

## Micro-patterns of Ruthenium (II) complexes produced by micromolding

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Ruthenium complexes exhibit attractive photophysical and electrochemical properties for many fundamental and applied studies due to their variety of luminescence properties with long excited state reactivity and relatively high chemical and thermal stability. It also has a large molar absorption coefficient in the visible-light region and the excited state performs oxidative and reductive electron transfer to various receptors and donors. Such unique features of Ruthenium complexes make them suitable for optical sensors [1–3], photo catalysts [4], photo electrodes for solar cells [5], and nonlinear optical materials [6].

Nano and micro particles lattice with strictly controllable size and space are necessary for high-tech research and applications. Micro particle lattices made of Ruthenium complexes have important potential applications in the research of optical devices, chemical

sensors, microelectronics. The traditional micro fabrication method is photolithography; it produces micro-patterns with UV light and photosensitive resists, but it is difficult to be used in other fields. Micromolding is a soft lithography method [7–11]. This technology can produce microstructures with varying chemical materials and works well on curved surface because of the good elasticity of the polydimethylsiloxane (PDMS) stamp. Micro features of the final product can be controlled well by using different masters to cast the stamp. In this paper, we demonstrate the experiment of producing Ruthenium (II) complexes micro-patterns by micromolding.

The pattern-transfer element used for micromolding used was an elastomeric stamp made of PDMS. PDMS was mixed with the curing agent in a ratio of 10:1 (w/w) and vacuumed to drive out air bubbles. Then it was

