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Electronic Supplementary Information

Hydrothermal Synthesis and Inkjet Printing of Hexagonal-Phase NaYF₄: Ln³⁺

Hollow Microtubes for Smart Anti-Counterfeiting Encryption

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Experimental section

Preparation: $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%), $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%), $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%), $\text{TmCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%), poly(acrylic acid) (PAA) (average molecular weight = 240,000 g/mol, 25 wt% solution in water) were obtained from Acros. Sodium fluoride (NaF), anhydrous ethanol and glycerin were purchased from Shanghai Aladdin Chemistry Co., Ltd. (China). All other chemicals were of analytical reagent grade which were used without further purification. All solutions used in this work were prepared with deionized water. The printing substrate of A4 duplicating paper was purchased from Double A (1991) Public Co., Ltd.

Synthesis: The $\text{NaYF}_4: \text{Ln}^{3+}$ UCHMs were synthesized via a poly(acrylic acid) (PAA) assisted hydrothermal process with rare earth chloride as lanthanide ions sources, sodium fluoride as sodium and fluoride sources. Taking the synthesis of $\text{NaYF}_4: 20\% \text{Yb}^{3+}, 2\% \text{Er}^{3+}$ UCHMs as a typical example, 236.6 mg (0.78 mmol) $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, 77.5 mg (0.20 mmol) $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, 7.6 mg (0.020 mmol) $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ were firstly dissolved in 5 mL H_2O with magnetic stirring to form the rare earth chloride aqueous solution. Then, a mixture of 15 mL ethanol and 6 mL PAA (10 wt%) aqueous solution containing PAA (2.8×10^{-6} mol) was added into the rare earth chloride aqueous solution. After stirring for 30 min, 8 mL (1.0 M) of NaF (8.0 mmol) aqueous solution was slowly added into the above reaction system under vigorous stirring to form a well-dispersed milky solution. The pH value of the mixture was adjusted at 5.0 by hydrochloric acid (2.0 M). The reaction mixture was stirred at room temperature for 1

h and then transferred into a Teflon bottle held in a stainless steel autoclave, sealed, and maintained at 200 °C for 24 h. After the completion of the hydrothermal reaction, the autoclave was cooled to room temperature naturally. The resulting precipitates were separated by centrifugation at 3000 rpm for 10 min, washed with ethanol/deionized water (v/v = 1:1) three times, and finally dried at 60 °C for 12 h to obtain the NaYF₄: 20% Yb³⁺, 2% Er³⁺ UCHMs as a white powder. The sample was denoted as UCHMs-G. Moreover, the NaYF₄: 10% Er³⁺, 2% Tm³⁺ and NaYF₄: 25% Yb³⁺, 0.3% Tm³⁺ UCHMs were prepared using similar procedures to that of NaYF₄: 20% Yb³⁺, 2% Er³⁺ by doping with different lanthanide ions and tailoring the molar ratio. The samples were denoted as UCHMs-R and UCHMs-B, respectively.

Inks preparation: The hydrophilic UCHMs printing inks were prepared by dispersing the as-synthesized UCHMs in a mixture solvent of ethanol, deionized water and glycerol. To obtain inks with the optimal performance such as viscosity and surface tension, the weight ratio of ethanol, water and glycerol was kept at 40: 40: 20. Typically, certain amount of UCHMs was added to 10.0 g mixture solvent (4.0 g ethanol, 4.0 g deionized water and 2.0 g glycerol). Then, the resulting mixture was vigorously stirred for 20 minutes and followed by 10 minutes of sonication to achieve the well dispersion of UCHMs. To produce three-primary-color inks with similar perceived upconversion brightness, the contents of UCHMs-R, UCHMs-G and UCHMs-B in three-primary-color inks were kept at 1.0 wt%, 0.20 wt% and 0.50 wt%, respectively.

