Electronic Supplementary Information

Anti-counterfeiting Patterns Encrypted with Multi-Mode Luminescent Nanotaggants

Tianying Sun,[a] *Bingzhe Xu,*[b] *Bing Chen,*[a] *Xian Chen,*[a] *Mingyu Li,**[,c] *Peng Shi,**[,b] *and Feng Wang**[,a,d]

[a]Department of Physics and Materials Science City University of Hong Kong, 83 Tat Chee Avenue, Hong Kong SAR, China. E-mail: fwang24@cityu.edu.hk

[b]Department of Medical and Biomedical Engineering, City University of Hong Kong, 83 Tat Chee Avenue, Hong Kong SAR, China. E-mail: pengshi@cityu.edu.hk

[c]State Key Laboratory of Modern Optical Instrumentation, Zhejiang University, Hangzhou 310027, China. E-mail: limy@zju.edu.cn

[d]City University of Hong Kong Shenzhen Research Institute, Shenzhen 518057, China.

Reagent:

$Gd(CH_3CO_2)_3 \cdot xH_2O$, (99.9%), $Y(CH_3CO_2)_3 \cdot xH_2O$, (99.9%), $Yb(CH_3CO_2)_3 \cdot xH_2O$, (99.9%), $Nd(CH_3CO_2)_3 \cdot xH_2O$, (99.9%), $Er(CH_3CO_2)_3 \cdot xH_2O$, (99.9%), $Tm(CH_3CO_2)_3 \cdot xH_2O$, (99.9%), $Ce(CH_3CO_2)_3 \cdot xH_2O$, (99.9%), $Tb(CH_3CO_2)_3 \cdot xH_2O$, (99.9%), $Eu(CH_3CO_2)_3 \cdot xH_2O$, (99.9%), NaOH, (>98%), NH_4F, (>98%), 1-octadecene (90%), oleic acid (90%), were all purchased from Sigma-Aldrich. Absolute ethanol (99.85%), methyl alcohol (99.99%), and cyclohexane (99.9%) were purchased from VWR International. Photoresist SU-8 was purchased from MicroChem. All reagents were used as received without further purification.

Synthesis of lanthanide-doped nanoparticles:

The lanthanide-doped nanoparticle was synthesized by following our previous coprecipitation protocols. In general, lanthanide acetates in water solution was added to a binary solvent mixture of OA and ODE in a 50 mL flask. The mixture was heated at 150^{o}C for 50 min to form the lanthanide-oleate precursor solution before cooling down to 45^{o}C. Thereafter, an appropriate amount of methanol solution containing NH_4F and NaOH was added, and the resultant solution was stirred for 90 min. After the methanol was evaporated, the solution was heated to 290^{o}C under argon atmosphere for 1 h and then cooled down to room temperature. The resulting nanoparticles were precipitated by addition of ethanol, collected by centrifugation at 6000 rpm for 3 min, washed with ethanol for several times, and redispersed in cyclohexane. The core-shell nanoparticles were synthesized by a layer-by-layer growth process using preformed nanoparticles as seeds.

Preparation of anti-counterfeiting patterns by photolithography: The as-prepared nanotaggants were mixed with SU-8 photoresist at 25 wt% to form a uniform nanotaggant/SU-8

composite, followed by a standard photolithography procedure using a Hybralign series 500 mask alignment and exposure system. The patterning procedure can be described as spinning, soft-baking, exposure, post-exposure bake, developing and rinsing.

Preparation of anti-counterfeiting patterns by contact printing:

Two stamps with pre-designed symbols were fabricated by Trodat, Inc. One stamp is a circlet and another one is an equilateral cross. Combining those two would give a complete sun cross symbol. Two types of aqueous dispersion nanoparticle ink were injected into the ink cartridge of the stamps, respectively before being imprinted onto a white copy paper. The aqueous dispersions of nanoparticles were prepared by removing the oleate ligands through acidic treatment.[1]

Characterizations: XRD patterns were recorded on a Bruker AXS D2 phaser with a graphite-monochro-matized Cu Kα radiation (1.5406 Å). TEM measurements were carried out on a JEOL-JEM 2100F transmission electron microscope operating at an acceleration voltage of 200 kV. SEM images were obtained with a Hitachi S-4800 field emission scanning electron microscope. Emission spectra were recorded with F-4600 spectrophotometer (Hitachi). Optical micrographs of patterns were recorded using an advanced research microscope (ECLIPSE Ni-U, Nikon) equipped with a streak camera (DS-Ri2, Nikon). Luminescence photos were taken with an Apple iPad through a 650 nm shortpass filter. All measurements were performed at room temperature.

