

# Reversible colorimetric ion sensors based on surface initiated polymerization of photochromic polymers†

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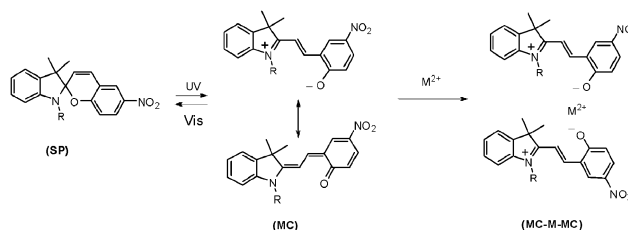
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**Spiropyran containing polymer brushes were used as reversible, photoswitchable optical sensors that show selectivity for different metal ions and drastic changes in surface wettability.**

Chemical sensors are molecules that are able to bind selectively and reversibly an analyte of interest with a simultaneous change in one or more physical properties of the system, such as absorption, fluorescence, or electrochemical potential. Specifically, colorimetric chemical sensors based on organic polymeric thin films (optodes) have been investigated extensively in the last decade.<sup>1–3</sup> In a typical sensor configuration, organic indicator dyes are immobilized in some host polymer matrix through either chemi- or physisorption. Depending on the type of immobilization, several problems can occur that limit the sensor stability, such as leaching of the indicator,<sup>4–6</sup> inaccessibility of the dye after functionalization due to steric constraints and/or diffusion of the analyte through the polymer matrix.<sup>7,8</sup> Also, immobilized indicator often prohibits a reversible response of analyte, because of very strong binding interactions. With increased usage, fouling that leads to sensor drift is unavoidable.

Recently, Byrne and Diamond have proposed the use of molecular switches that can adopt active or passive forms using external control as a way to improve sensor lifetime.<sup>9</sup> A switchable sensor would also simplify any method of calibration that might be necessary due to drift in the sensor response with time. In this context, they have used a photochromic spiropyran self-assembled monolayer, tethered to a poly(methyl methacrylate) support through alkyl diamine spacers, to reversibly bind cobalt(II) ions in solution.<sup>10</sup>

Spiroyrans are a group of photo-switchable organic molecules whose photochromism involves light induced cleavage of the spiro C–O bond. This allows reversible switching between a colorless closed form and a strongly colored merocyanine open form.<sup>11,12</sup> The photoinduced geometry change between the ring closed spiropyran (SP) and the ring-opened merocyanine (MC) form (Scheme 1) is accompanied by a large change in dipole moment. If confined to an interface, the change in dipole moment affects the surface free energy, which in turn, gives rise to a switching of wettability. We and others have exploited this change to generate surfaces that can be



**Scheme 1** Isomeric structures of spiropyran (SP) and two canonical forms of merocyanine (MC). The dimeric complex of MC with metal ions is also shown.

switched from hydrophobic to hydrophilic using light of the appropriate wavelength.<sup>13–17</sup>

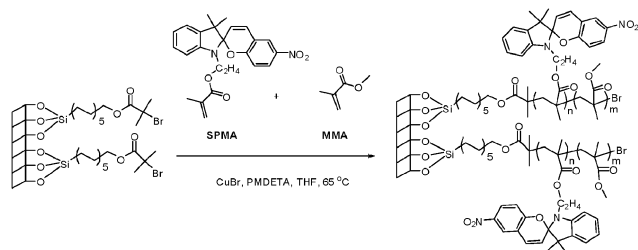
The ring-opened merocyanine (MC) form exists as a resonance hybrid between two canonical forms: the charged zwitterion and a neutral quinoidal structure (Scheme 1). It has been known for some time that the merocyanine (MC) zwitterion can bind metal ions through complexation with the phenolate anion.<sup>11,18,19</sup> This interaction is weak enough to allow dissociation of the ion and ring closing to occur upon irradiation with visible light, which provides a system capable of reversible binding.

In this work, we have synthesized polymer brushes containing spiropyran moieties using atom transfer radical polymerization (ATRP). Through a grafting-from approach, the number of functional groups present at a surface can be greatly enhanced through the three-dimensional arrangement of tethered polymer chains. This allows for a brush-like morphology, with extended chain conformations and high density of molecules in a limited area.<sup>20</sup> The increased functionality can also be used to amplify the stimuli responsive nature of the polymer coating at a surface. These brushes were used as reversible, photoswitchable optical sensors that show selectivity for different metal ions. Different metal complexation was also used to create surfaces with drastic changes in wettability. Covalently bound polymer chains allow for an increase in sensor stability, impart a rapid response to analyte, and provide reversible, switchable sensor surfaces with longer lifetimes.