Instruments and characterizations: The phase purity and crystallinity of the as-prepared UCHMs were characterized by X-ray diffraction (XRD) using a Rigaku Model D/max-2500 diffractometer, with Cu K α radiation in the 2θ range of 10-80° with a step size of 0.02°. Fourier transform infrared spectroscopy (FTIR) was recorded on a Nicolet 380 spectrometer using 32 scans and a 4 cm⁻¹ resolution. Field emission scanning electron microscopy (FE-SEM) images were obtained with Hitachi S-3000N instrument. Energy-dispersive X-ray spectroscopy analysis (EDXS) of the samples was performed during FE-SEM measurements to obtain the elemental composition of the samples. Transmission electron microscopy (TEM) was obtained from a JEM-1011 instrument operating at an accelerating voltage of 100 kV. The upconversion emission spectra of the products were carried out using a Hitachi F-4500 5J2-0004 spectrophotometer with an external CNI (5W) 980 nm IR fiber coupled laser system (Changchun New Industries Optoelectronics Tech. Co., Ltd). The photoluminescence mapping of luminescent microtubes was performed using a WITech alpha 300R+ confocal photoluminescence microscope system, where 980 nm diode lasers act as a source of excitation. The kinematic viscosities of the UCHMs inks were obtained by using a 0.4-0.5 mm diameter Capillary Tube Viscometer at 20 °C (Shanghai Loikaw Instrument Co., Ltd, the viscometer constant $k = 0.00589$ mm²/s²). The surface tension of the UCHMs inks was measured with capillary tubes (Shanghai Chang Cheng Scientific Instrument Factory) of 0.9-1.1 mm diameter. The inkjet printing of the UCHMs inks was performed on a Canon PIXMA ip2780 inkjet printer equipped with 25-pL (PG-815) and 2.5-pL cartridges (PG-816). The nozzle

diameter of the cartridge we used (PG-815) is about 37 μm . The photographs of the sample under the 980 nm laser irradiation (5W) were obtained using a Nikon D7000 camera with an infrared filter. The exposure time was 15 s, aperture size used was F14 and photosensitivity (ISO) was 3200.

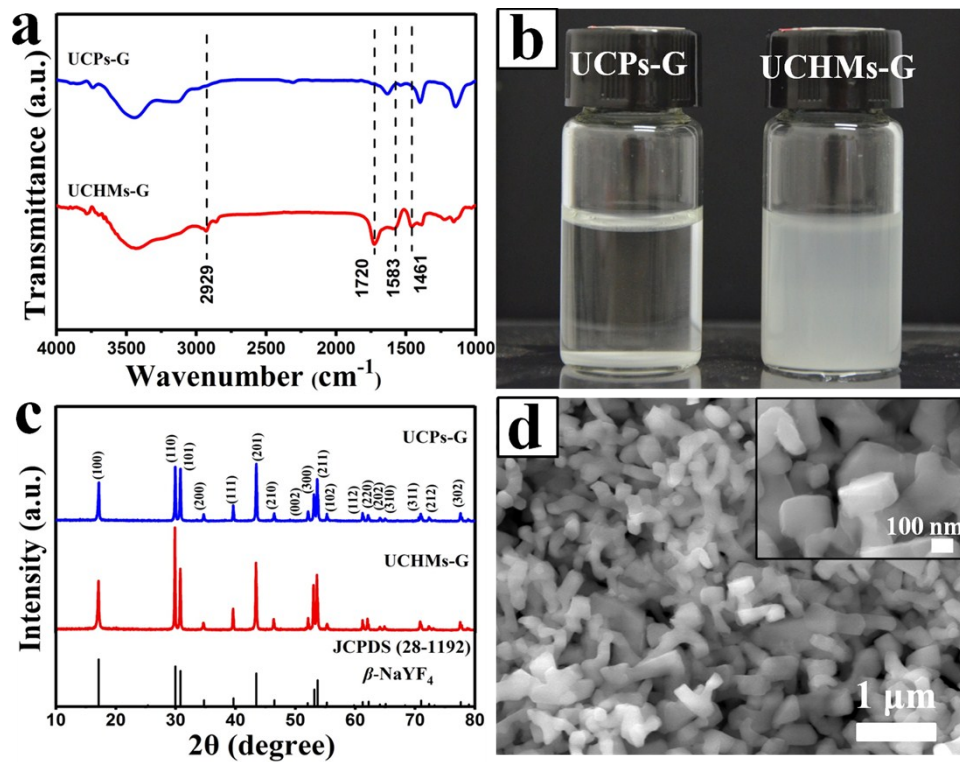


Fig. S1. The (a) FTIR spectra of UCPS-G and UCHMs-G, (b) Comparison of the dispersion of UCPS-G and UCHMs-G in water with the concentration of 5 mg/mL, (c) XRD patterns of the UCPS-G and UCHMs-G, (d) FE-SEM image of UCPS-G.

