

**Electronic Supplementary Information (ESI)**

**Highly-selective recognition of latent fingerprints by La<sup>3+</sup>-sensitized  
Ce nanocomposite via electrostatic binding**

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## **Experimental section**

### **Materials:**

Terbium (III) oxide ( $\text{CeO}_2$ ) and lanthanum (III) oxide ( $\text{La}_2\text{O}_3$ ), at 99.99% purity, were purchased from Shanghai Yuelong Rare Earth New Materials Co., Ltd., China. sulfosalicylic acid (SSA, AR), 1,10-phenanthroline (Phen, AR), dimethyl sulfoxide (DMSO, AR), absolute ethyl alcohol (EA, AR), acetone (AR), sodium hydroxide (NaOH, AR), concentrated hydrochloric acid (HCl, AR) and potassium bromide (KBr, AR) were provided by Sinopharm Chemical Reagent Co., Ltd., China. Supercoiled pBR322 plasmid DNA (3 kb) was purchased from Shanghai Sangon Biotech Co., Ltd. All the chemicals were used without further purification, and ultrapure millipore water (18.2 M $\Omega$  cm) was prepared throughout all the experiments.

### **Synthesis:**

The synthesis procedure for  $\text{Ce}_x\text{La}_{1-x}(\text{SSA})_3\text{Phen}$  complexes was carried out by an optimized route based on our previous work. Different calculated weights of  $\text{CeO}_2$  and  $\text{La}_2\text{O}_3$  ( $\text{Ce}_x\text{La}_{1-x}(\text{SSA})_3\text{Phen}$ , ( $x=1, 0.875, 0.75, 0.5, 0.25, 0.125, 0$ )) were dissolved in excess concentrated HCl and were evaporated to near dryness at 100 °C for 11 h. Then, 80 mL of ethanol was added to the crystal with stirring after cooling. A homogeneous solution of  $\text{Ce}_x\text{La}_{1-x}\text{Cl}_3$  in ethanol was then obtained. SSA (12 mmol) and Phen (4 mmol) were dissolved in 30 mL 95% ethanol in a three-necked flask. The mixture solution was adjusted to pH 6.5 with NaOH (6 mmol). Then, 40 mL of  $\text{Ce}_x\text{La}_{1-x}\text{Cl}_3$  solution (4 mmol) was slowly dropped into the previous solution with constant stirring at 60 °C for 30 minutes. The mixture was quickly transferred to a polytetrafluoroethylene reactor and incubated at 140 °C for 4 h and was then precipitated, filtered, washed with ethanol three times, and dried in a vacuum at 60 °C to dryness. The nanopowder was collected, ground, and stored away from light for characterization and application.

### **Characterization of the $\text{Ce}_x\text{La}_{1-x}(\text{SSA})_3\text{Phen}$ complexes**

The morphology and size of the  $Ce_xLa_{1-x}(SSA)_3Phen$  complexes were characterized by SEM (NanoLab 600i, FEI Corp.). A total of 10 mg sample was dissolved in 5 mL of ethanol, and the supernatant was placed on a special conductive adhesive that was dried in air. The SEM images were acquired at an electron acceleration voltage of 5 kV.

The contents of carbon, hydrogen, oxygen, and nitrogen in the complexes were characterized using an elemental analyzer (PE2400, Perkin Elmer, USA). The content of RE(III) was determined from ethylenediaminetetraacetic acid (EDTA) titration. The mass spectrometry (Bruker autoflex III, USA) was performed to analyze the final composition of complexes at positive ion mode using acetonitrile as the solvent. The structure and thermal behaviors of the complexes were studied with a thermogravimetric analyzer (TGA/DSC 1, Mettler, Switzerland) under nitrogen atmosphere with the rate of temperature rise at 10 °C/min from room temperature to 900 °C/min.

The state-solid photoluminescence excitation (PLE), photoluminescence (PL) spectra, quantum yield (QY) and luminescence decay curves were measured at room temperature on a fluorescence spectrometer (Hitachi F-700, Hitachi High-Technologies Corporation, Tokyo, Japan), with an integrating sphere, and a 450 W xenon lamp was used as the light source. UV-vis absorption spectra were obtained with a UV-vis spectrophotometer (UV-3600, Shimada UV, Japan).

