



# Realization of Optical Network Structures for Robust Films through Immobilization of Europium Complexes

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## Abstract

In this study, the bio-inspired self-cracking substrate can be employed as a template to control the formation of a robust micropatterning film. Uniform materials with variable diameters are achieved by optimizing the egg white/water ratios and reaction temperature. The incorporated europium ions exhibit its typical  $f-f$  transitions in patterned films. Moreover, the mechanical property and excellent transmittance features have been demonstrated. The current approach can be extended to design two-dimensional nanofabrication of different materials.

**Keywords** Micropatterning · Luminescence · Microstructure

## Introduction

Recent development in micro-patterning techniques enables precise control surface structures and well-defined patterns derived from micro-fabrication strategies have been found to be valuable in a wide variety of fields such as bio-imaging, electronic display device, anti-counterfeiting barcode and light-emitting devices (LEDs) [1–3]. The miniaturization effects may generate superior photophysical property for devices in comparison to bulk materials as their counterparts. As for the selection of emission sources, certain pioneering studies concerning lanthanide chemistry have aroused considerable interests [xxx]. The excited lifetime

of lanthanide ions has been determined in the range of microsecond to millisecond. Therefore, the employment of time-gated detection procedure will realize the clear cases of discrimination between lanthanide emission and noisy signals or light scattering [4, 5].

However, lanthanide complex in the form of powder will be difficult to collect and possesses lower stability. It may dissociate easily especially in the aqueous solution which will significantly interfere with its application potentials. Hence, novel lanthanide materials with regular shapes or portable features would be required and a few studies involved the exploration of lanthanide nano-scale devices with simplicity or flexibility [6–9]. In this research, lanthanide complex was stamped onto the flexible and transparent PDMS substrate and a novel luminescent device was assembled. The current self-cracking strategy was completely different from the micro-contact printing, micro-transfer molding or solvent-assisted micro-molding method. It was inspired by spontaneous consolidation and cracking of egg white liquid. Finally, a functional template was afforded [10, 11]. Compared with lithography technique with multiple steps, the egg white solution with eco-friendly feature was low-cost and easy to operate during synthesis procedure. Results demonstrated the fine control of network distributions via the parameter changes of water content or temperature. This study supported that micro-patterning technique would be an efficient route for the immobilization of lanthanide species into robust substrate.

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## Experimental Section

### Materials

NaOH, 2,6-pyridinedicarboxylic acid and 2,4-pentanedione were purchased from J&K chemical company.  $\text{Eu}_2\text{O}_3$  (98%) was purchased from Aladdin company and the oxide was dissolved into nitric acid to obtain their corresponding lanthanide nitrates. All the raw materials were obtained from commercial suppliers and used as received. Raw materials of polydimethylsiloxane (PDMS) film, the silicone Elastomer base and silicone elastomer curing agent, were obtained from Dow Corning Company and used without further purification. The synthesis of europium complexes with 2,6-pyridinedicarboxylic acid and 2,4-pentanedione was according to the literature [12].

