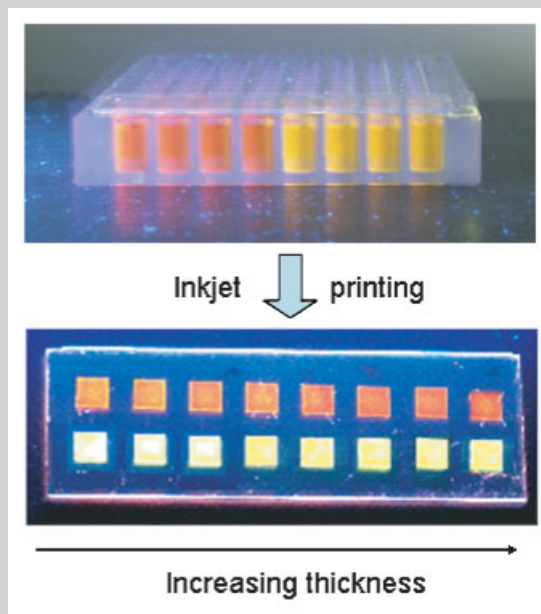


**Summary:** Defined films of luminescent ruthenium(II) polypyridyl-poly(methyl methacrylate) (PMMA) and iridium(III) polypyridyl-polystyrene (PS) copolymers could be prepared by ink-jet printing. The copolymers were deposited on photoresist-patterned glass substrates. Films as thin as 120 nm could be printed with a roughness of 1 to 2%. In addition, the film thickness could be varied in a controlled way through the number of droplets deposited per unit area. The topography of the ink-jet printed films was analyzed utilizing an optical profilometer. The absorbance and emission spectra were measured using fast parallel UV-vis and fluorescence plate reader.

Photo of the solutions of luminescent ruthenium (left) and iridium (right) containing polymers in a glass microtiter plate (top). The subsequently prepared films using ink-jet dispensing techniques are shown below.



# Ink-Jet Printing of Luminescent Ruthenium- and Iridium-Containing Polymers for Applications in Light-Emitting Devices

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Received: October 23, 2004; Revised: November 29, 2004; Accepted: November 30, 2004; DOI: 10.1002/marc.200400507

**Keywords:** ink-jet printing; inks; iridium ions; light-emitting devices; optical property screening; ruthenium ions; thin film libraries

## Introduction

Ink-jet printing is a very attractive technique for the controlled deposition of small quantities of solutions (down to picoliters) of functional materials at well defined places on a substrate.<sup>[1–3]</sup> Recently, growing efforts have been made in the field of ink-jet printing technology in relation with the fabrication of organic transistors (polytronics),<sup>[4–6]</sup> color emissive polymer displays,<sup>[7–11]</sup> ceramics,<sup>[12]</sup> and biomolecular arrays.<sup>[13,14]</sup>

In particular, ink-jet printing is an indispensable technique for the integration of different polymers in a certain

pattern on the same substrate (e.g., deposition of red, green, and blue emitters for potential applications in full color displays).<sup>[15–18]</sup> Furthermore, less material is wasted as compared to other deposition methods, such as spincoating. Moreover, insensitivity to substrate defects for the fabrication of large-area devices is offered.<sup>[10]</sup>

Usually, polymer films deposited by ink-jet printing suffer from a ring-formation effect.<sup>[19,20]</sup> This makes them unsuitable for applications in the production of high quality electronic devices. Previously conducted studies in our group focused on this topic and showed how to minimize the ring-formation effect either for small polymer dots<sup>[21]</sup> or

for macroscopic films<sup>[20]</sup> by a careful selection of solvent, substrate, and printing methods.