### **Latent fingerprint recognition**

The latent fingerprint samples were from the right thumb of the same male donor and were prepared by lightly rubbing the finger on the nose and forehead before touching the surface. Various substrates, including transparent glass, plastic sheets, aluminum alloys, ceramic tiles, painted wood, artificial leather and coated paper were used for depositing latent fingerprints. The powder dusting method was employed to develop the latent fingerprints using a soft feather brush. In contrast, some traditional

developing methods, e.g., commercial phosphor, cyanoacrylate fuming methodology, and magnetic powder were chosen as controls. The fingerprint images were detected under day-light or 312 nm irradiation detection, and were then recorded with a digital camera (EDS 6D, Canon, Japan). More ridge details were captured using a digital microscope (VHX-6000, Keyence, Japan). Finally, an automatic fingerprint identification system (AFIS) was applied for the evaluation of the image quality of the developed fingerprints.

### **Interaction experiment between fingerprint residues and $Ce_xLa_{1-x}(SSA)_3Phen$ complexes**

The transparent glass was cleaned up with ultrapure water and was dried and prepared as the substrate for the interaction experiment. Particularly, stained fingerprints using  $Ce_{0.125}La_{0.875}(SSA)_3Phen$  complex as the developing powder were scraped from the glass and were collected as the sample for the FTIR and zeta potential analyses. Fourier transform infrared spectra (FTIR) were performed on a PerkinElmer Spectrum (PerkinElmer, USA) using KBr pellets. Zeta potentials of the  $Ce_{0.125}La_{0.875}(SSA)_3Phen$  and  $Ce_{0.125}La_{0.875}(SSA)_3Phen$  / fingerprint residues were examined with a Malvern Nano-ZS, Model ZEN3600 (Malvern Instruments, Malvern, UK).

### **Interaction experiment between DNA and $Ce_xLa_{1-x}(SSA)_3Phen$ complexes**

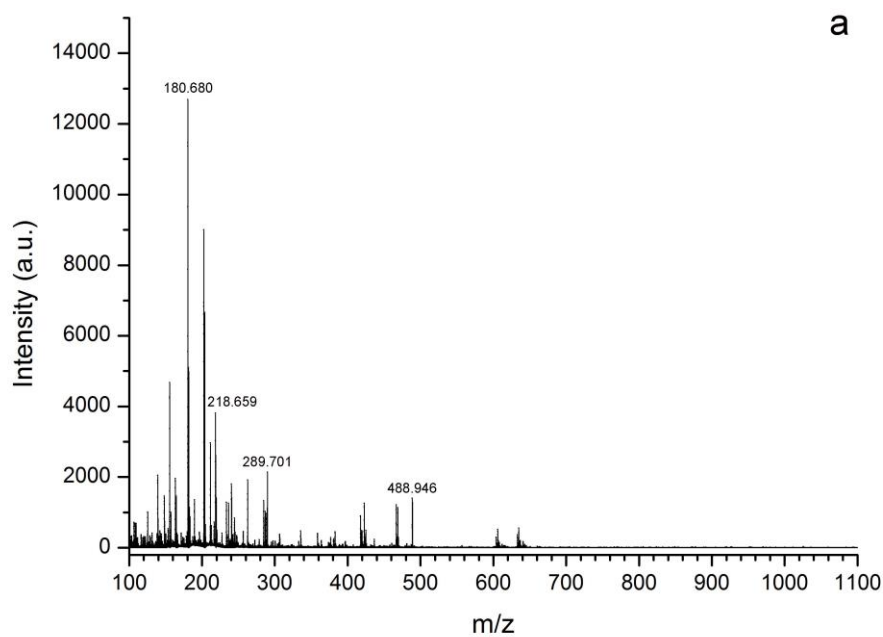
An agarose gel electrophoresis system was used to analyze the interaction mode of our complex and DNA. The complexes/plasmid DNA were prepared freshly prior to use. The pure plasmid DNA was prepared with concentrations of  $3.5 \times 10^{-6}$  mol/L in ultrapure water, and  $Ce_{0.125}La_{0.875}(SSA)_3Phen$  complexes was added to the DNA solution with the concentrations of  $5.0 \times 10^{-6}$ ,  $10.0 \times 10^{-6}$ ,  $15.0 \times 10^{-6}$ ,  $20.0 \times 10^{-6}$  mol/L, respectively. For each lane, a 20  $\mu$ L volume of sample was loaded containing same concentration of DNA and different ratio of complexes, and additional ultrapure water are needed. The mixed samples were allowed to incubate at 37 °C for 20 min, and were then separated on a 1.5% agarose gel for 1 h at 120 V in Tris-acetate-EDTA (TAE) buffer, containing 1.5% agarose gel. Ethidium bromide (0.5  $\mu$ g/mL) was then