### Characterizations

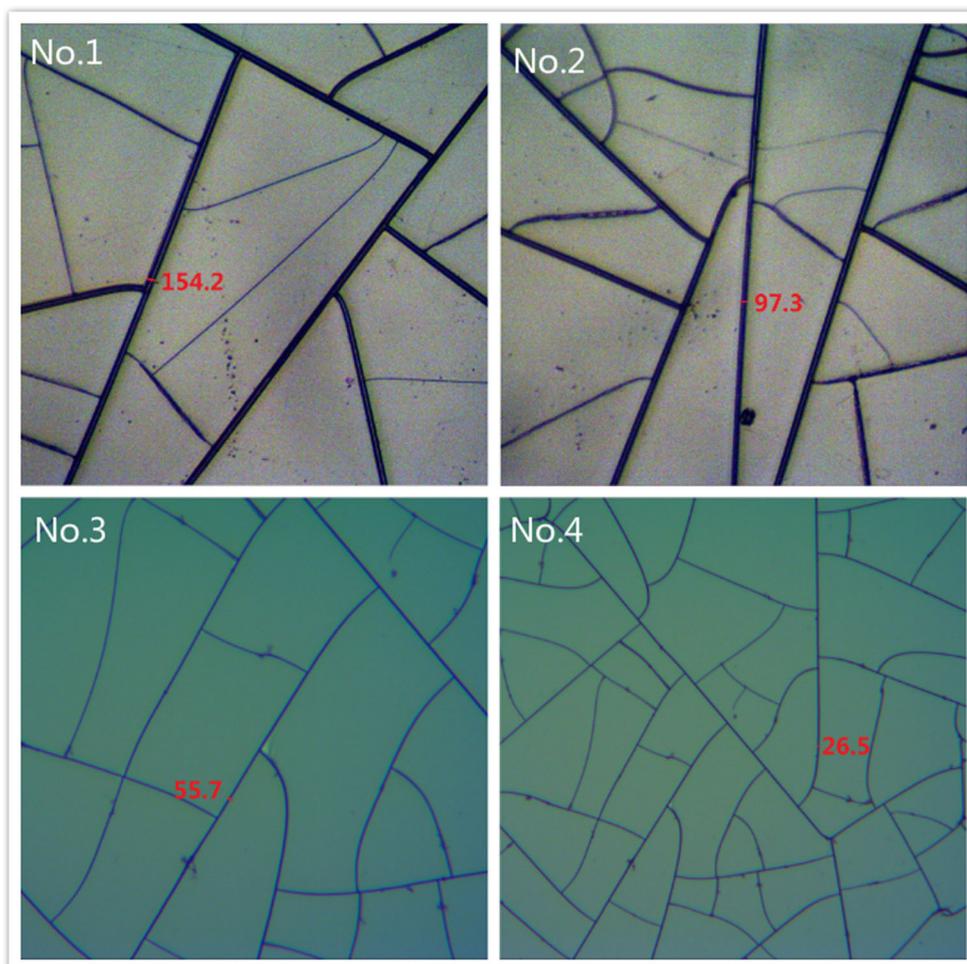
The luminescent spectra were measured by a Hitachi FL2700 spectrophotometer with a 150 W lamp. The optical

transmittance data were recorded by Transmittance tester. Elemental analysis was carried out in an ElementarVario EL elemental analyzer. The micro optical pictures were collected by an optical microscope MA2002 equipped with a Mingmei digital imaging system and the length on the picture was also measured in the system. The element content was determined by atomic absorption spectroscopy via Varian AA-220FS.

