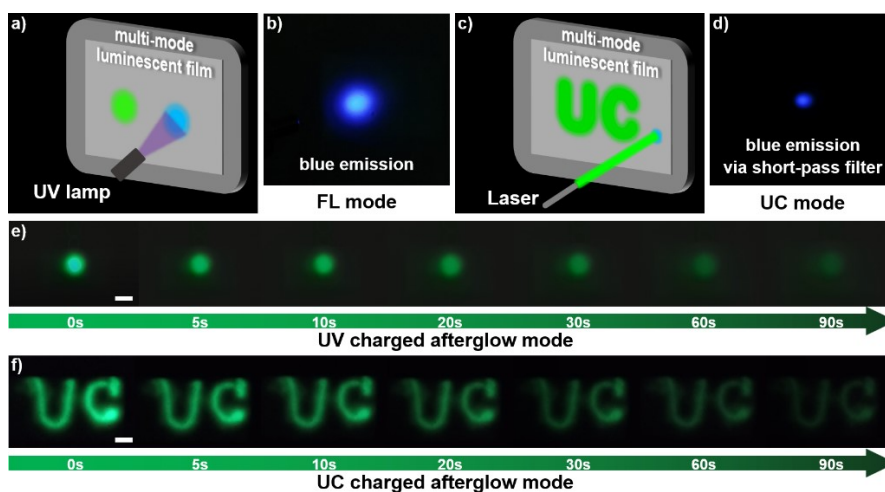
**Fig. S21** Photographs of the pattern sample (PtOEP/DPA/phosphor@PαP/PIB) under the excitation of a 532 nm area light source (3W). (a) Photograph taken without any filters. (b) Photograph taken through a 532 nm negative filter. (c) Photograph taken through a 520 nm short pass filter.



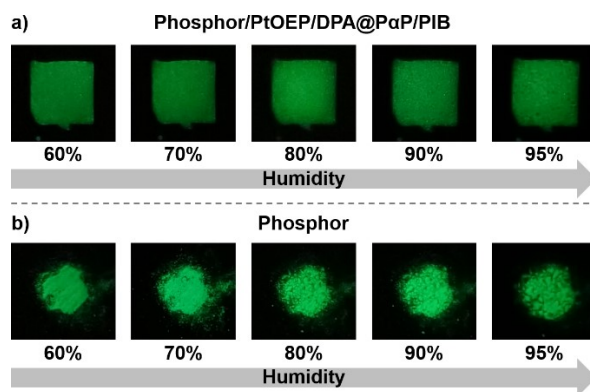
**Fig. S22** “Drop-on-demand” patterning system based on a direct-writing method. (a) Photograph of the printer (Sonoplot, Microplotter II). (b) Pattern drawn on the software of the printer. Each color represented a type of ink with a specific afterglow color. Bird: PtOEP/white phosphor; cloud: PtOEP/blue phosphor; river: PtOEP/cyan phosphor; sun: PtOEP/DPA/orange phosphor; mountain: PtOEP/DPA/green phosphor. (c) The printed pattern based on (b) (scale bar: 2 mm). (d) Afterglow pattern after UV irradiation. (e) Afterglow pattern after 532 nm laser irradiation.



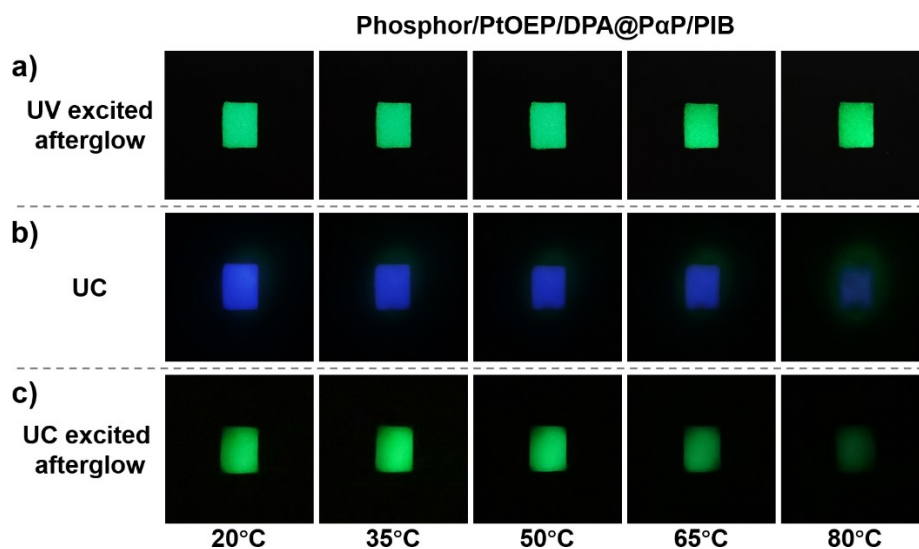
**Fig. S23** (a) Luminescent pattern printed from ink with the phosphor well dispersed. The printed sample displayed even luminescent pattern under the FL and UV excited afterglow modes. (b) Luminescent pattern printed from ink with the phosphor aggregates. The printed sample only displayed even luminescent pattern under the FL mode. Excitation: 365 nm UV light, the afterglow emission images were recorded after 10s UV irradiation.