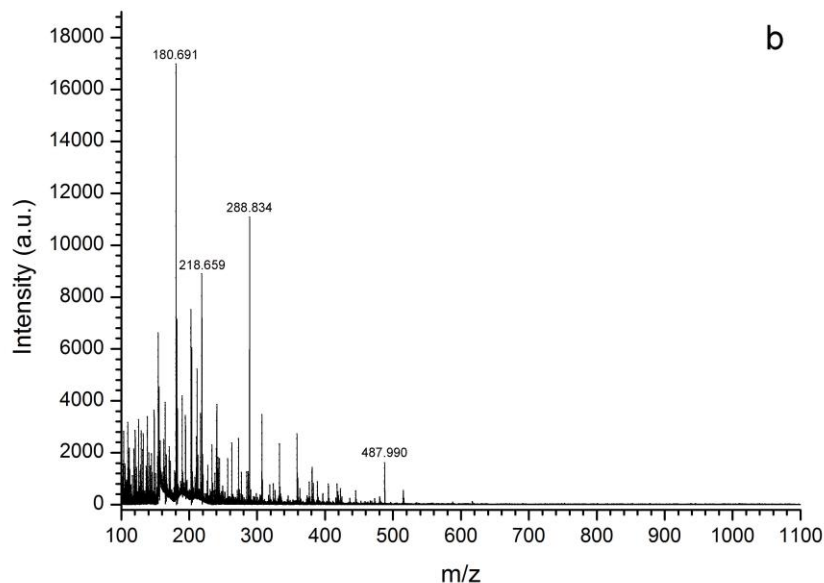
used to stain gels, which were imaged under UV light.

For Circular dichroism (CD) spectra measurements (CHIRASCAN, Applied Photophysics, GB), moderate amounts of DNA and  $\text{Ce}_{0.125}\text{La}_{0.875}(\text{SSA})_3\text{Phen}$  were mixed in a 25 mL tube and diluted to 10 mL volume by ultrapure water. The pure plasmid DNA and mixed sample and with the concentration of  $3.5 \times 10^{-5}$  and  $3.8 \times 10^{-5}$  mol/L were respectively analyzed by CD spectrum using 1 cm quartz absorption cell, with a 220~320 nm scan range and ultrapure water as a blank.

**Table S1** Elemental percentages of the Ce<sub>x</sub>La<sub>1-x</sub>(SSA)<sub>3</sub>Phen complexes.

X values	weight (wt%)									
	Ln		C		H		N		S	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
1	14.59	14.37	40.89	40.63	2.72	2.67	2.90	2.87	9.82	9.85
0.875	14.54	14.36	40.91	40.63	2.72	2.67	2.94	2.87	9.83	9.85
0.75	14.52	14.34	40.88	40.63	2.71	2.67	2.94	2.87	9.82	9.85
0.5	14.48	14.32	40.88	40.64	2.74	2.67	2.93	2.87	9.81	9.85
0.25	14.47	14.29	40.90	40.66	2.71	2.67	2.89	2.87	9.88	9.86
0.125	14.47	14.28	40.93	40.67	2.72	2.67	2.95	2.88	9.85	9.86
0	14.40	14.26	40.99	40.67	2.75	2.67	2.91	2.88	9.86	9.86





**Fig. S1** MS spectra of (a)  $\text{Ce}(\text{SSA})_3\text{Phen}$  and (b)  $\text{Ce}_{0.125}\text{La}_{0.875}(\text{SSA})_3\text{Phen}$ .