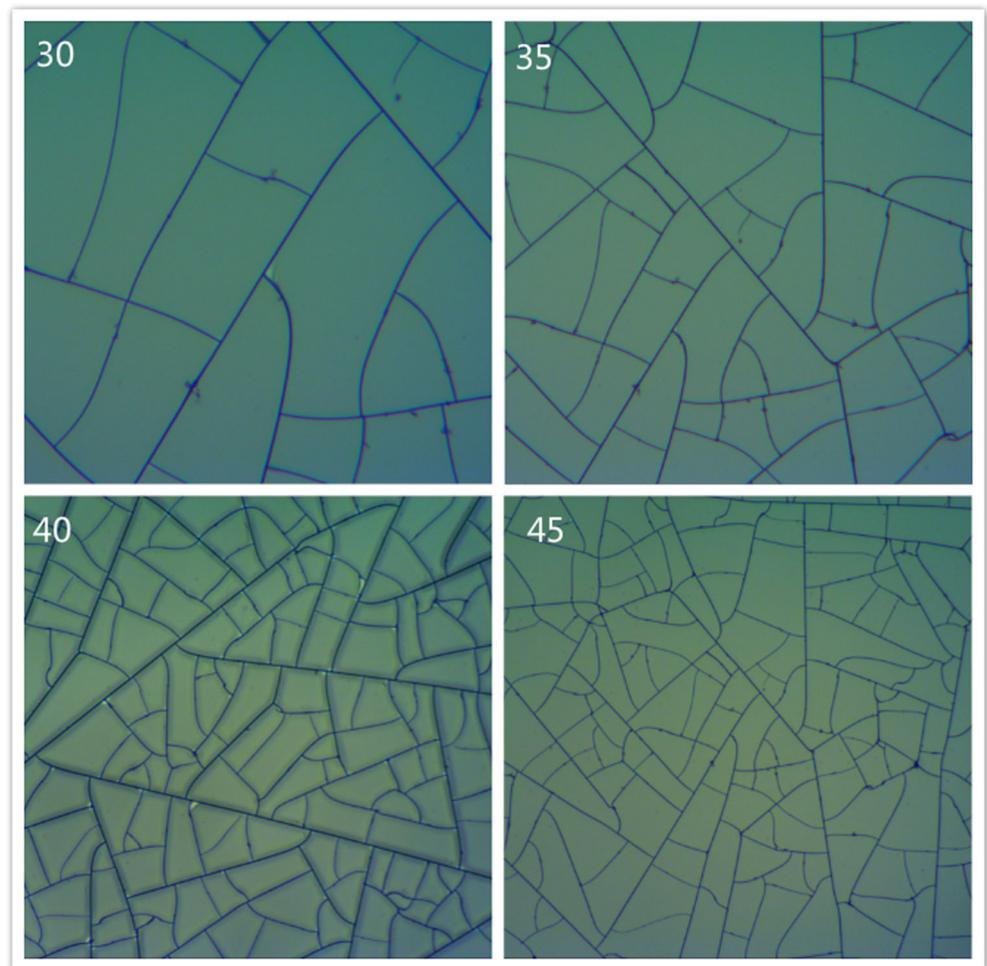
### Syntheses of Lanthanide Complex

With 2,6-pyridinedicarboxylic acid and 2,4-pentanedione as organic ligands, two kinds of lanthanide complex were obtained by reaction with  $\text{Eu}_2\text{O}_3$  and named as complex A and complex B. NaOH was chosen to adjust pH value during the period. The powder of the product was obtained after air-dried and confirmed by elemental analysis (EA). Calcd: C, 29.98; H, 1.78; N, 4.79, Found: C, 30.02; H, 1.83; N, 4.81 for compound  $\text{ANa}_3[\text{Eu}(\text{C}_7\text{H}_3\text{NO}_4)_3]\cdot 3\text{H}_2\text{O}$  and Calcd: C, 35.78; H, 5.36; Found: C, 35.81; H, 5.36 for compound  $\text{B Eu}(\text{C}_5\text{H}_7\text{O}_2)_3\cdot 3\text{H}_2\text{O}$ .

**Fig. 1** Optical microscope images of films fabricated by egg white solution with different proportion with deionized water



