

# MICRO-CAPILLARY SYSTEMS INTEGRATING PHOTO-CONTROLLED MOLECULAR CRANES FOR METAL ION ACCUMULATION, SENSING AND RELEASE IN CONTINUOUS FLOW

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## ABSTRACT

A simple and innovative photo-controlled micro-capillary system, capable of metal ion detection, accumulation and release, in continuous flow, has been realised through out the integration of the beneficial characteristics of both micro-fluidic platforms (micro-capillary) and photochromic dyes. This system involves the coating of the inner walls of fused-silica micro-capillaries with polymeric brushes based on spiropyran using the “grafting from” approach. Upon irradiation with UV light the passive spiropyran (SP) unit undergoes a heterocyclic ring cleavage that results in the merocyanine (MC) formation, molecular crane performance. In contrast to the uncharged and colourless spiropyran form, the MC is highly charged and can be used as ligand for other charged species. Based on the coordination-induced photochromism characteristic of the MC form, we show here, that our micro-capillary integrated system can be successfully used for the accumulation, optical detection and on demand release of different metal ions ( $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ) that are passing through the capillary in a continuous flow mode.

## KEYWORDS

Spiropyran, metal ions, coatings, micro-capillary, continuous flow.

## INTRODUCTION

The real-time analysis of metal ions is important for chemical monitoring as well as environmental and clinical applications, which are fast developing areas in micro-fluidic technology. Recently, great scientific effort have been focused on producing sensors that are capable of detecting metal ions in a fast and reversible manner. Building arrays of sensors composed of multiple ligands specific for the detection of each metal ion is difficult to realise and rather time-consuming. In this respect, a single material that is capable of binding multiple metal ions and give a unique spectral response to each metal ion-ligand complex would be preferred. Moreover, if the chelator itself could be switch between a passive and an active state, then very simple, reusable and cost-effective sensors could be developed. In this context, spiropyran (SP) derivatives have attracted a lot of attention. SPs are organic photochromic compounds that upon irradiation with UV or visible light, isomerise between the closed and open forms, in which the open form is comparatively more polar. Metal ions can influence this isomerisation process by associating with the open form through the electron-rich oxygen atom (Figure 1) - molecular crane performance. In contrast, visible light produces a high concentration of the closed form, and thus hinders metal-binding. The use of light to trigger the chelator offers unique opportunities as the binding/releasing process is now reversible and can be controlled externally in a non-invasive manner.

A relatively new and promising approach of producing chemical sensor involves the integration of polymeric optical-sensing materials and fluidic functionalities at the micro-scale to leverage their combined advantages [1]. The micro-fluidic part, which in this case is represented by a micro-capillary, possesses many advantages as such reduced consumption of reagents and analytes, improved time efficiency in the analysis, shrinkage in the size and weight of the system, increased portability, and low cost in fabrication. By combining the advantages of the micro-capillary platform with SP-polymeric coatings, real-time and controllable detection of metal ions, photo-accumulation and on demand photo-release can be achieved. Moreover, the use of light to activate the molecular cranes offers unique opportunities that minimise waste generation and power requirements.

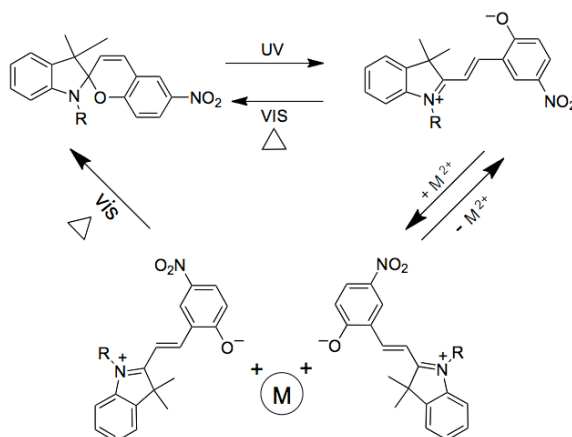


Figure 1. Metal ion binding scheme related to SP-MC switching.