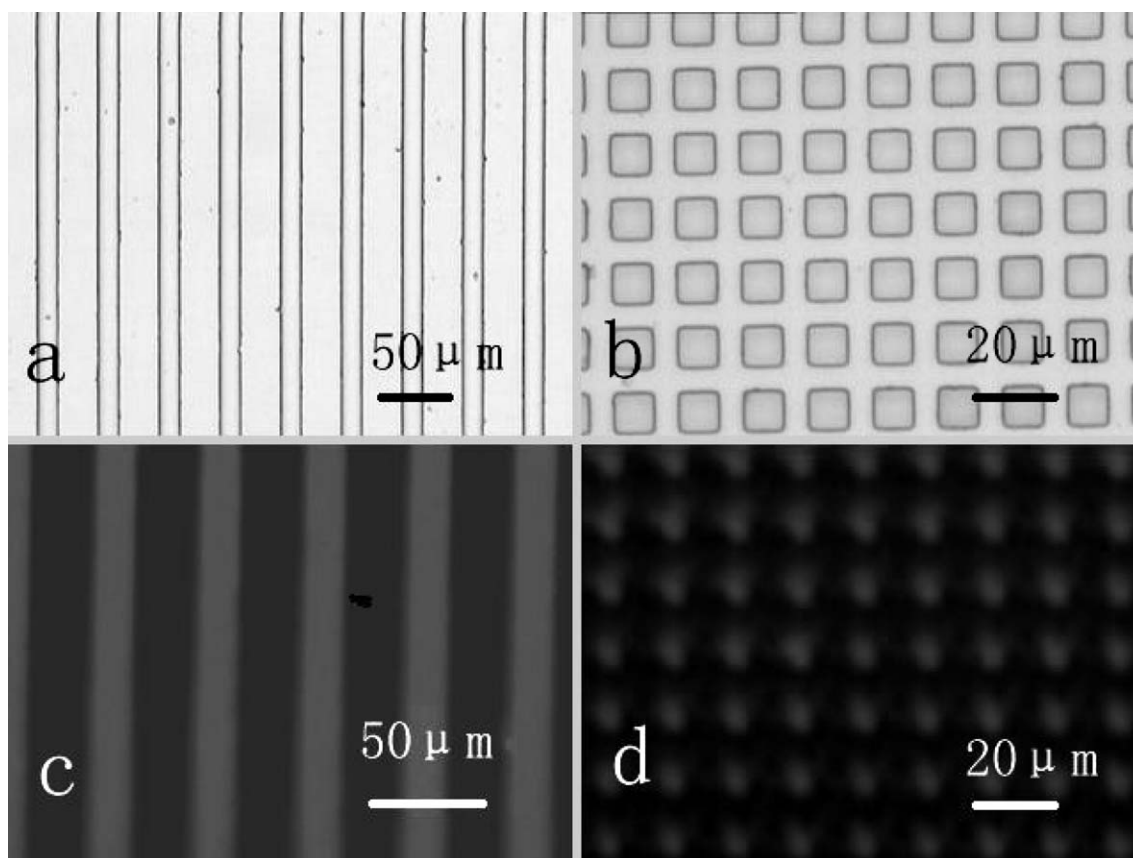
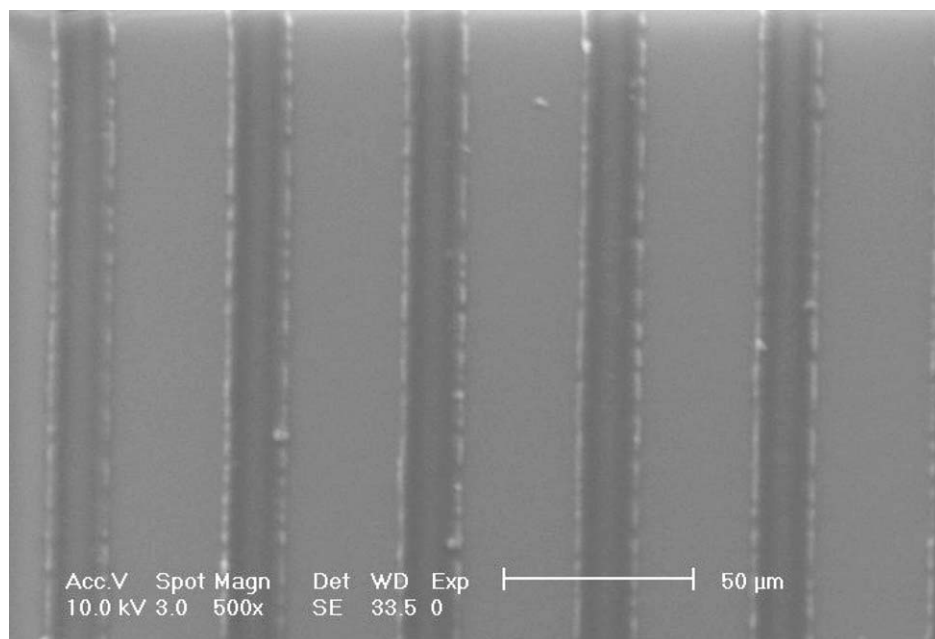
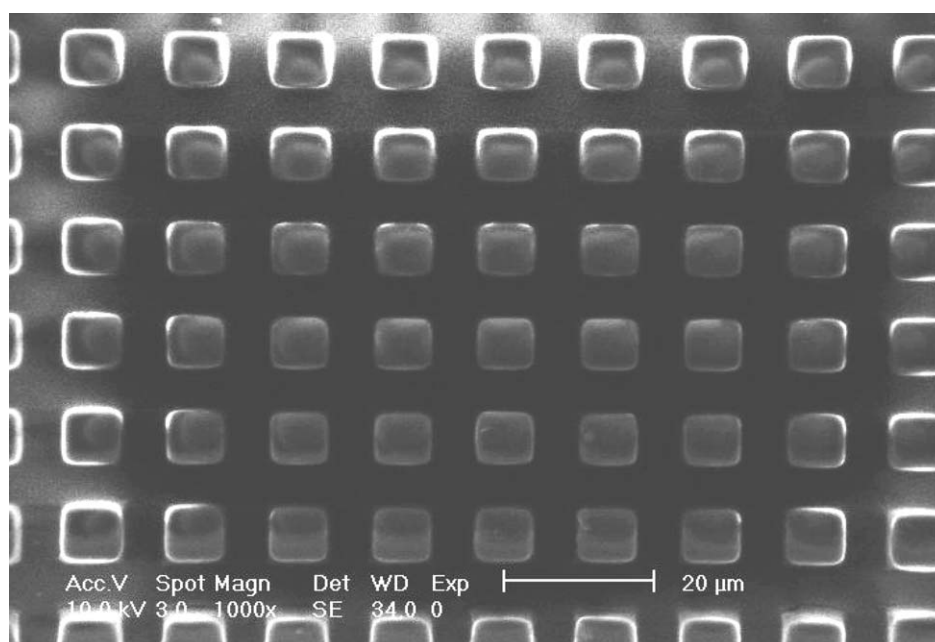


