Supplementary Information

Micro-capillary Coatings Based on Spiropyran Polymeric Brushes for Metal Ion Binding, Detection and Release in Continuous Flow

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S1. polySP polymeric brushes functionalised micro-capillary

**Figure S1.** Schematic representation of the polySP polymeric brush structure and functionalised micro-capillary.

**Figure S2.** Scanning Electron Microscopy image of the polySP polymeric brushes functionalised micro-capillary.
S2. Set-up for absorbance measurements of micro-capillaries

Figure S3. Set-up used to study the absorbance spectra of the micro-capillary when M$^{2+}$ solutions (in ACN) are passed through the micro-capillary in continuous flow. The set-up is composed of a two fiber-optic light guides connected to a light source and a Miniature Fiber Optic Spectrometer (USB4000, Ocean Optics) and aligned using a cross-shaped cell. The M$^{2+}$ solution (in ACN) is passed through the micro-capillary using a syringe pump.

S3. Photo-induced binding and releasing of metal ions

Figure S4. Microscopy photos of a section of a micro-capillary modified with spiropyran polymer brushes (polySP) before (left) and after irradiation for 20 s with UV light (middle) followed by the addition of Co$^{2+}$ (right). The micro-capillary returns to colourless (due to the conversion of the polyMC to polySP) after irradiation with white light for 1 min, resulting in the release of Co$^{2+}$ ions.

In order to prove the release of the bound metal ion from the SP-polymer brushes coated micro-capillary through irradiation with white light, the release of metal ion was demonstrated in the case of Co$^{2+}$ through detection post modified micro-capillary using a chelating reagent, 4-(2-pyridylazo)resorcinol (PAR). PAR can coordinate to
metal ions through a heterocyclic nitrogen group, azo group, and o-hydroxyl group, as shown in Figure S5[1-3].

![Chemical structures of 4-(2-pyridylazo) resorcinol (left) and metal complexed 4-(2-pyridylazo) resorcinol (right).](image)

**Figure S5.** Chemical structures of 4-(2-pyridylazo) resorcinol (left) and metal complexed 4-(2-pyridylazo) resorcinol (right).

Firstly, the absorbance spectra of the chelating reagent (PAR) and its Co$^{2+}$ complex were recorded (Figure S6) by passing a solution of PAR (1 mM) and PAR-Co$^{2+}$ (PAR: Co$^{2+}$ 1:1) through an unmodified glass micro-capillary at 2 µL min$^{-1}$. The spectra (Figure S6) show the typical absorbance bands corresponding to PAR (black) and PAR-Co$^{2+}$ (red). The absorbance maximum for PAR-Co$^{2+}$ was recorded at ~ 510 nm.

![Absorbance spectra of the chelating reagent (PAR) and its Co$^{2+}$ complex.](image)

**Figure S6.** Absorbance spectra of the chelating reagent (PAR) and its Co$^{2+}$ complex.
For the detection of the photo-released Co\textsuperscript{2+}, the previous set-up (Figure S3) was modified (Figure S7) to include the injection of Co\textsuperscript{2+} solution in ACN (1 mM), and the following steps were undertaken:

1. The pump (left) was turned on (flow rate = 20 µL min\textsuperscript{-1}; mobile phase = ACN).
2. The syringe pump (right) was turned on (flow rate = 20 µL min\textsuperscript{-1}; mobile phase = post column reagent PAR 0.1 M).
3. The polySP modified micro-capillary was irradiated with UV light for 20 s.
4. Co\textsuperscript{2+} solution (1 mM) from the injection loop was injected in the system at a flow rate of 20 µL min\textsuperscript{-1} for approximately 5 min.
5. When all the expected Co\textsuperscript{2+} solution left the detection area, both pumps (ACN and PAR) were turned OFF and the while light was turned ON.
6. After about 5 min, both pumps (ACN and PAR) were turned back ON.
7. The absorbance at \(\lambda_{\text{max}}\) specific for PAR-Co\textsuperscript{2+} (510 nm) was recorded during the whole experiment (steps 1-6) and plotted in Figure S8.

**Figure S7.** Scheme of the set-up used for the determination of metal ions photo-released from the polySP modified micro-capillary using PAR. Step 3 (irradiation of the spiropyran modified micro-capillary with UV light) and 5 (irradiation of spiropyran modified micro-capillary with white light) are depicted in the scheme.
It is expected that, after the irradiation of the micro-capillary with white light (step 5), the Co$^{2+}$ ions will be released and then, with both pumps turned ON, the two confluent flows will react and PAR-Co$^{2+}$ will be formed. When reaching the detection area, PAR-Co$^{2+}$ will generate a change in the absorption spectra, generating a new absorbance band at 510 nm. This absorbance band (Figure S8) was recorded during the experiment (steps 1 to 6) and shows an increase in the absorbance band at 510 nm when both the PAR flow (step 2) and Co$^{2+}$ flow (step 4) are turned ON. When the Co$^{2+}$ flow is turned OFF (step 5), a decrease in the band at 510 nm is observed until this reaches an absorbance of ~0 a.u. indicating that all Co$^{2+}$ has exited the detection area. Following this, the PAR flow is also switched OFF and the SP-M polymeric brushes functionalised micro-capillary is irradiated with white light for 5 minutes. Finally, the ACN and PAR flows are switched ON. This causes an increase in the band at 510 nm (Figure S8, step 6) indicating that indeed Co$^{2+}$ was released upon white light irradiation from the modified micro-capillary.

**Figure S8.** Absorbance at 510 nm recorded on a USB400 spectrometer using the set-up depicted in Figure S7 during experimental steps 1-6. The increase of the absorbance band centred at 510 nm indicates the presence of PAR-Co$^{2+}$ complex.

**S4. Videos**

Video S1 shows in real time the colour change of the spiropyran norbornene monomer crystals under different illumination conditions. In the video, the UV light was turned ON at 0:45 and switched OFF after ~2 min (time 2:49), followed by ~3 min of white light irradiation (white light ON at 5:13 and switched OFF at 8:21). The video was recorded on a benchtop Aigo digital Microscope GE5, at a magnification of 180x.
S5. References

1. Ghasemi, J.; Niazi, A.; Maeder, M. Spectrophotometric studies on the protonation and nickel complexation equilibria of 4-(2-pyridylazo) resorcinol using global analysis in aqueous solution. *Journal of the Brazilian Chemical Society* **2007**, *18*, 267-272.

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3. Chen, Q.; Feng, Y.; Zhang, D.; Zhang, G.; Fan, Q.; Sun, S.; Zhu, D. Light - triggered self - assembly of a spiropyran - functionalized dendron into nano - /micrometer - sized particles and photoresponsive organogel with switchable fluorescence. *Advanced Functional Materials* **2010**, *20*, 36-42.