The mass spectrometry was performed to analysis the final composition of complexes. As shown in Fig. S1a, it could be observed that the  $m/z=218.659$  matched well with the ligand SSA (M.W.=218.21), since the two  $\text{H}_2\text{O}$  combined would be removed when ionization. The  $m/z=180.680$  matched well with the ligand Phen (M.W.=180.2). Based on formula of  $(m+z)/z$ , it an be deduced that the peak at 289.701 can be assigned to the  $\text{Ce}(\text{SSA})_2$   $((140.116+218.21 \times 2+2)/2=289.268)$ . The  $m/z=488.946$  could be extrapolated to be the  $\text{Ce}(\text{SSA})_3\text{Phen}$   $((974.946+2)/2=488.473)$ . Similar results could be observed in Fig. S1b. For sample of  $\text{Ce}_{0.125}\text{La}_{0.875}(\text{SSA})_3\text{Phen}$ , the  $m/z=180.691$  and 218.659 matched well with the ligand Phen (M.W.=180.2) and the ligand SSA (M.W.=218.21), respectively. In addition, the  $m/z=138.586$  matched well with the La (M.W.=138.9). Based on previous formula, the peak at 288.834 could be assigned to the  $\text{Ce}_{0.125}\text{La}_{0.875}(\text{SSA})_2$   $((140.116 \times 0.125+138.9055 \times 0.875+218.21 \times 2+2)/2=288.738)$ . We also extrapolated that the peak at 487.990 would be the  $\text{Ce}_{0.125}\text{La}_{0.875}(\text{SSA})_3\text{Phen}$   $((973.887+2)/2=487.943)$ .

### Solid-state Quantum efficiency of $Ce_xLa_{1-x}(SSA)_3Phen$ complexes

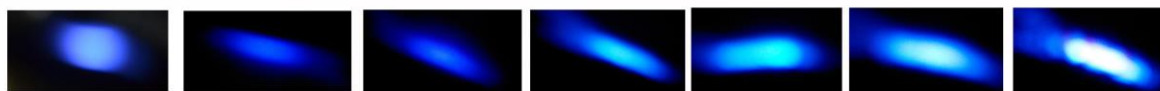
For luminescence, the quantum yield is an important parameter for a phosphor and determines its performance directly. The inner quantum yield is defined by:

$$\eta_{in} = \int L_S / (\int E_R - \int E_S)$$

where  $L_S$  is the emission intensity of the sample, and  $E_S$  and  $E_R$  are the spectra of the excitation light with and without the sample in the integrating sphere, respectively.

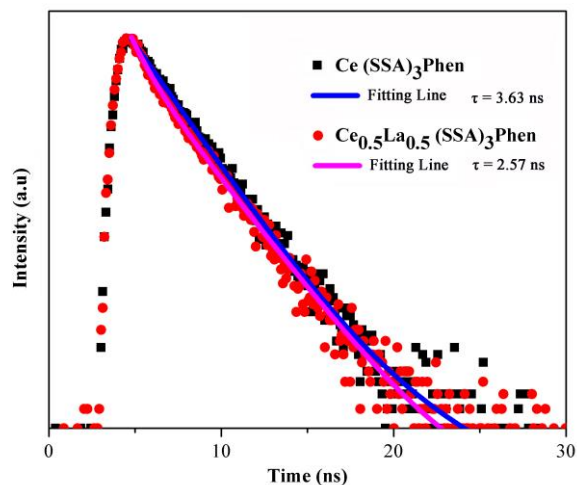
**Table S2** Solid-state quantum yields of  $Ce_xLa_{1-x}(SSA)_3Phen$  complexes.

X values	Quantum yields (%)
1	38.8
0.875	9.5
0.75	9.9
0.5	12.7
0.25	44.8
0.125	51.2
0	20.1