Figure 1 Microscope images of PDMS stamp ((a) the strip patterns and (b) the dot array patterns) and fluorescent microscope images of the micro-patterns containing  $\text{Ru}(\text{dpphen})_3^{2+}$  ((c) the strip patterns and (d) the dot array patterns).

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(a)



(b)

Figure 2 SEM images for the patterned structure containing  $\text{Ru}(\text{dpphen})_3^{2+}$ .

cast on the master, which had been prepared by photolithography. After 3-h curing at  $70^\circ\text{C}$ , the PDMS stamp was taken off carefully and micro-patterns were copied on the surface of the stamp.  $\text{Ru}(\text{dpphen})_3^{2+}$  (dpphen = 4,7-diphenyl-1,10-phenanthroline) was dissolved in AR grade ethanol with the concentration of  $2100 \text{ mol/m}^3$ . Then poly[1-(2-oxo-1-pyrrolidinyl)-ethylene] (PVP) was also dissolved in the same solution with the concentration of 2% (w/w). The mixture solution was kept in a refrigerator before the micromolding experiments. To improve the qualities of the micro-patterns, a drop of mixed solution was deposited onto the surface of the PDMS stamp first and smoothed out. Excess solution was scraped off. For making the strip patterns, the PDMS stamp with the strip patterns was used and placed on a glass substrate with the feature face

in contact with the substrate. Thus the micro-channels could be formed. Then the mixture solution was put on the open end of the micro-channels and dried at room temperature for 24 h. The system was placed in a drying chamber for further drying. Then the PDMS stamp was taken off carefully and the micro strip patterns of PVP containing  $\text{Ru}(\text{dpphen})_3^{2+}$  complexes were complete. For producing the dot array patterns, micro transfer molding was used. The PDMS stamp containing the mixture solution in the space between dots was placed on the glass substrate with the feature face in contact with the substrate as before. The solution in the dot array patterns of the PDMS stamp was transferred onto the substrate. Using the same procedure, the micro dot array patterns of PVP containing  $\text{Ru}(\text{dpphen})_3^{2+}$  complexes were formed.

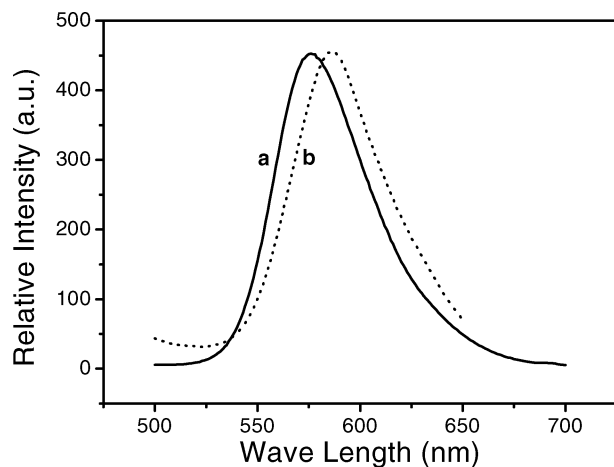


Figure 3 Photo-induced emission spectra of  $\text{Ru(dpphen)}_3^{2+}$  in powder (a) and in PVP matrix in the micro-patterns (b).