Table S1. Synthetic conditions for core-shell nanoparticles of different structures and compositions.

Nanoparticle	core	1st shell	2nd shell	3rd shell	4th shell
$NaYF_4$ @$NaYbF_4$:Er(2%) @$NaYF_4$	OA:ODE=3:7 F:RE=3.95	OA:ODE=3:7 F:RE=3.95	OA:ODE=3:7 F:RE=3.95	---	---
$NaYF_4$:Yb/Tm(39%/1%) @$NaYF_4$:Yb/Nd(30%/15%) @$NaYF_4$	OA:ODE=3:7 F:RE=3.95	OA:ODE=3:7 F:RE=3.95	OA:ODE=3:7 F:RE=3.95	---	---
$NaGdF_4$:Ce/Tb(15%/5%)	OA:ODE=4:6 F:RE=3.1	---	---	---	---
$NaYF_4$:Yb/Er(38%/2%) @$NaYF_4$	OA:ODE=3:7 F:RE=3.95	OA:ODE=3:7 F:RE=3.95	---	---	---
$NaGdF_4$:Yb/Nd(30%/30%) @$NaGdF_4$:Yb/Er(38%/2%) @$NaGdF_4$	OA:ODE=4:6 F:RE=3.2	OA:ODE=4:6 F:RE=3.2	OA:ODE=4:6 F:RE=3.2	---	---
$NaGdF_4$:Ce(15%) @$NaGdF_4$:Eu(5%)	OA:ODE=4:6 F:RE=3.1	OA:ODE=4:6 F:RE=3.1	---	---	---
$NaGdF_4$:Yb/Tm(49%/1%) @$NaGdF_4$	OA:ODE=4:6 F:RE=3.3	OA:ODE=4:6 F:RE=3.3	---	---	---
$NaGdF_4$:Yb/Tm(49%/1%) @$NaGdF_4$ @$NaYbF_4$: Nd(50%) @$NaGdF_4$:Yb/Er(38%/2%) @$NaGdF_4$	OA:ODE=4:6 F:RE=3.3	OA:ODE=4:6 F:RE=3.3	OA:ODE=4:6 F:RE=3.3	OA:ODE=4:6 F:RE=3.3	OA:ODE=4:6 F:RE=3.3
$NaYF_4$ @$NaYbF_4$:Tm(1%) @$NaYF_4$	OA:ODE=3:7 F:RE=3.95	OA:ODE=3:7 F:RE=3.95	OA:ODE=3:7 F:RE=3.95	---	---
$NaYF_4$:Yb/Er(38%/2%) @$NaYbF_4$:Nd(50%) @$NaYF_4$	OA:ODE=3:7 F:RE=3.95	OA:ODE=3:7 F:RE=3.95	OA:ODE=3:7 F:RE=3.95	---	---

OA, oleic acid; ODE, 1-octadecene; F, fluoride; RE, rare-earth ions.

Table S2. The composition of nanotaggants for each set of pattern in Fig. 3.

#	Composition of nanoparticles
1	$NaYF_4$:Yb/Er(38%/2%)@$NaYF_4$ $NaYF_4$:Yb/Tm(39%/1%)@$NaYF_4$:Yb/Nd(30%/15%)@$NaYF_4$ $NaGdF_4$:Ce/Tb(15%/5%)
2	$NaYF_4$@$NaYbF_4$: Er(2%)@$NaYF_4$ $NaGdF_4$:Yb/Nd(30%/30%)@$NaGdF_4$:Yb/Er(38%/2%)@$NaGdF_4$ $NaGdF_4$:Ce(15%)@$NaGdF_4$:Eu(5%)
3	$NaGdF_4$:Yb/Tm(49%/1%)@$NaGdF_4$ $NaGdF_4$:Yb/Nd(30%/30%)@$NaGdF_4$:Yb/Er(38%/2%)@$NaGdF_4$ $NaGdF_4$: Ce/Tb(15%/5%)
4	$NaYF_4$@$NaYbF_4$:Er(2%)@$NaYF_4$ $NaGdF_4$:Yb/Nd(30%/30%)@$NaGdF_4$:Yb/Er(38%/2%)@$NaGdF_4$ $NaGdF_4$:Ce/Tb(15%/5%)
5	$NaGdF_4$:Yb/Tm(49%/1%)@$NaGdF_4$ $NaGdF_4$:Yb/Nd(30%/30%)@$NaGdF_4$:Yb/Er(38%/2%)@$NaGdF_4$ $NaGdF_4$:Ce(15%)@$NaGdF_4$:Eu(5%)