**Fig. 2** Optical microscope images of films fabricated under different temperature

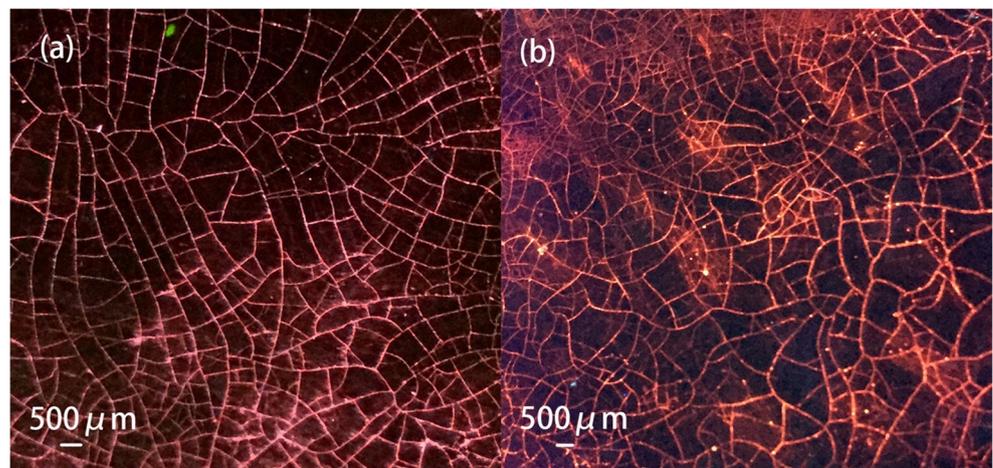


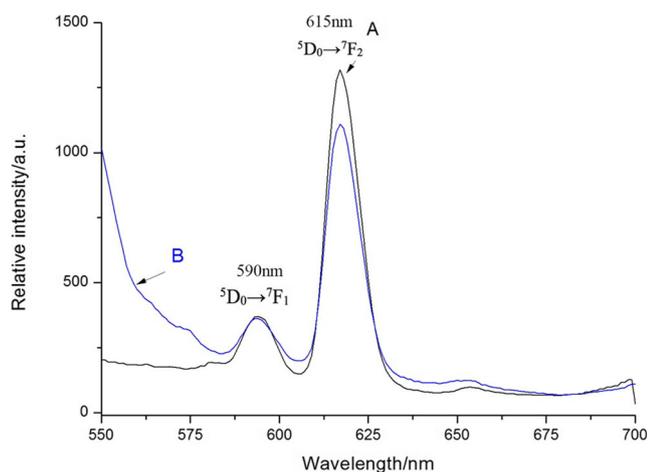
### Preparation of Self-Cracking Template

The PDMS substrate was prepared by mixing elastomeric base and curing agent (in 8:1 weight ratio) on a clean glass and heated under 85 °C to be consolidated. The bio-inspired

template was formed by self-cracking property of natural egg. Firstly, the egg white solution was prepared as follows: the egg white of a fresh egg was separated from egg yolk and then mixed with appropriate amount of deionized water and stirring for five minutes and the homogenous slightly white color

**Fig. 3** Optical pictures of patterned luminescent materials onto flexible PDMS film under 365 nm UV irradiation (a. complex A; b. complex B)



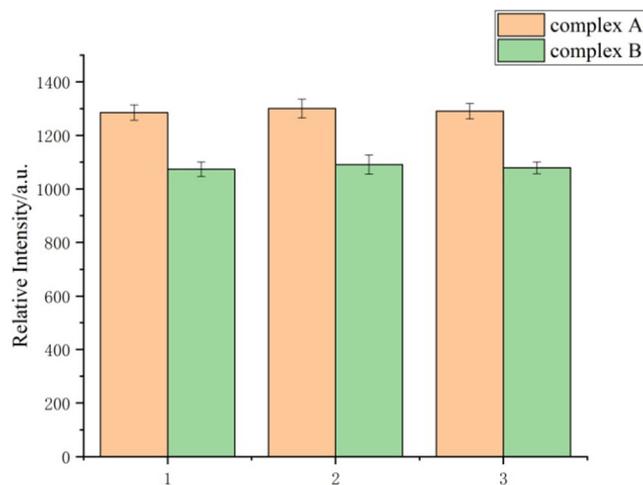


**Fig. 4** Emission spectra of two europium complexes encapsulated PDMS films

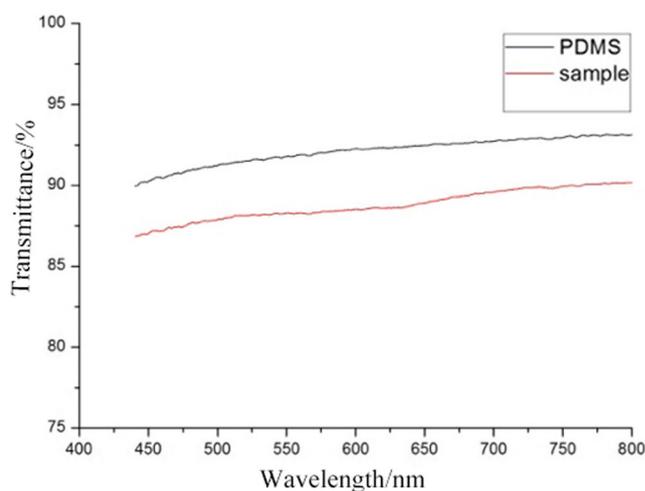
solution was obtained. Then, this egg white solution was dropped on the prepared PDMS film and spread around. Finally, we can obtain the functional films depending on optimized experimental conditions. In the next step, the lanthanide complex in the mix solvent ( $\text{CH}_3\text{CH}_2\text{OH}$  and  $\text{CHCl}_3$ ) was added on the substrate. After evaporation of the solvent at room temperature, the branched and distributed optical networks can be achieved and observed by naked eyes under UV light irradiations.