In combinatorial research, ink-jet printing opens the way to the preparation of libraries of thin films and dots of polymers, polymer blends, or composites, with a systematic variation of parameters such as chemical composition or thickness.<sup>[14,20]</sup>

Ru- and Ir-complexes are promising materials for light-emitting diodes because of their photophysical, photochemical, and electrochemical properties (Figure 1).<sup>[17,18,22,23]</sup> For device applications, films of luminescent materials must be very thin (in the range of about 100 nm) and very flat (less than 5% roughness).

The focus of this paper is directed to the development of a method for the high-throughput preparation of thin films of these luminescent polymers using ink-jet printing, as well as the subsequent rapid screening of their optical properties. Photoresist patterns on glass substrates were employed to confine the printed liquid and thus to produce well-defined films. Using this method, thin-film libraries with various thicknesses could be obtained in a controlled way.

## Experimental Part

### Materials

The synthetic procedures to obtain Ru/polypyridyl-poly-(methyl methacrylate) (PMMA) ( $\bar{M}_n = 15\,000\text{ g}\cdot\text{mol}^{-1}$ ) and Ir/polypyridyl-polystyrene (PS) ( $\bar{M}_n = 3\,000\text{ g}\cdot\text{mol}^{-1}$ ) are described elsewhere<sup>[24–27]</sup> and their structures are shown in Figure 1. Isopropyl acetate (99%) and acetophenone (99%) were purchased from Sigma-Aldrich. The negative tone photoresist SU-8 2005 and SU-8 developer were purchased from Micro Chem. This epoxy-based photoresist results in a highly cross-linked layer that is insoluble in organic solvents. Microscopic slides ( $3 \times 1\text{ inch}^2$ ) from Marienfeld (Lauda-Königshofen, Germany) were used as a glass substrate.

### Preparation of Photoresist Patterns on Glass

Because most organic solvents spread on glass, the printing of polymer solutions sometimes results in irregular films. To obtain well-defined arrays of films, glass substrates were patterned using a photoresist to confine the deposited solution. Before patterning, the glass substrates were ultrasonicated for 5 min in acetone. Subsequently, they were rubbed and ultrasonicated for 10 min with sodium dodecyl sulfate solution and washed with demineralized water to remove the soap. Afterwards, they were ultrasonicated in isopropyl alcohol to remove the water, and then dried under airflow. To remove any organic contamination, the substrates were finally treated in a UV-ozone photoreactor (UVP PR-100, Upland, CA) for 20 min. Photoresist SU-8 2005 was spin-coated onto the glass substrate at 1 000 rpm for 2 min to obtain a layer of about 8  $\mu\text{m}$  thickness. The substrate was then baked on a heating plate at 90 °C for 7 min. A transparent plastic mask containing rectangular dark areas ( $5 \times 5\text{ mm}^2$ ) was placed on top of the substrate, which was then exposed to UV light (300–400 nm) for 1–2 min. Afterwards, the sample was post baked at 95 °C for 5 min and subsequently immersed in the developer. After rinsing with isopropyl alcohol and drying under airflow, the substrate was hard-baked at 150–200 °C for 10 min to maximize the cross-link density.<sup>[28]</sup> The structure of this photoresist pattern and the printing onto this substrate are shown in Figure 2. The films were printed into the microtiter-plate well positions (each  $5\text{ mm} \times 5\text{ mm}$  in size). This provides a parallel investigation of libraries with high-throughput screening technologies like UV-vis and fluorescence plate reader.

### Instrumentation

Ink-jet printing was carried out using an Autodrop printer (Microdrop, Norderstedt, Germany). The system is equipped with an XYZ-stage and a stroboscopic video camera. The positioning accuracy of the print head is 3  $\mu\text{m}$  and the available workspace is  $200 \times 200 \times 80\text{ mm}^3$ . As a print head, a standard AD-K-501 micropipette (having a single nozzle) was used. The