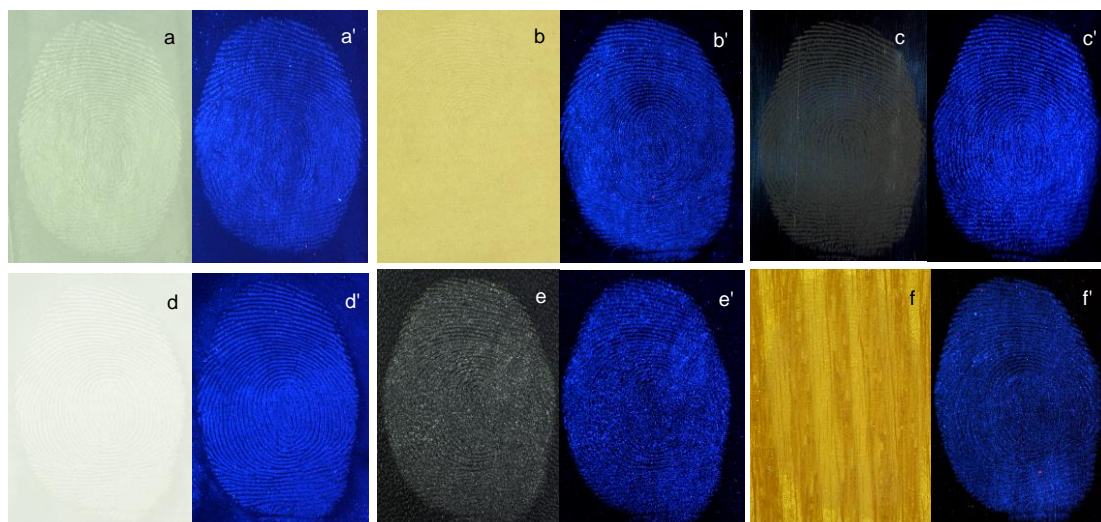
**Fig. S2** Luminescence photographs of  $Ce_xLa_{1-x}(SSA)_3Phen$  complexes (from left to right refers to different samples when  $x=0.875, 0.75, 0.5, 0, 1, 0.25$  and  $0.125$ , respectively).



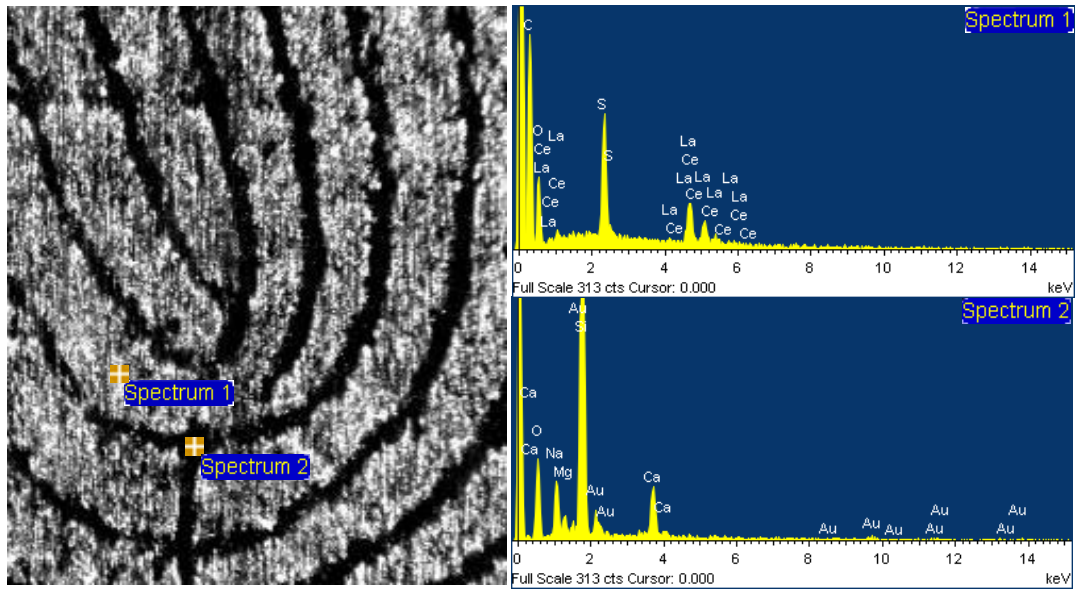


**Fig. S3** PL decay of Ce(SSA)<sub>3</sub>Phen and Ce<sub>0.5</sub>La<sub>0.5</sub>(SSA)<sub>3</sub>Phen at 297 K. a<sub>0</sub>