## EXPERIMENTAL

### Fused silica micro-capillaries coating protocol

The protocol used to coat micro-capillaries with spiropyran polymer brushes is described in Fig. 2, steps 1-4. Prior to functionalisation, the inner surface of fused-silica micro-capillaries was first activated with 7-octenyl trichlorosilane. The inner micro-capillary surface was quickly washed with acetone and water, then flushed with a solution of NaOH 0.2 M for 30 min at a flow rate of  $0.25 \mu\text{L min}^{-1}$  using a syringe pump, and then rinsed with deionised water. Next, the micro-capillary was flushed with a solution of HCl 0.2 M for 30 min at a flow rate of  $0.25 \mu\text{L min}^{-1}$ , rinsed with water, and with dry toluene. A 0.1 M solution of the silanisation agent (7-octenyl trichlorosilane) 0.1 M in dry toluene was pumped through the micro-capillaries for 90 min at a flow rate of  $0.25 \mu\text{L min}^{-1}$  (Fig. 2 – step 1). The micro-capillaries were then washed with acetone, dried under nitrogen stream, and left at room temperature for 24h. Later, the micro-capillary was filled with a solution of Grubbs Catalyst Second Generation 0.02 M in degassed  $\text{CH}_2\text{Cl}_2$ , closed at both ends using rubber septa (this procedure was performed in the glove box due to the air sensitivity of the catalyst) and put in a water bath for 1h at  $45^\circ\text{C}$  (Fig. 2 – step 2). After, the catalyst-attached micro-capillary was thoroughly washed with degassed  $\text{CH}_2\text{Cl}_2$  in an inert atmosphere (glove box). Finally, the micro-capillary was filled with a solution of spiropyran-norbornene functionalised monomer, 0.5 M in degassed  $\text{CH}_2\text{Cl}_2$ , closed at both ends using rubber septa, removed from the glove box and put in a water bath at  $50^\circ\text{C}$  for 4 h (Fig. 2 – step 3). The polymerisation was quenched by passing ethyl vinyl ether into the micro-capillary (Fig. 2 – step 4). Finally the micro-capillary was thoroughly washed with acetone to remove any physisorbed materials.

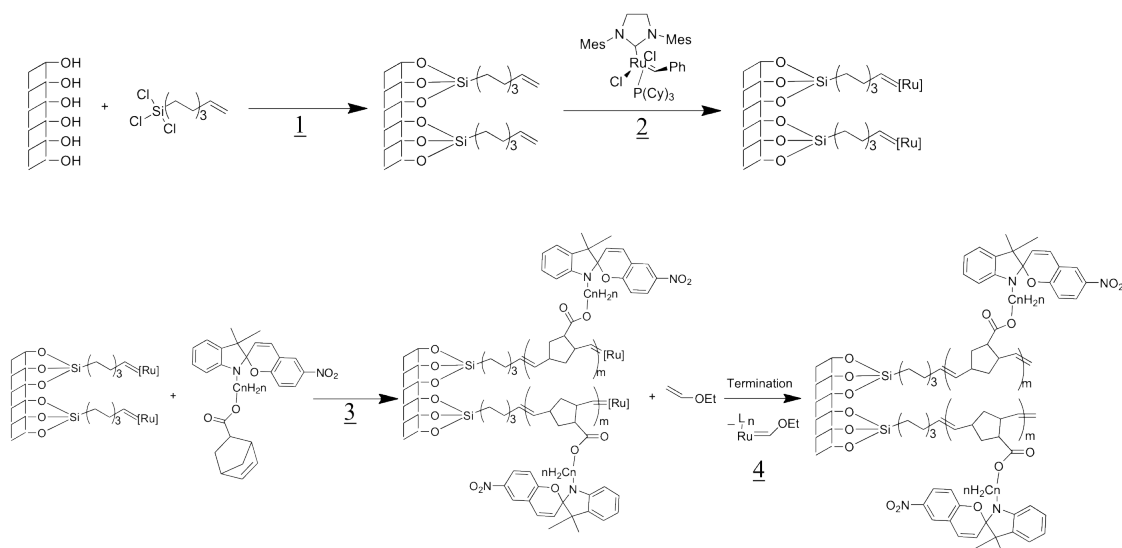


Figure 2. Functionalisation protocol of fused silica micro-capillaries with spiropyran based polymeric brushes.

### Optical characterisation of spiropyran coatings

The optical switching of the spiropyran moiety inside the capillary has been studied using USB 4000 Fiber Optic Spectrometer – Ocean Optics, Inc, when the light source was a LS-1 tungsten halogen lamp (white light) obtained from Ocean Optics, Inc. A representation of the set-up used for absorbance measurements is described in Fig. 3. The solvent acetonitrile (ACN) and metal ions solutions in ACN were passed through the capillary at constant flow rate ( $0.5 \mu\text{L min}^{-1}$ ) using a syringe pump (PHD 2000 Syringe) purchased from Harvard Apparatus.

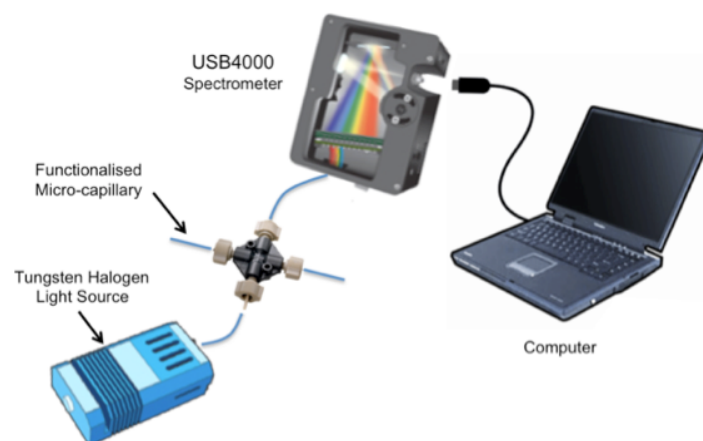


Figure 3. Schematic of the set-up used for absorbance measurements of the micro-capillary coatings.