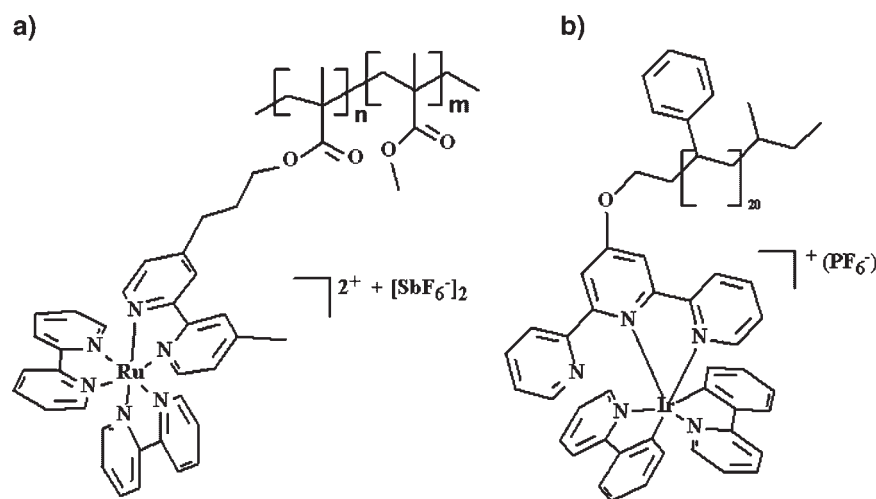


Figure 1. a) Schematic representation of the Ru<sup>II</sup>/polypyridyl-PMMA copolymer; and b) schematic representation of the Ir<sup>III</sup>/polypyridyl-PS copolymer.

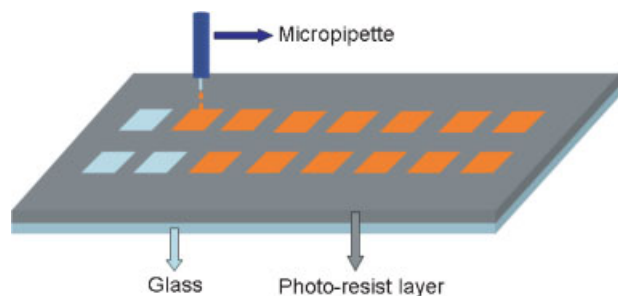


Figure 2. Schematic illustration of the photoresist-patterned glass substrate and the corresponding ink-jet printing into the wells of this substrate using a micropipette.

diameter of the nozzle is 70  $\mu\text{m}$ . It has already been shown that the device is capable to print dilute solutions (1–2% by weight) of high-molecular-weight polymers ( $\bar{M}_w \sim 100$  kD).<sup>[29]</sup> The micropipette can aspirate small quantities of fluid from a 96-well microtiter plate, and can dispense them at any desired place (e.g., on glass plates, silicon wafers, polycarbonate, a second microtiter plate, etc.). The pipette can be cleaned by repeated aspiration and flushing with solvent. The piezo actuator serves as a built-in ultrasonic cleaning device when operating at its eigenfrequency, i.e., 12 kHz, and was used to remove persistent contamination. After use, the micropipette was flushed with acetone and dried by purging with air.

UV-vis and fluorescence spectra of the ink-jet printed films were measured on a Flashscan 530 spectrophotometer from AnalytikJena (Jena, Germany). All spectra were referenced to an empty plate and measurements were performed with four flashes. The actual time for the measurement of one microtiter plate with 96 full UV-vis spectra was approximately 40 s.

An optical-profilometer, the Fogale Zoomsurf, was used to determine the surface topography and to measure the thickness of the polymer films. Its vertical resolution is 1 nm, when a red light source is employed, and 7 nm for white light; the horizontal resolution is 150 nm. However, to scan large areas a low-resolution magnifying objective (5 times) was used. AFM imaging was performed on a Solver P47-H scanning probe microscope (NT-MDT, Moscow, Russia). The measurement was obtained in semi-contact mode with silicon tips (NSG11, NT-MDT).