### Leaching Experiments

In the leaching experiments, the films were immersed into a leaching medium (deionized water, pH = 2 and pH = 10) at the beginning. At different time intervals, the solution samples were taken and explored for europium ions via atomic absorption spectroscopy. The leaching efficiency “ $\eta$ ” was



**Fig. 5** Emission intensities for three batches of samples of the two europium complexes encapsulated PDMS films



**Fig. 6** Transmittance of PDMS and thin film incorporated with Eu complex

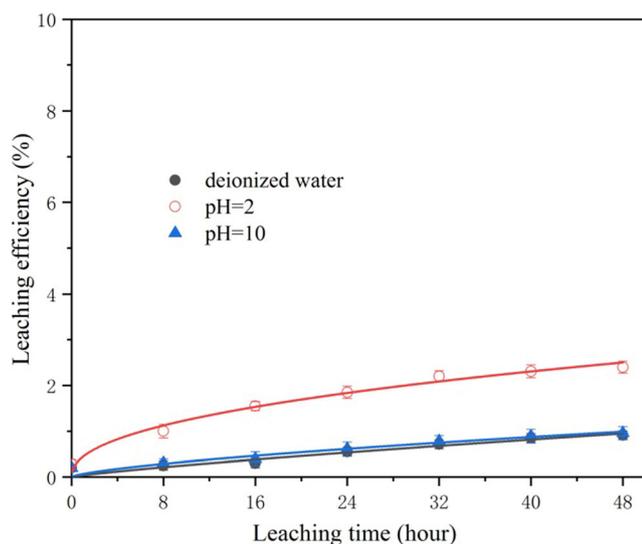
determined by equation of  $\eta = [m]_t/[m]_0$ , in which  $[m]_0$  and  $[m]_t$  refers to the europium content in the films before leaching experiments and the released content in the given time scale.  $[m]_0$  was retrieved by the europium content in the incorporated europium complex. Each experiment was performed by three times and the error bars were added in the curves.

### Results and Discussion

Compared with bulk materials, the assembly of thin films will be a valuable strategy for forming patterned networks with micro or nano dimensions. Incorporating of emissive materials into the robust films will contribute for the high-resolution display in opto-electronics fields. Previously, we have studied the fundamental properties of self-cracking network and utilized this flexible thin film as a portable pH sensor [13]. In this study, we focused on the investigation of detailed experimental conditions that controls the



**Fig. 7** Flexibility and transparency of bended thin film



**Fig. 8** Leaching experiments for europium-2,6-pyridinedicarboxylic acid complex encapsulated PDMS film in deionized water, or at pH = 2 and pH = 10

formation of microstructures and types of patterns. At first, the concentration of egg white solution was studied. We mixed the egg white with deionized water at different ratios from 1:1 to 1:4. These four samples were classified as No.1 to No.4. During the treatments, all the mixed solutions can self crack under heating but they gave rise to different widths. According to the observation from optical microscope (Fig. 1), the solution with higher water concentration formed narrow networks or scaffolds. The average diameter for the sample No.1 was estimated to be around 150 nm. In terms of the increase of water content, No.2 was reduced to 100 nm. A size shrinkage of network was observed in No.3 (60 nm) and No.4 (30 nm). The variation of egg white/water ratios would finely affect the evolution of crack structures and the dimension could be controlled. The egg white solution with high concentration of water was apparently more dilute and the thickness of the film was much less than sample No.1. Therefore, it behaved differently during the cracking process. In this way, we could control 2D nanoscale arrays in the range between 30 and 150 nm.

