Quantitative Photo-binding and Sensing of Divalent Metal Ions Using Photo-responsive Polymeric Brushes in Micro-capillaries

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Introduction

Here, we report for the first time quantitative photo-induced binding and sensing of a wide range of divalent metal ions in continuous flow regime using spiropyran photochromic brushes coated micro-capillaries. The polymeric brushes approach offers a nanostructured to microstructured responsive coating ensuring small diffusion paths and fast response times.

Micro-capillary Functionalisation Process

The inner walls of fused silica micro-capillaries were successfully coated with spiropyran polymeric brushes using surface-initiated ring-opening metathesis polymerisation. Scanning Electron Microscopy imaging of the SP brushes inside the micro-capillary showed that coatings having lengths of about 2-3 µm were obtained.

Qualitative Binding

SP-polymer brushes modified micro-capillaries are capable of detecting different metal solutions that are passing through the modified micro-capillary in continuous flow, based on changes in colour (absorbance spectra) of the coating after irradiation with UV light. Five different metal ions solutions of Co²⁺, Ni²⁺, Cu²⁺, Cd²⁺ and Zn²⁺ were detected.

Quantitative Binding

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Metal Ions Sensing

Quantitative determination of the binding capacity of SP-coated micro-capillary; non-binding form (○), binding form (△), Cu²⁺ (-president), PADAP (●). 1 → Opening of the SP to the MC by UV light irradiation; 2 → Introduction of Cu²⁺; 3 → Binding of Cu²⁺ to the MC form and washing of non-bound Cu²⁺; 4 → Introduction of PADAP; 5 → Elution of PADAP-Cu²⁺ complex and regeneration of micro-capillary coating.

Conclusions

A new, simple and innovative micro-capillary platform capable of metal ion detection, accumulation and release has been presented. The binding capacity of the SP coated capillary was estimated as ~7x10⁻⁸ Cu²⁺ mol/mm² coating. This indicates that these photo-responsive, inherently self-indicating capillaries have significant metal ion binding capacity and could be used for photocontrolled separations, sample pre-concentration and selective metal ion extraction.