## Results and Discussion

In a previous study, it had been found that the addition of small amounts of high-boiling solvent to a low-boiling-solvent-based ink can prevent ring formation. This finding was used to print polystyrene films with a thickness of between 6 and 20  $\mu\text{m}$  and a roughness smaller than 5%.<sup>[20]</sup>

To print thin films (in a range of 100 nm) of luminescent polymers and to subsequently screen their optical properties in a fast and reliable way, Ru/polypyridyl-poly(methyl methacrylate) (PMMA) and Ir/polypyridyl-polystyrene (PS) copolymers were selected as suitable candidates. Dilute solutions of these copolymers (1 wt-%) were prepared using a mixture of isopropyl acetate/acetophenone (85/15, w/w) to minimize the ring-formation effect (see ref.<sup>[20,21]</sup>). These

solutions could be printed at a voltage of 85 V and a pulse width of 35  $\mu\text{s}$ . However, when printing onto a glass surface, ring formation was still not completely eliminated. To confine the deposited material and to obtain well-defined films, the solutions were printed on a glass surface surrounded by photoresist barriers, as shown in Figure 2 (see experimental part for more detailed information). The effect of employing barriers was compared to printing onto a normal glass surface (Figure 3). It can be clearly seen from the

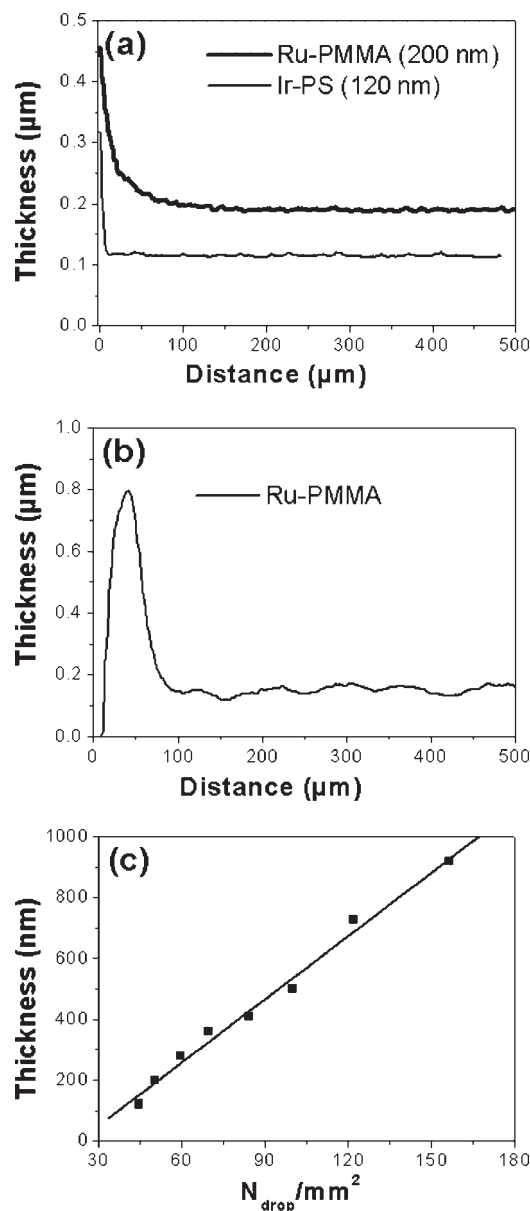


Figure 3. a) Lateral cross-section of the Ru<sup>II</sup>/polypyridyl-PMMA and Ir<sup>III</sup>/polypyridyl-PS copolymer films printed into the photoresist barriers ( $x = 0$  represents the edge of the photoresist); b) Cross-section of the Ru<sup>II</sup>/polypyridyl-PMMA copolymer film directly printed onto a normal glass surface; c) Thickness of the films as a function of the number of drops per square millimeter ( $N_{\text{drop}} \cdot \text{mm}^{-2}$ ).