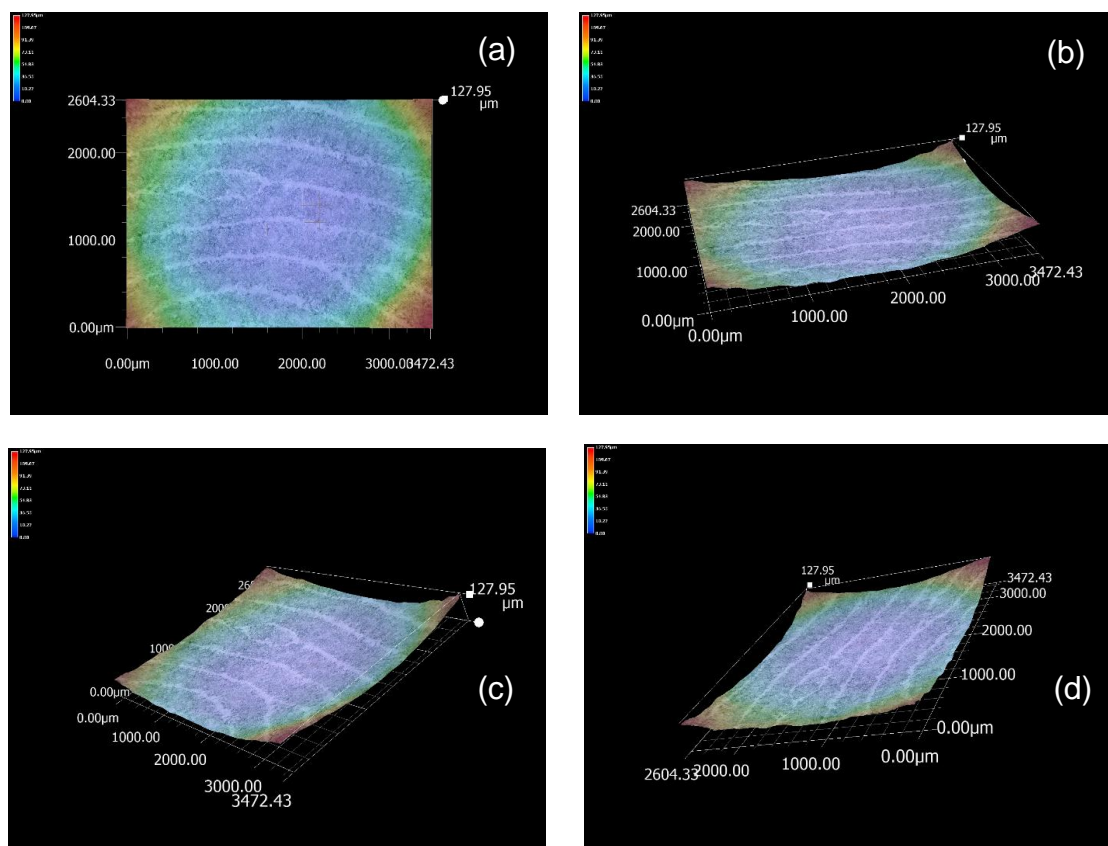
The energy transfer efficiency ( $E_p$ ) between La<sup>3+</sup> and Ce<sup>3+</sup> cations is estimated based on the equation  $E_p = 1 - \tau_{DA}/\tau_D$ , where  $\tau_{DA}$  and  $\tau_D$  are the lifetime values in the presence and absence of La<sup>3+</sup> cation, which provides an  $E_p$  of 29.2%.



**Fig. S4** Stained fingerprints on various surfaces: (a, a') transparent plastic sheet, (b, b') ceramic tile, (c, c') aluminum alloy, (d, d') coated paper, (e, e') artificial leather, and (f, f') painted wood in (a–f) bright field and then developed by (a'– f')  $\text{Ce}_{0.125}\text{La}_{0.875}(\text{SSA})_3\text{Phen}$  nanopowder by 312 nm UV light in a dark field.