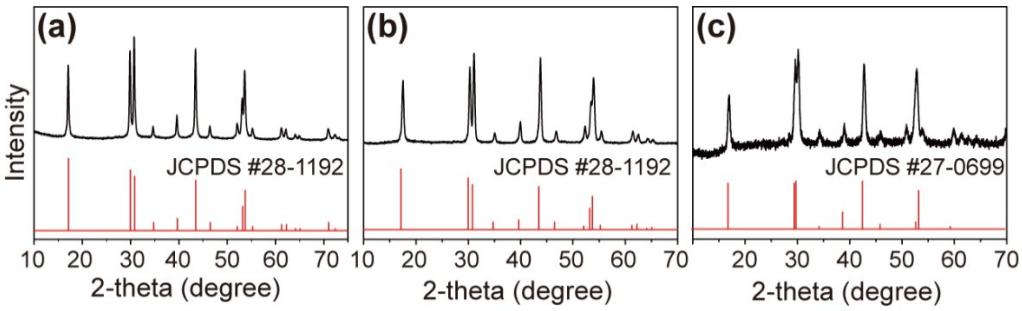

Fig. S1 XRD patterns of (a) $NaYF_4$@$NaYbF_4$:Er@$NaYF_4$, (b) $NaYF_4$:Yb/Tm@$NaYF_4$:Yb/Nd @$NaYF_4$, and (c) $NaGdF_4$:Ce/Tb nanoparticles. The line spectra are literature data for hexagonal-phase $NaYF_4$ (a and b) and hexagonal-phase $NaGdF_4$ (c).

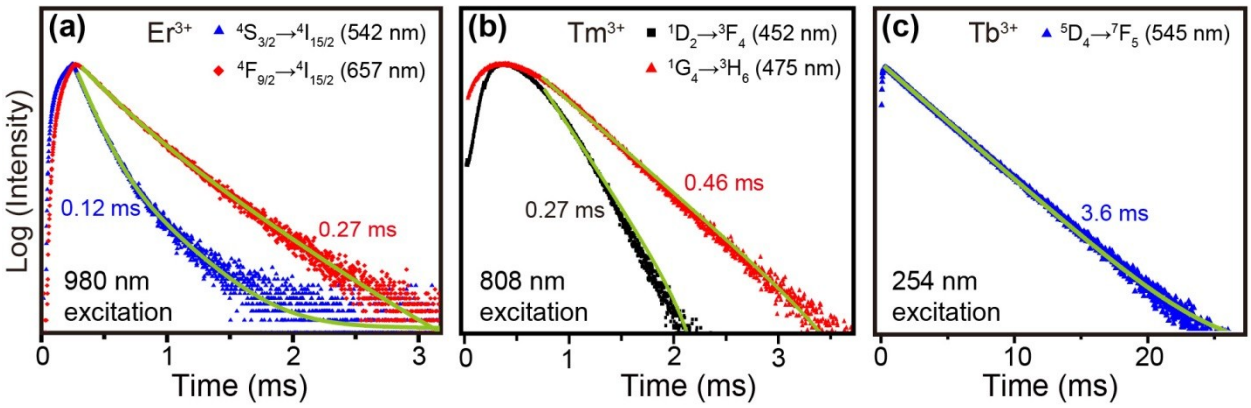

Fig. S2 Luminescent decay curves of (a) $NaYF_4$@$NaYbF_4$:Er@$NaYF_4$, (b) $NaYF_4$:Yb/Tm@ $NaYF_4$:Yb/Nd@$NaYF_4$, and (c) $NaGdF_4$:Ce/Tb nanoparticles under excitation at 980 nm, 808 nm, and 254 nm, respectively. Quantum yields of the samples are 0.5%, 0.1% and 90%, respectively.