cross-section that the ink-jet printed copolymer films in barriers are much flatter than those printed onto glass (Figure 3a and 3b). However, the edges of the cross-sections of the films shown in Figure 3a are slightly parabolic. This could be caused by hydrophobic interactions between the photoresist and the printed material. To find the actual reason and to avoid this effect, further investigations are certainly needed. On the other hand, films printed onto a normal glass surface exhibit a clearly visual ring-formation effect: most of the material was transferred to the edges (Figure 3b). This effect is completely or partially invisible when printing between photoresist barriers. It is obvious that the topography of the films printed on patterned glass have a more homogeneous thickness distribution.

The roughness of the films, as determined from the profilometer images, was approximately 4 to 6 nm. The roughness of these films was also examined using atomic force microscopy (AFM). Typically  $10 \times 10 \mu\text{m}$  areas were measured. For instance, the roughness of an  $\text{Ir}^{\text{III}}$ /polypyridyl-PS copolymer film having a thickness of 120 nm was 1 nm and for a  $\text{Ru}^{\text{II}}$ /polypyridyl-PMMA film having a thickness of 200 nm, the roughness was around 1 to 3 nm. These values correspond to 1–2% of the thickness of the films.

When printing onto a glass surface, many organic solvents show strong spreading. As a consequence of this spreading the obtained films are, therefore, irregular in shape and the thickness control after deposition becomes impossible. Therefore, the material needs to be confined in a certain area. To check the dependency of the thickness of the polymer layer after drying on the number of deposited droplets per unit area, a library of  $\text{Ru}^{\text{II}}$ /polypyridyl-PMMA and  $\text{Ir}^{\text{III}}$ /polypyridyl-PS copolymer films with variable thicknesses were printed. These films were obtained by deposition of an array of droplets on the surface. The array is characterized by the number of droplets in the X- and Y-directions, and the spacing in between (dot spacing). Films can be printed by reducing the spacing between the droplets, so that they merge on the surface. When we decrease the dot spacing ( $\Delta x$ ), the film thickness ( $h$ ) should increase according to  $h \propto (\Delta x)^{-2}$ , as the amount that is deposited will be increased.

To determine the film thickness, the printed films were scratched with a scalpel. The depth of the film was measured by scanning over the scratch using the profilometer. Dot spacing, the corresponding number of deposited droplets per  $\text{mm}^2$ , and the resulting film thicknesses are summarized in Table 1. The thickness versus number of deposited droplets per area is plotted in Figure 3c. The observed linear relation proves the control on the film thickness.

The positions of the luminescent films correspond to the (standardized) positions of the wells of a 96-well microtiter plate. This allows the use of a UV-vis/fluorescence plate reader to screen the optical properties of the copolymers in

Table 1. Dot spacing and corresponding number of droplets per area that were used to print luminescent polymers with various thicknesses. The resulting thicknesses were measured by an optical profilometer.

Dot spacing	Number of droplets per $\text{mm}^2$	Thickness
mm		nm
0.15	45	120
0.14	50	199
0.13	60	282
0.12	70	370
0.11	84	405
0.10	100	500
0.09	122	729
0.08	156	920

the film. All absorption and emission spectra of the prepared  $\text{Ru}^{\text{II}}$ /polypyridyl-PMMA and  $\text{Ir}^{\text{III}}$ /polypyridyl-PS copolymer libraries with various thicknesses were measured at the same time. The maximum absorption of the metal-to-ligand charge-transfer band of the  $\text{Ru}^{\text{II}}$ /polypyridyl-PMMA copolymer was observed at 455 nm (Figure 4a). The respective emission spectra were recorded upon excitation at 455 nm. Maxima at 620 nm were exhibited, which are characteristic for an electroluminescent trispyridyl ruthenium(II) complex (Figure 4b). Because of the rigidity of the environment, the