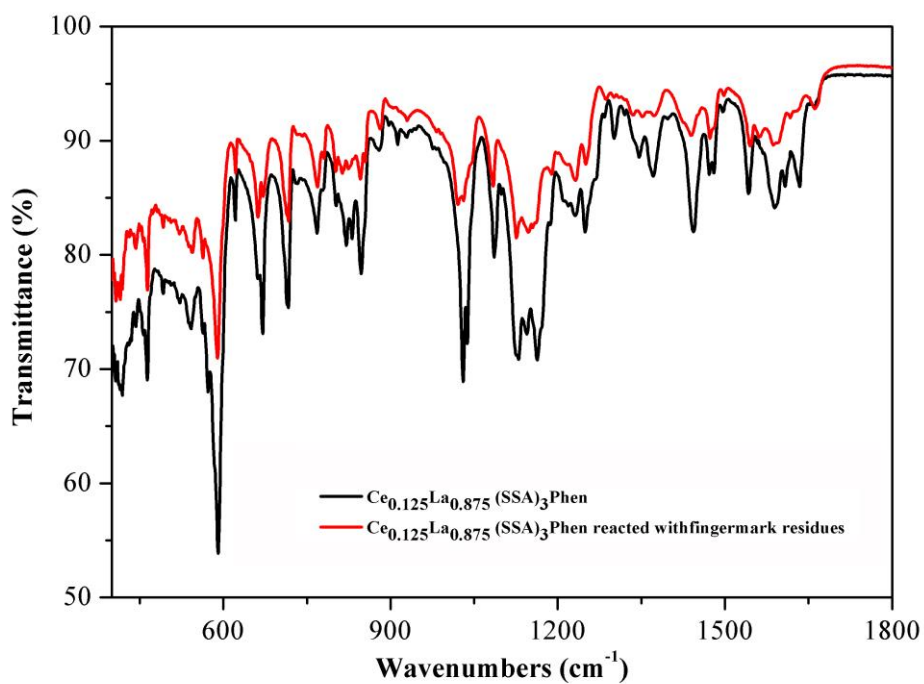
**Fig. S5** EDS analysis of a developed fingermark on transparent glass by  $\text{Ce}_{0.125}\text{La}_{0.875}(\text{SSA})_3\text{Phen}$  nanopowder: (Spectrum 1) ridge, (Spectrum 2) furrow.

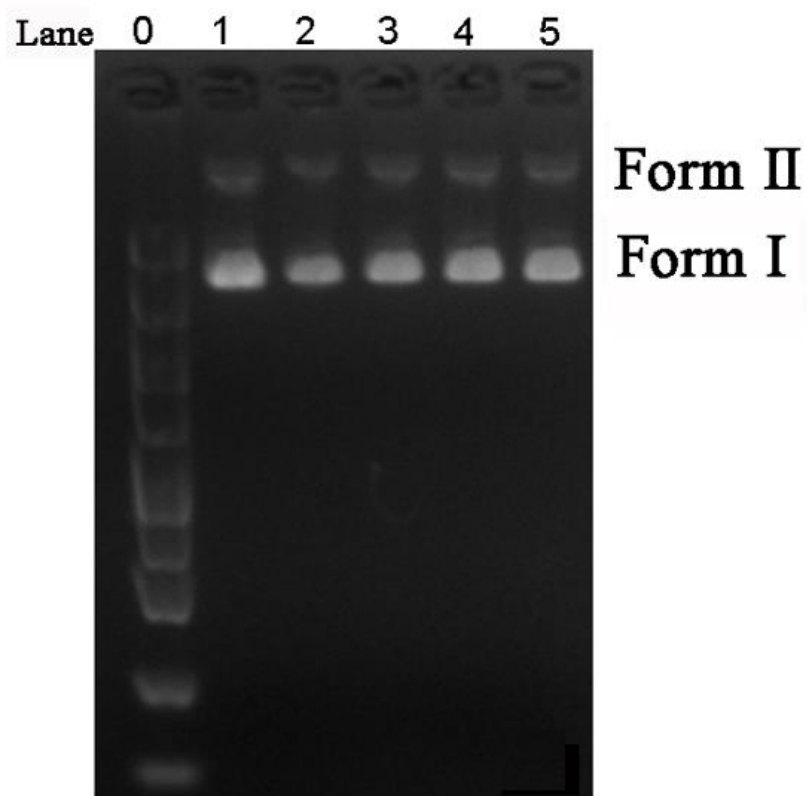


**Fig. S6** 3D images of a developed fingerprint on PVC sheet by  $\text{Ce}_{0.125}\text{La}_{0.875}(\text{SSA})_3\text{Phen}$  nanopowder (a ~ d were captured at different angles of view).