## RESULTS AND DISCUSSION

SP-polymer brushes modified micro-capillaries are capable of detecting different metal solutions when passing through the micro-capillary and this detection is based on changes in colour of the coating after irradiation with UV light (Figure 4A). The absorbance spectra of the coatings were recorded using the system described in Figure 3. As depicted from Figure 4B, upon irradiation with UV light, the different metal ions that are passed through the modified capillary in continuous flow will form complexes with the MC-coating that absorb at different wavelengths. When only the solvent, ACN, is passed through the modified micro-capillary, the irradiation of the capillary with UV light for 20 s, causes the formation of the ring-opened merocyanine (MC-coating), characterised by an intense absorption band at 563 nm. Upon complexation with  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ , the absorption band is shifted at lower wavelengths, which is metal-ion-dependent. The MC-  $\text{Ni}^{2+}$ -MC, complex yields the smallest blue shift of only 29 nm ( $\lambda_{\text{max}} = 534$  nm), but the MC- $\text{Cd}^{2+}$ -MC and MC- $\text{Co}^{2+}$ -MC complexes give blue shifts of 41 nm ( $\lambda_{\text{max}} = 522$  nm) and 55 nm ( $\lambda_{\text{max}} = 508$  nm), respectively. The higher shifts are observed in the case of MC- $\text{Zn}^{2+}$ -MC and MC- $\text{Cu}^{2+}$ -MC complexes which present a  $\lambda_{\text{max}} = 489$  nm and  $\lambda_{\text{max}} = 480$  nm, respectively. Moreover, the sensing behaviour of the SP-polymer brushes micro-capillaries can be switched ON/OFF using light at appropriate wavelengths. After the metal ion binding process, which is manifested by a change in colour of the micro-capillary coating, the micro-capillary is irradiated with white light for 1 min, MC-polymer coating will go back to the closed SP-polymer coating form and the metal ion previously bound will be released. As a consequence, the micro-capillary goes back to colourless. This process is depicted in the case of  $\text{Co}^{2+}$  in Figure 5.

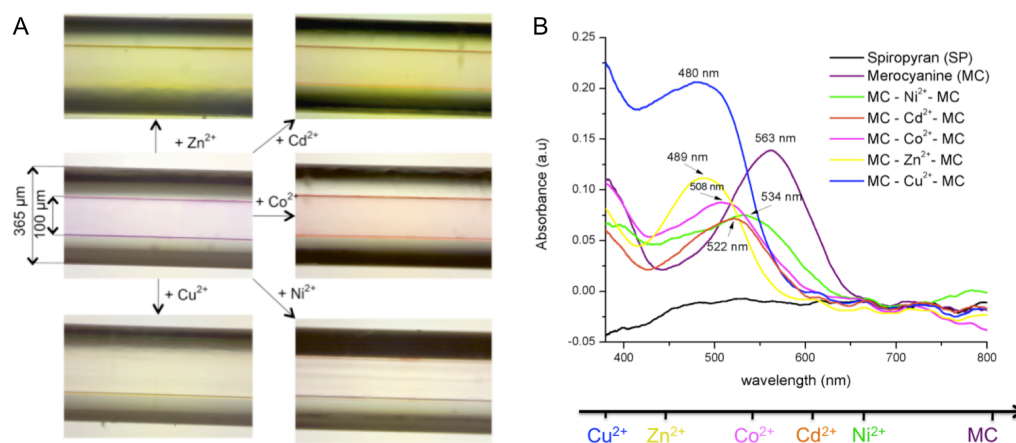


Figure 4. Photos (A) and absorbance spectra (B) of the SP-polymeric brushes coated micro-capillary in the presence of different metal ions after irradiation with UV light (20 s).

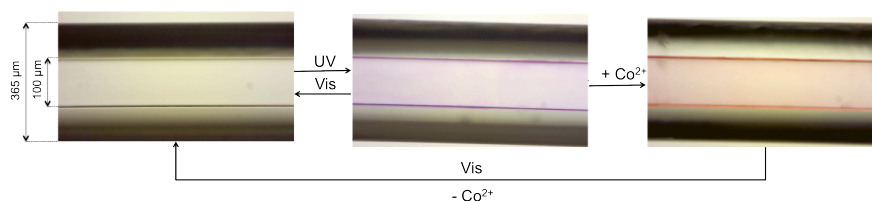


Figure 5. Photos of a section of a micro-capillary showing the binding and releasing of  $\text{Co}^{2+}$ .

## CONCLUSION

In conclusion, a new, simple and innovative micro-capillary platform capable of metal ion detection, accumulation and release has been presented. The SP-polymer brushes functionalised micro-capillary acts as photonicallly controlled self-indicating system for metal ion detection that operates in continuous flow facilitating real-time measurements and fast analysis protocols.

## ACKNOWLEDGEMENTS

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## REFERENCES

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