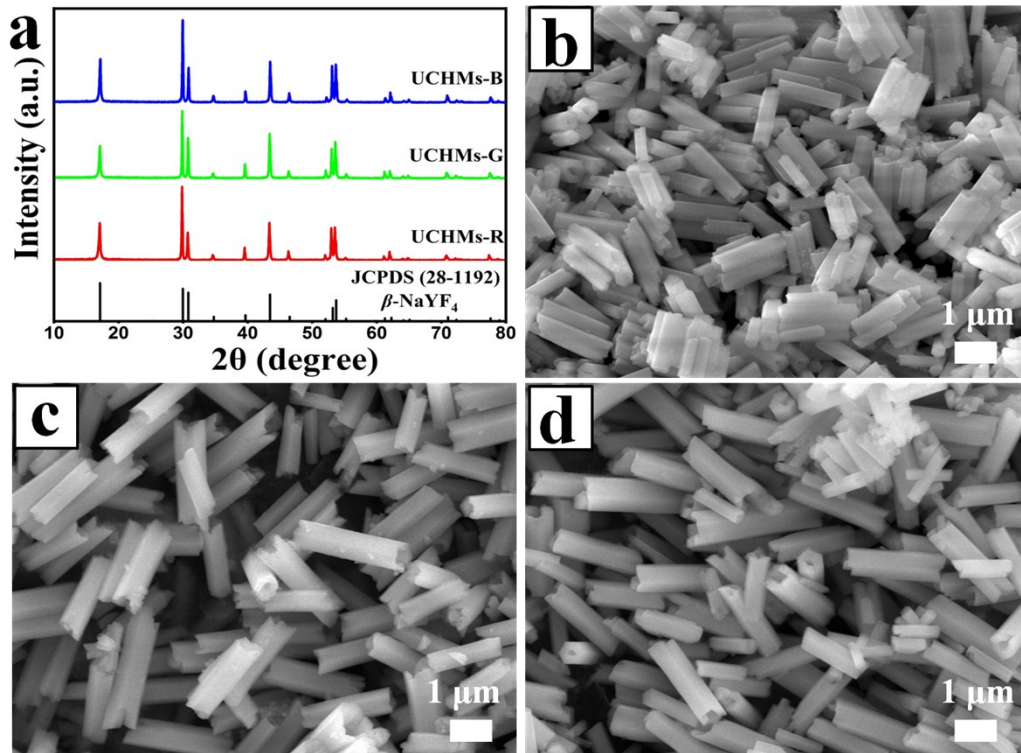


Fig. S2. (a) The XRD patterns of three-primary-color UCHMs and the FE-SEM images of (b) NaYF₄: 10%Er³⁺, 2%Tm³⁺ (UCHMs-R), (c) NaYF₄: 20%Yb³⁺, 2%Er³⁺ (UCHMs-G) and (d) NaYF₄: 25%Yb³⁺, 0.3%Tm³⁺ (UCHMs-B), respectively.