Another important factor will be the temperature during the cracking process. The No. 2 sample was employed to carry out the formation experiments at 30 °C, 35 °C, 40 °C, 45 °C, 50 °C and 55 °C respectively. The results obtained at higher temperature such as 50 °C and 55 °C samples were not very satisfactory. The corresponding egg white solution achieved wrinkled surface rapidly upon heating treatment and we have difficulty in obtaining smooth film for further steps. However, samples at lower temperature could meet the technical requirements. They possessed transparent and uniform networks with variable widths (Fig. 2). The irregular networks were densely distributed according to the temperature increase. The

diameter could be controlled from 120 nm to 70 nm based on different temperature.

One approach to design functional devices is to incorporate the emission species into the substrate [14–18]. In this work, we selected two europium complexes with 2,6-pyridinedicarboxylic acid and 2,4-pentanedione. The mixture of  $\text{CH}_3\text{CH}_2\text{OH}$  and  $\text{CHCl}_3$  was used as solvent to dissolve the powder complex and the homogenous solutions were formed. The liquid was drop onto the as-prepared template and heated until the evaporation of organic solvents for about 20 min. When the sample was cooled down in room temperature, the PDMS moiety could be peeled off from the glass substrate and the flexible luminescent thin film was generated. Under the irradiation via 365 nm UV light, the two samples both exhibited strong red emissions and clear network structures were identified (Fig. 3). Emission spectrum of europium complex with 2,6-pyridinedicarboxylic acid (Fig. 4) illustrated typical europium peaks at around 590 nm and 615 nm. These signals were attributed to f-f transitions of  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  ( $J = 1, 2$ ) derived from europium ions. Optical property for europium  $\beta$ -diketone complex demonstrated analogous curves. These results supported that lanthanide edifices can be effectively integrated into such self-cracking template and their unique optical features were maintained. In addition, the reproducing property was investigated with three batches of samples for the two europium complexes encapsulated PDMS films (Fig. 5). It is obvious that the fluctuations of emission intensities were negligible and the experiment results suggested excellent reproducibility of optical films.

Moreover, the mechanism property of the achieved thin films was also investigated for future optical application. Based on the PDMS substrate and homogenous egg white solution, this patterned film possessed highly transmittance. As illustrated in Fig. 6, The transmittance value of the sample film encapsulated by europium complex (88.4%) could be comparable with pure PDMS film (91.7%). In addition, the film would be elastic and could be recovered after a bending or stretching forming process (Fig. 7). This study demonstrated the capability to expand the application range for molecular-based optical materials.

The stability of the film was also evaluated by leaching experiments (Fig. 8). The parallel experiments were concentrated on europium dissolution at different conditions (deionized water, pH = 2 and pH = 10). The leaching efficiency of europium under all the circumstances was very low. Even at acidic environment (pH = 2) for 48 h, the leaching ratio was still less than 2.5%. The results revealed the robust film possessed enough durability for practical uses.

## Conclusions

In view of material science, it will be very important to tailor the structure to achieve particular morphologies for distinct applications. Herein, the robust and luminescent lanthanide

film was synthesized with the uniform self-cracking template. Detailed experimental conditions including egg white/water ratios and reaction temperature were investigated and the dimensions could be controlled. The suitable concentration of egg white solution and the self-cracking temperature were identified and the evolution feature was discussed. Two optical materials composed of europium (III) complexes with 2,6-pyridinedicarboxylic acid and 2,4-pentanedione were measured and the micro-patterned films were achieved. The photoluminescence from the network was dominated by  $f-f$  transitions from europium ions. Both of its transmittance and elasticity were recorded. This new structuring method for the control of spatial distribution of optical centers on transparent films will act as an interesting alternative to routine techniques.

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