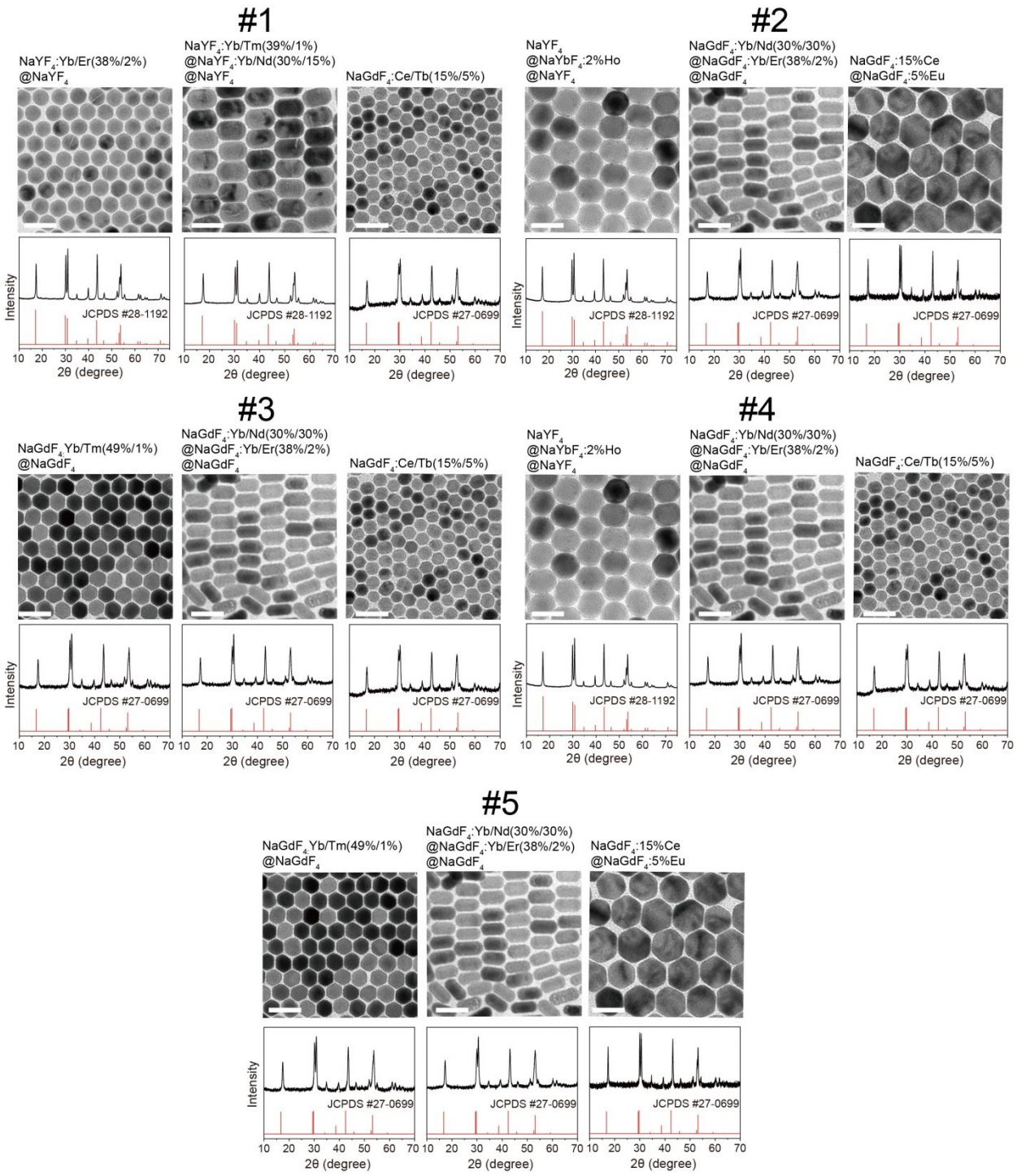

Fig. S3 TEM images and XRD patterns of the nanotaggants in Fig. 3. Scale bars for TEM images are 50 nm. The line spectra are the literature data for hexagonal-phase $NaYF_4$ (JCPDS #28-1192) and hexagonal-phase $NaGdF_4$ (JCPDS #27-0699).