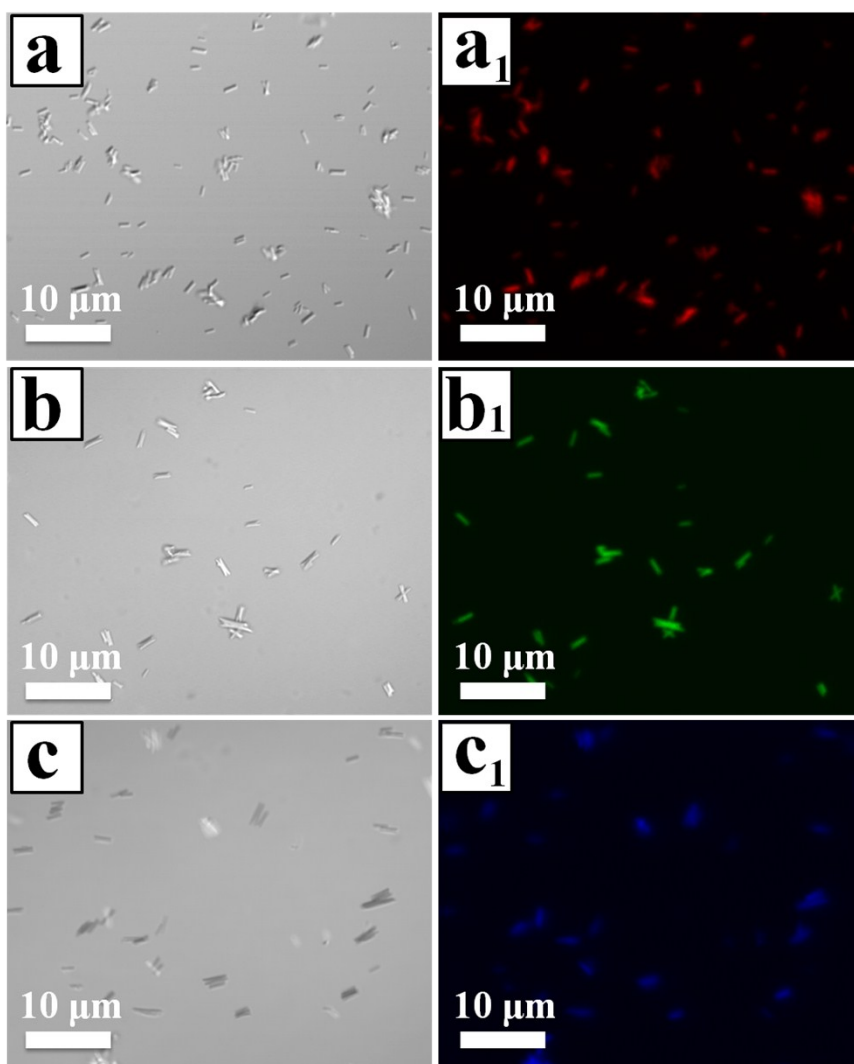


Fig. S3. (a, b, c) Bright field and (a₁, b₁, c₁) upconversion micrographs of the three-primary-color UCHMs dispersed on a glass substrate, respectively.

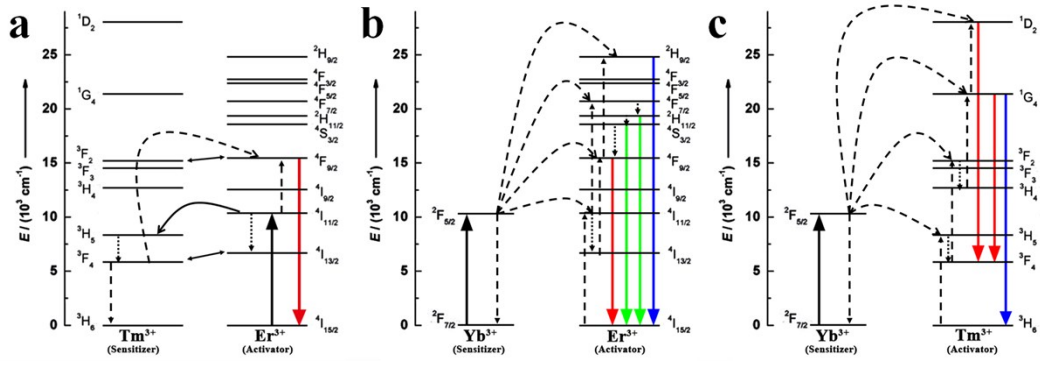


Fig. S4. Proposed energy transfer mechanisms showing the UC processes in (a) Tm³⁺/Er³⁺, (b) Yb³⁺/Er³⁺, (c) Yb³⁺/Tm³⁺ doped crystals under 980 nm laser excitation, respectively. The black full, dashed, dotted and color full arrows represent photon excitation, energy transfer, multiphonon relaxation and emission processes, respectively. Only visible and NIR emissions were shown here.