Fig. 1a and b shows microscope images of the PDMS stamp with the strip patterns and the dot array patterns. It is found that the micro-patterns can be copied well from the photolithography template. Because shrinkage will happen during the crystallization process, this would introduce some fracture in the final microstructures when using  $\text{Ru(dpphen)}_3^{2+}$ -ethanol solution only. To improve the quality of the resulting micro-patterns, the  $\text{Ru(dpphen)}_3^{2+}$ -PVP-ethanol mixture solution was used. Fig. 1c and d shows fluorescent microscope images (OLYMPUS IX-70 with OLYMPUS DP-50) of the micro-patterns prepared by micromolding and micro transfer molding with  $\text{Ru(dpphen)}_3^{2+}$ -PVP-ethanol mixture solution. The light (red) area was the part containing  $\text{Ru(dpphen)}_3^{2+}$  and the dark one the blank area. There was no crack or fracture in the final patterns. In comparison with the dot array patterns, both boundary and color contrast were sharper in the strip patterns. The reason was related to the different micro fabrications. The micro strip patterns were prepared by micromolding in a capillary, in which the drop of mixture solution would replenish the solution in the capillary continually when shrinkage occurred during the procedure. However, the micro dot array patterns were prepared by micro transfer molding, in which there was no additional mixture solution available during the procedure. Thus the amount of  $\text{Ru(dpphen)}_3^{2+}$  that entered the strip patterns by micromolding in the capillary would be more than that in the dot array patterns made by micro transfer molding. No remarkable local phase separation in the strips or dots could be found in the fluorescent microscope images. All these results suggested that  $\text{Ru(dpphen)}_3^{2+}$  was dispersed homogeneously into the micro-patterns and these micro-patterns containing  $\text{Ru(dpphen)}_3^{2+}$  were homogeneous enough for application in optical devices.

SEM measurements (Philips XL30 ESEM, acceleration voltage 10 kV) were performed to collect information concerning the micro-patterns of PVP containing  $\text{Ru(dpphen)}_3^{2+}$ . Fig. 2a shows an SEM image for the patterned strip structure prepared by micromolding in capillaries with PVP- $\text{Ru(dpphen)}_3^{2+}$ -ethanol solution. Fig. 2b shows an SEM image for the patterned dot array

structure prepared by micro transfer molding with PVP- $\text{Ru(dpphen)}_3^{2+}$ -ethanol solution. From Fig. 2, we could clearly draw the conclusion that defect-free patterns were produced. In Fig. 2a, the period was  $46 \mu\text{m}$  with a strip width of  $13 \mu\text{m}$ . In Fig. 2b, the dots array had a period of  $15 \mu\text{m}$  with the dot size of  $8 \mu\text{m}$ . All the results suggested that homogeneous and smooth patterns have been fabricated.

The photo-induced emission spectra of  $\text{Ru(dpphen)}_3^{2+}$  in powder and in PVP matrix in the micro-patterns are shown in Fig. 3. The photo-induced emission spectra of  $\text{Ru(dpphen)}_3^{2+}$  in strip patterns and dot array patterns were similar. The fluorescence maximum of  $\text{Ru(dpphen)}_3^{2+}$  in PVP matrix in the micro-patterns was observed at 576 nm, which showed slightly blue shift compared with  $\text{Ru(dpphen)}_3^{2+}$  in powder (586 nm).  $\text{Ru(dpphen)}_3^{2+}$  in PVP matrix in the micro-patterns emitted light of shorter wavelengths, suggesting some interaction between  $\text{Ru(dpphen)}_3^{2+}$  and PVP due to the close molecular packing in the micro-patterns. All these results indicate that the introduction of PVP cannot affect greatly the optical properties of  $\text{Ru(dpphen)}_3^{2+}$ , and these micro-patterns containing  $\text{Ru(dpphen)}_3^{2+}$  were suitable for application in optical devices.

In conclusion, a promising method was proposed for fabricating micro-patterns containing  $\text{Ru(dpphen)}_3^{2+}$ .  $\text{Ru(dpphen)}_3^{2+}$  was dispersed homogeneously into the micro-patterns and these micro-patterns containing  $\text{Ru(dpphen)}_3^{2+}$  were homogeneous enough for application in optical devices. This method may be extended to other functional molecular systems.

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