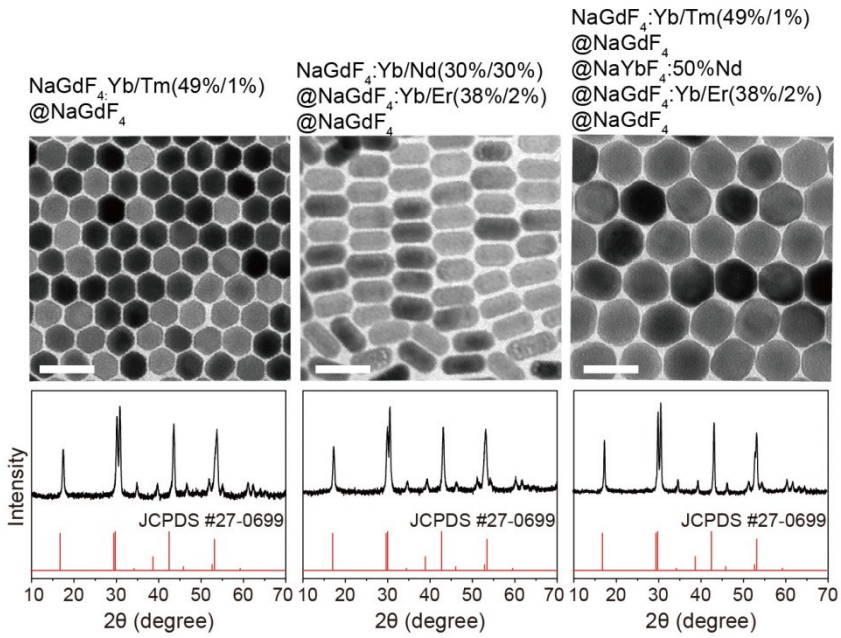

Fig. S4 TEM images and XRD patterns of the nanotaggants in Fig. 4. Scale bars for TEM images are 50 nm. The line spectra are the literature data for hexagonal-phase $NaGdF_4$.

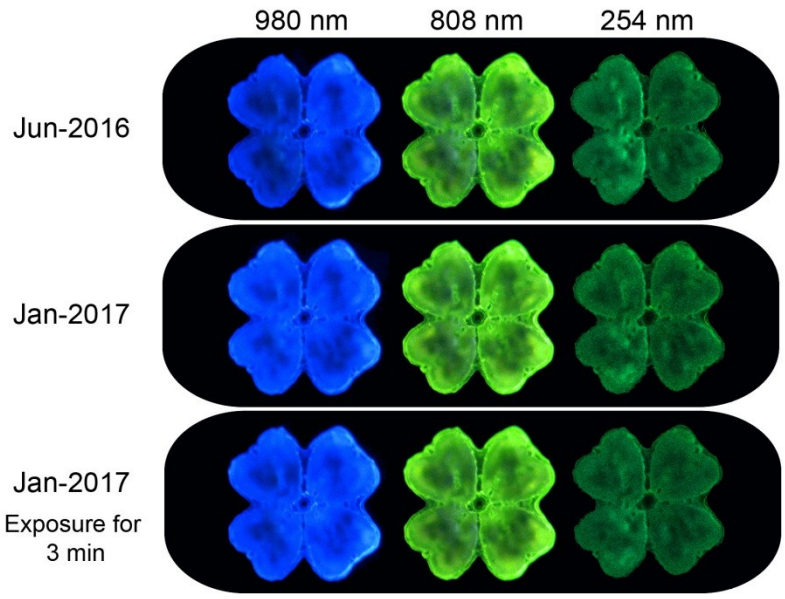

Fig. S5 Evaluation of chemical and optical stability of a pattern. No signs of chemical degradation or photobleaching are observed after the pattern is stored for six months and exposed to laser irradiation for three minutes.

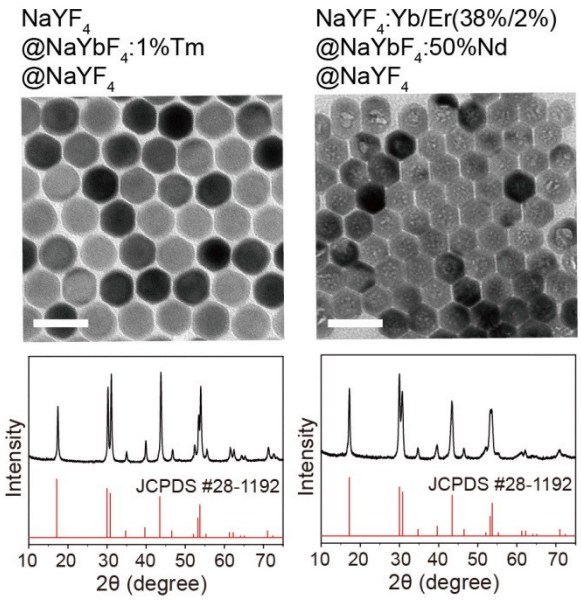

Fig. S6 TEM images and XRD patterns of the nanotaggants in Fig. 5. Scale bars for TEM images are 50 nm. The line spectra are the literature data for hexagonal-phase $NaYF_4$.

Reference for Supporting Information

1 N. Bogdan, F. Vetrone, G. A. Ozin, J. A. Capobianco, *Nano. Lett.*, 2011, **11**, 835.