In Er³⁺/Tm³⁺ codoped NaYF₄ lattice (Fig. S4a), the Tm³⁺ ion acts as a sensitizer and the Er³⁺ ion acts as the activator producing visible emission. Firstly, the ground state of Er³⁺ absorbs directly the 980 nm photons and transits to an excited state $^4\text{I}_{11/2}$ level. Then the energy transfer from $^4\text{I}_{11/2}$ and $^4\text{I}_{13/2}$ of Er³⁺ ion can populate the $^3\text{F}_4$ level of the Tm³⁺ ion. In addition, the $^4\text{F}_{9/2}$ red emitting state of Er³⁺ is populated via cross-relaxation of $^4\text{I}_{11/2}(\text{Er}^{3+}) + ^3\text{F}_4(\text{Tm}^{3+}) \rightarrow ^3\text{H}_6(\text{Tm}^{3+}) + ^4\text{F}_{9/2}(\text{Er}^{3+})$, leading a red $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ (656 nm) emission occurs. For Yb³⁺/Er³⁺ and Yb³⁺/Tm³⁺ system, Yb³⁺ ions have a larger absorption cross section for infrared light, a longer excited state lifetime and a higher doping concentration than Er³⁺ and Tm³⁺ ions. Thus, the main pathway to populate the upper emitting states is the energy transfer from Yb³⁺ ions to Er³⁺ and Tm³⁺ ions. In Yb³⁺/Er³⁺ codoped NaYF₄ lattice (Fig. S4b), the ground state of Yb³⁺ absorbs the 980 nm photons and transits to an excited state $^2\text{F}_{5/2}$ level. The

Er^{3+} ions in the ground state are excited to $^4\text{I}_{11/2}$ state via energy transfer of neighboring Yb^{3+} and Er^{3+} . Subsequent nonradiative relaxations of $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$ also populate the $^4\text{I}_{13/2}$ levels. In the second-step excitation, the same laser pumps the excited-state electrons of $^4\text{I}_{11/2} \rightarrow ^4\text{F}_{7/2}$ level via energy transfer or $^4\text{I}_{13/2} \rightarrow ^4\text{F}_{9/2}$ state via phonon-assisted energy transfer. Subsequent nonradiative relaxations of $^4\text{F}_{7/2} \rightarrow ^4\text{S}_{3/2}$ ($^2\text{H}_{11/2}$) populate the $^4\text{S}_{3/2}$ ($^2\text{H}_{11/2}$) state. Then, following nonradiative relaxations of $^4\text{S}_{3/2} \rightarrow ^4\text{F}_{9/2}$ populate the $^4\text{F}_{9/2}$ state, while the same laser pumps the excited-state electrons from $^4\text{F}_{9/2}$ to $^2\text{H}_{9/2}$ levels via energy transfer. As a consequence, two-photon green $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ (525 nm), $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ (546 nm) emissions, red $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ (656 nm) emission and purple $^2\text{H}_{9/2} \rightarrow ^4\text{I}_{15/2}$ (408 nm) emission are occurred in different energy transfer paths. Similarly, for $\text{Yb}^{3+}/\text{Tm}^{3+}$ system (Fig. S4c), in a first nonradiative energy-transfer step, the Yb^{3+} ion in the $^2\text{F}_{7/2}$ ground state absorbs a 980 nm photon and transits to excited state $^2\text{F}_{5/2}$. The Tm^{3+} ions in the $^3\text{H}_6$ ground state are excited to $^3\text{H}_5$ state via energy transfer of neighboring Yb^{3+} and Tm^{3+} . Subsequent nonradiative relaxations of $^3\text{H}_5 \rightarrow ^3\text{F}_4$ can populate the $^3\text{F}_4$ levels. After multistep excitation energy transfer, the Tm^{3+} is promoted to the $^1\text{G}_4$ emission level, red $^1\text{G}_4 \rightarrow ^3\text{F}_4$ (475 nm) and blue $^1\text{G}_4 \rightarrow ^3\text{H}_6$ (644 nm) emission are occurred. In addition, the Tm^{3+} ion in the $^1\text{G}_4$ level can ulteriorly excite to $^3\text{H}_5$ state via energy transfer, then another blue $^1\text{D}_2 \rightarrow ^3\text{F}_4$ (450 nm) emission is occurred.