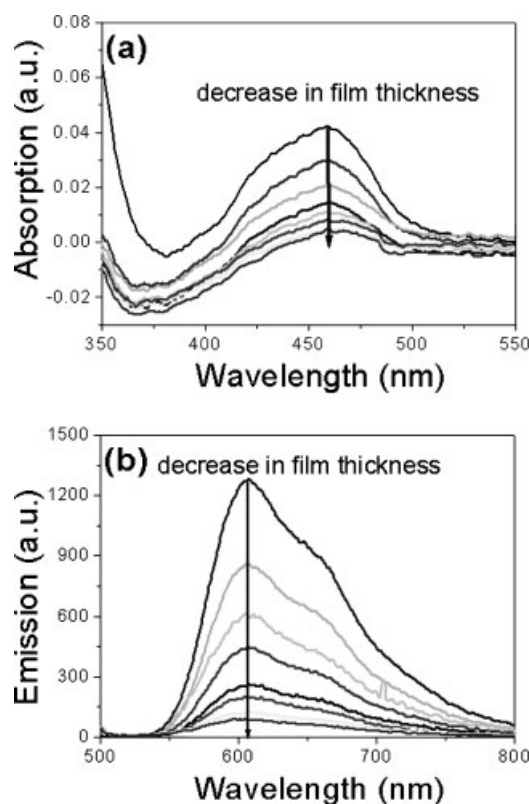


Figure 4. The absorption (a) and emission (b) spectra of ink-jet printed  $\text{Ru}^{\text{II}}$ /polypyridyl-PMMA copolymer films with variable thickness ranging from 120 to 900 nm.



Table 2. The droplet number per mm<sup>2</sup> in correlation with the maximum intensities of the absorption and emission spectra of the Ir and Ru polymers.

Number of droplets per mm <sup>2</sup>	Abs <sub>max.</sub> Ru-PMMA	Em <sub>max.</sub> Ru-PMMA	Abs <sub>max.</sub> Ir-PS	Em <sub>max.</sub> Ir-PS
	a.u.	a.u.	a.u.	a.u.
45	0.0420	1 266	0.319	1 735
50	0.0295	861	0.296	1 510
60	0.0204	607	0.272	1 290
70	0.0141	442	0.253	974
84	0.0106	257	0.233	700
100	0.0078	198	0.229	514
122	0.0045	125	0.222	378
156	0.0043	86	0.212	366

emission band is more pronounced. Ir<sup>III</sup>/polypyridyl-PS copolymer films have absorption and emission bands at 370 and 570 nm, respectively. In both cases, the emission and absorption intensity of the copolymers regularly decreased with the decrease of film thickness. We found a linear relationship between film thickness and the maximum absorbance or emission, when intensities were plotted versus the number of drops per mm<sup>2</sup> (see Table 2).

## Conclusion

The high-throughput preparation of thin-film libraries of Ru<sup>II</sup>/polypyridyl-PMMA and Ir<sup>III</sup>/polypyridyl-PS copolymers with various thickness were successfully performed onto one common substrate using ink-jet printing, which is not possible using conventional methods such as spincoating. Photoresist-patterned glass substrates were employed to confine the deposited material. Using this method, ring formation decreased and uncontrolled spreading of the ink is prevented. Films as thin as 120 nm with a roughness of 1% were successfully printed. By changing the number of droplets per unit area, the thickness of the films could be varied in a controlled way. Furthermore, the optical properties of the luminescent films were rapidly screened by utilizing a UV-vis/fluorescence plate reader. Emission and absorption spectra of the copolymers regularly decreased with film thickness. Emission and absorption were found to be a linear function of the number of drops per mm<sup>2</sup>, as expected. Future experiments will be directed towards a parallel investigation of the opto-electronic properties of arrays of different dyes for device applications.

**Acknowledgements:** This work forms part of the DPI research program (projects 401 and 448, cooperation with projects 324 and 360). The authors thank the *Fonds der Chemischen Industrie* for financial support.

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