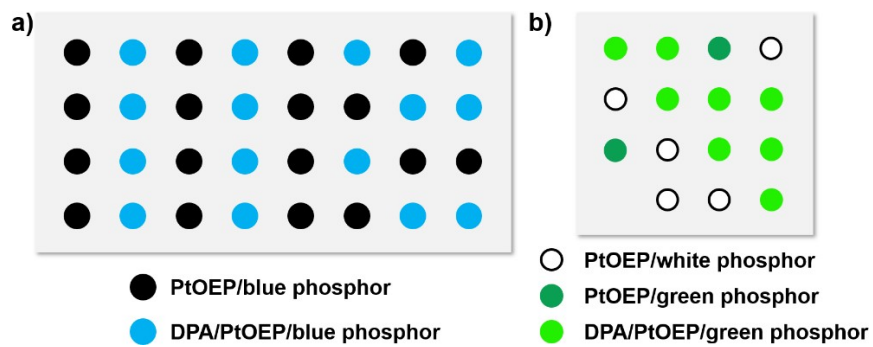
**Fig. S24** The writing panel application of the multi-mode luminescent film. (a) Schematic illustration of the afterglow trace left by the light spot of UV light. (b) Blue emission light spot under the excitation of UV light. (c) Schematic illustration of the “writing” process by the path of the light spot trace of a 532 nm laser pointer (35 mW). (e) Afterglow patterns after different persistent time left by a UV light spot. Scale bar: 2 cm. (f) Afterglow patterns after different persistent time drawn by a 532 nm laser pointer. Scale bar: 5 mm.



**Fig. S25** Afterglow luminescence stabilities of the multi-mode luminescent system (phosphor/PtOEP/DPA@P $\alpha$ P/PIB) and the phosphor alone under different humidity (60-95%). (a) The afterglow luminescent images of the pattern showing the initial afterglow intensity under different humidity. Excitation: CW 532 nm laser, 50mW. (b) The afterglow luminescent images of the phosphor showing the initial afterglow intensity under different humidity. Excitation: 365 nm UV light. All the images were recorded after 10s irradiation of the excitation light source.

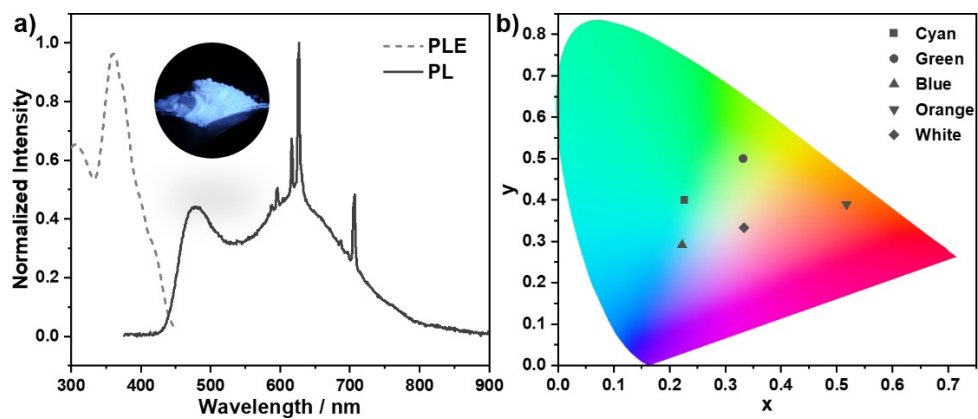


**Fig. S26** The luminescence stabilities of the multi-mode luminescent pattern under different temperature. (a) The afterglow luminescent images of the pattern showing the initial afterglow intensity under different temperature. Excitation: 365 nm UV light. (b) UC luminescence images of the pattern under different temperature. Excitation: CW 532 nm laser, 50 mW. (c) The afterglow luminescent images of the pattern showing the initial afterglow intensity under different temperature. Excitation: CW 532 nm laser, 50 mW. All the afterglow images were recorded after 10s irradiation of the excitation light source.