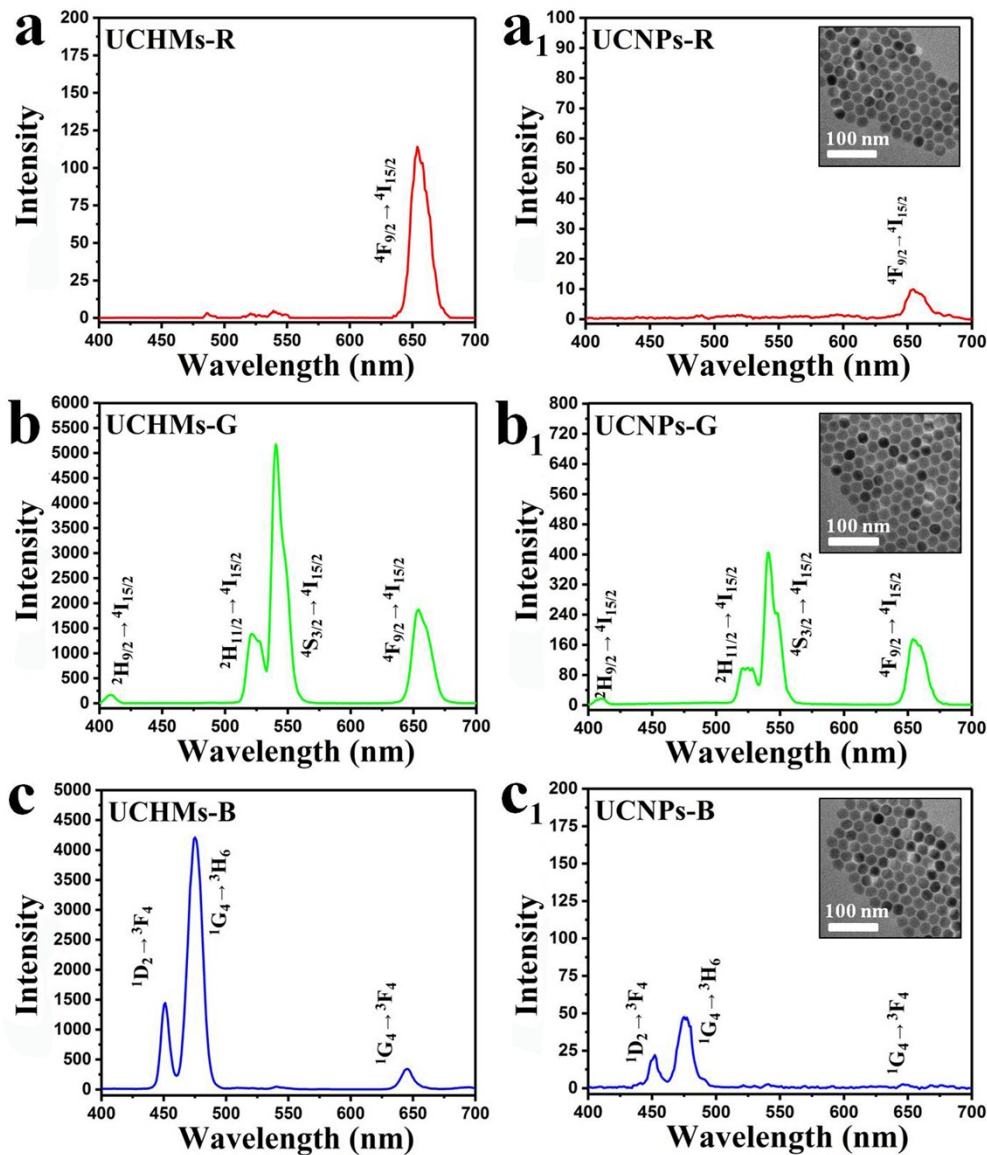


Fig. S5. The comparison of upconversion emission spectra of RGB UCHMs (a, b, and c) and RGB UCNPs (a₁, b₁, and c₁) aqueous dispersion. The TEM images of the synthesized UCNPs were shown in the inset of a₁, b₁ and c₁, respectively.

In order to demonstrate that the synthesized UCHMs possessed high upconversion fluorescence, we compared the luminescent property of UCHMs and upconversion nanoparticles (UCNPs) which have been previously used in inkjet printing. The UCNPs were synthesized by thermal decomposition method employing oleic acid as ligand and followed by PAA modification as discussed elsewhere.^[1] By

doping different lanthanide ions and tailoring the molar ratio of the doped lanthanide ions in UCNPs, three-primary-color (RGB) UCNPs were successfully produced. The synthesized RGB UCHMs exhibited uniform nanosphere morphology with the average diameter of 21 nm (UCNPs-R), 26 nm (UCNPs-G) and 25 nm (UCNPs-B), respectively, as shown in the inset TEM images of Fig. S5. To make a clear comparison, the RGB UCHMs and RGB UCNPs exhibited similar upconversion emission spectra were measured with a 980 nm laser as excitation source operating under the same concentration (1.0 mg/mL) and exciting power density (60 mW/mm²) at room temperature. By measuring the peak intensity of the highest peak in the fluorescence spectra, it was found that the fluorescence intensity of UCHMs-R and UCHMs-G was an order of magnitude higher than that the corresponding UCNPs. For the UCHMs-B sample, the fluorescence intensity was two orders of magnitude higher than the UCNPs-B.