**Table S3** Wavenumbers of main peaks of FTIR spectra of two samples ( $\text{cm}^{-1}$ ).

Samples	$\nu_{\text{O-H}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{N=C}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{C-H}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{C=O}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{C=C}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{O}\rightarrow\text{RE}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{N}\rightarrow\text{RE}}$ ( $\text{cm}^{-1}$ )
<b>Ce<sub>0.125</sub>La<sub>0.875</sub>(SSA)<sub>3</sub>Phen</b>	3224	1542	847, 716	1660	1589, 1472	591	464
<b>Ce<sub>0.125</sub>La<sub>0.875</sub>(SSA)<sub>3</sub>Phen reacted with fingerprint residues</b>	3215	1545	846, 717	1661	1587, 1473	589	464

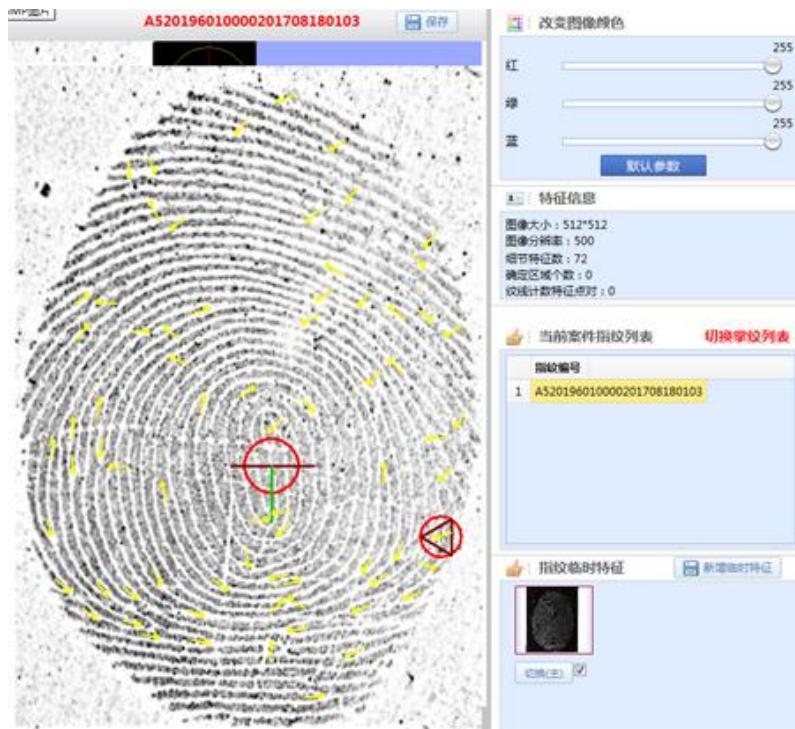
**Fig. S7** FTIR spectrum of the pure and the Ce<sub>0.125</sub>La<sub>0.875</sub>(SSA)<sub>3</sub>Phen reacted with fingerprint residues at the region of 450 ~ 1800  $\text{cm}^{-1}$ .



**Fig. S8** Electrophorogram for cleavage of plasmid DNA in the presence of complex. Lane 1: DNA only; Lane 2–5 in the different concentrations of complex:  $5.0 \times 10^{-6}$  mol/L,  $10.0 \times 10^{-6}$  mol/L,  $15.0 \times 10^{-6}$  mol/L,  $20.0 \times 10^{-6}$  mol/L.

**Table S4** Comparison of second-level feature recognition rate of four developing method on different aging time of latent fingerprints (unit: %)

Time \ Methods	Ce <sub>0.125</sub> La <sub>0.875</sub> (SSA) <sub>3</sub> Phen complex	Commercial phosphor	superglue fuming	magnetic ferric powder
1 d	98.6	97.3	97.3	95.9
7 d	97.3	93.2	86.3	79.5
15 d	95.9	84.9	75.3	63.0
24 d	91.7	75.3	64.4	47.9
32 d	90.4	65.8	58.9	41.1



**Fig. S9** AFIS analysis of a fresh fingerprint developed by Ce<sub>0.125</sub>La<sub>0.875</sub> (SSA)<sub>3</sub>Phen nanopowder.