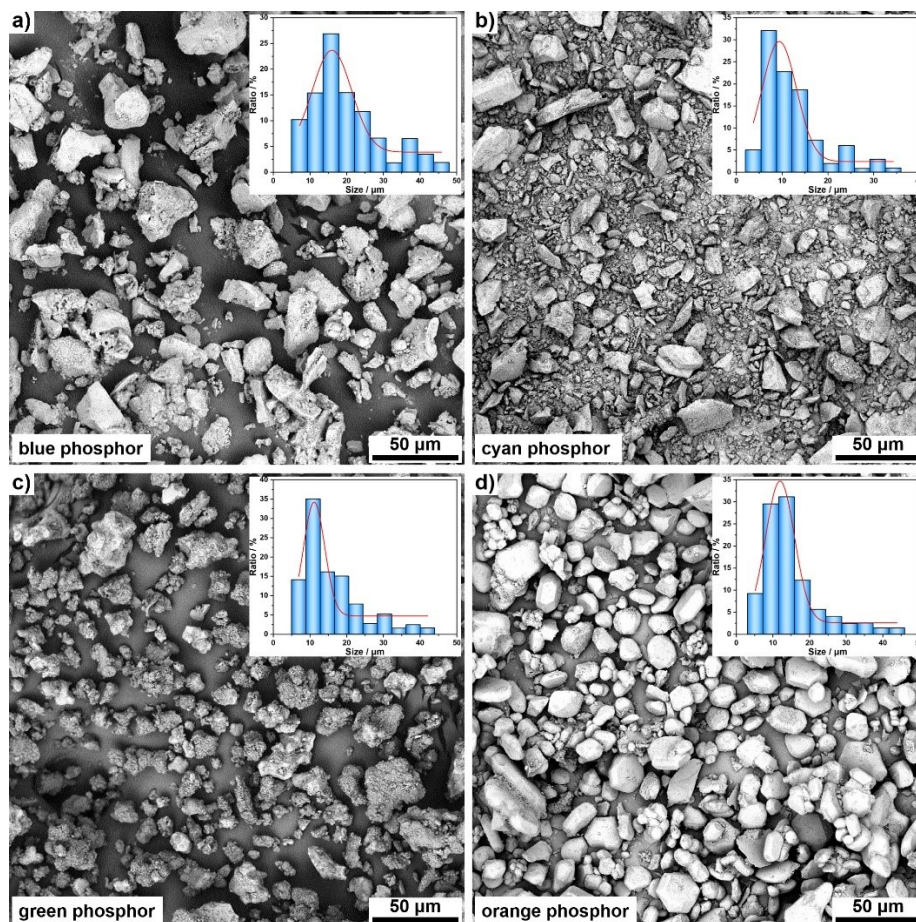


**Fig. S27** Schematic illustration of the composition setup of the printed arrays for the encoding applications. (a) The setup of the array in Fig. 4. (c) The setup of the array in Fig. 5.





**Fig. S28** (a) Excitation and PL spectra of the white afterglow phosphor (mixed by blue and orange phosphors with the weight ratio of 9:8). Emission: 627 nm for PLE spectrum; Excitation: 365 nm for PL spectrum. (b) CIE chromaticity coordinates of all the afterglow phosphors.



**Fig. S29** SEM observations of the four types of phosphors with different afterglow luminescent colors. Inset: size distribution of the sample calculated by measuring the size of the particles in the images. More than 50 particles were measured for each sample.

**Table S3** Statistical results of the phosphor powder size.

<b>Sample</b>	<b>Minimum (<math>\mu\text{m}</math>)</b>	<b>Maximum (<math>\mu\text{m}</math>)</b>	<b>Average (<math>\mu\text{m}</math>)</b>
blue phosphor	5.3	47.3	19.7
cyan phosphor	2.2	35.5	12.4
green phosphor	5.2	43.6	15.9
orange phosphor	4.0	45.1	14.9

## References

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