Ink properties

The viscosity of UCHMs-G inks can be got through the following formulas (Equation 1 and 2).

$$v = \kappa \times t \quad (1)$$

$$\eta = v \times \rho \quad (2)$$

where t is the time of certain volume UCHMs-G inks through capillary (s), κ is the viscometer constant (mm^2/s^2), v is calculated to the kinematic viscosity of UCHMs-G inks (mm^2/s), η and ρ are the viscosity ($\text{mPa}\cdot\text{s}$) and density (g/cm^3) of UCHMs-G inks, respectively.

The surface tension of UCHMs-G inks can be got through the following formula (Equation 3).

$$\gamma = \frac{1}{2} \rho g r \left(h + \frac{r}{3} \right) \left(1 - \frac{r}{r_1 - r_2} \right) \quad (3)$$

where r is the inner radius of the capillary (m), h is the liquid rise height of the capillary (m), r_1 is the inner radius of the cylindrical container (m), r_2 is the outer radius of the capillary (m), g is gravitational acceleration ($\text{kg}/\text{m}^2\cdot\text{s}$) and ρ is the density (g/cm^3) of UCHMs-G inks, respectively.

Table S1. Different mass ratio of UCHMs-G inks.

Sample	UCHMs (wt%)	Deionized water (wt%)	Ethanol (wt%)	Glycerol (wt%)
Ink1	0.2	20.0	20.0	60.0
Ink2	0.2	30.0	20.0	50.0
Ink3	0.2	20.0	40.0	40.0
Ink4	0.2	40.0	20.0	40.0
Ink5	0.2	40.0	40.0	20.0
Ink6	0.2	40.0	50.0	10.0

Table S2. Experimental parameters of viscosity test and surface tension test of Ink1-Ink6 UCHMs-G inks.

Sample	Viscosity test					Surface tension test				
	t	c	v	ρ	η	h	r	r_1	r_2	γ
	(s)	(mm ² /s ²)	(mm ² /s)	(g/cm ³)	(mPa·s)	(m)	(m)	(m)	(m)	(mN/m)
Ink1	3175	0.00589	18.701	1.154	21.581	0.0133	0.0005	0.02490	0.00057	37.292
Ink2	1738	0.00589	10.237	0.968	9.909	0.0127	0.0005	0.02500	0.00059	29.890
Ink3	1464	0.00589	8.623	0.996	8.589	0.0122	0.0005	0.02495	0.00058	29.558
Ink4	940	0.00589	5.537	1.035	5.731	0.0108	0.0005	0.02495	0.00058	27.238
Ink5	614	0.00589	3.616	0.949	3.432	0.0145	0.0005	0.02500	0.00055	33.404
Ink6	508	0.00589	2.992	0.909	2.720	0.0127	0.0005	0.02500	0.00055	28.069

Table S3. Experimental parameters of viscosity test and surface tension test of Ink7 (UCHMs-B ink) and Ink8 (UCHMs-R ink).

Sample	UCHMs (wt%)	Deionized water (wt%)	Ethanol (wt%)	Glycerol (wt%)
Ink7	0.5	40.0	40.0	20.0
Ink8	1.0	40.0	40.0	20.0

Sample	Viscosity test					Surface tension test				
	t	c	v	ρ	η	h	r	r_1	r_2	γ
	(s)	(mm ² /s ²)	(mm ² /s)	(g/cm ³)	(mPa·s)	(m)	(m)	(m)	(m)	(mN/m)
Ink7	619	0.00589	3.646	0.945	3.445	0.0143	0.0005	0.02495	0.00058	32.807
Ink8	617	0.00589	3.634	0.939	3.412	0.0140	0.0005	0.02490	0.00058	31.920

Reference

1. M. You, M. Lin, S. Wang, X. Wang, G. Zhang, Y. Hong, Y. Dong, G. Jin and F. Xu, *Nanoscale*, 2016, **8**, 10096-10104.