The SPMA monomer (Scheme 2) was copolymerized with MMA from glass substrates using a surface bound bromoisobutyryl initiator. When homopolymerization was attempted, no brushes with a thickness larger than 4 nm were possible under different catalyst/ligand/solvent combinations, presumably due to the steric bulk of the SPMA monomer. Under conditions similar to those reported by Piech and Bell,<sup>21,22</sup> we attempted to copolymerize SPMA with different methacrylates

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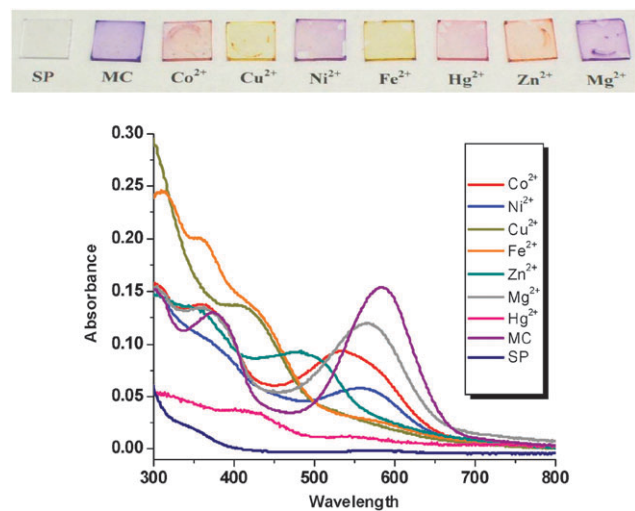


**Scheme 2** Surface initiated copolymerization of a spiropyran methacrylate derivative (SPMA) and methyl methacrylate (MMA).

in varying ratios, and thicknesses up to 80 nm were possible under controlled conditions with high graft density (see ESI for details<sup>†</sup>). The final film thickness decreased with increasing mol% SPMA, and for the rest of this work, a copolymer with 10 mol% SPMA–90 mol% MMA was used.

For sensing experiments, the films were irradiated with 365 nm light ( $30 \text{ mW cm}^{-2}$ ) in the solid state for two minutes, submerged into metal salt solution (25 mM in ethanol) for two minutes, and blown dry with air for 15 s. Chloride salts of each metal were used. To decomplex the metal, the films were irradiated in toluene for 10 min with visible light (30 W quartz halogen fiber optic illuminator, 2 cm from the source).

Fig. 1 shows the UV-Vis absorbance spectrum of the surface initiated SPMA copolymers in response to different metal ions. The thickness of the films used for metal ion sensing was set at 25 nm (16 h polymerization time). As can be seen from Fig. 1, the as-synthesized SPMA copolymer brush is transparent to the visible, with an absorption tail below 400 nm. When irradiated with UV light, the SP chromophores are converted to the MC form, which is characterized by an intense absorption band centered at 584 nm and a second band at approximately 374 nm. Upon complexation with different metal ions, there is a decrease in absorbance along with significant blue shift in absorbance maxima, which is metal ion dependent. The ion selectivity can easily be discriminated with the naked eye for most metal ions, as shown in the polymer coated glass substrates at the top of Fig. 1.<sup>‡</sup> The



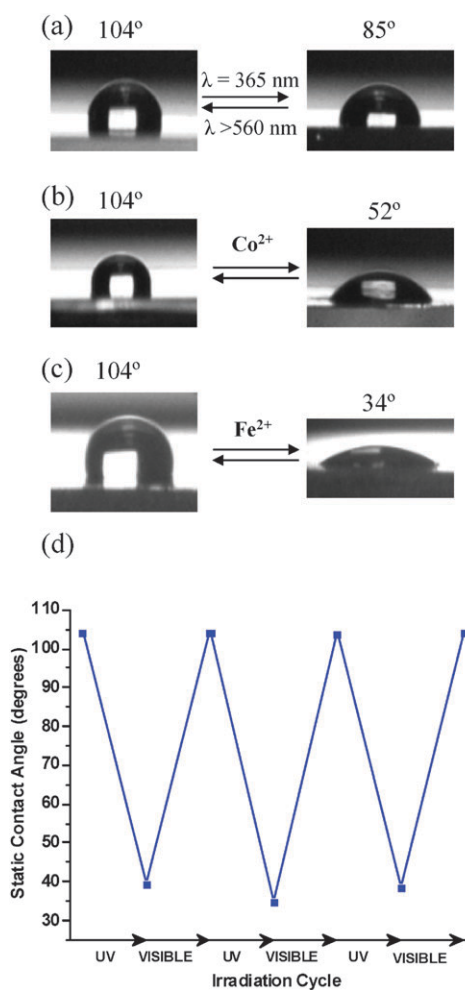
**Fig. 1** UV-Vis of polymer brush in the presence of different metal ions.

SPMA–metal complex is stable, even under irradiation with visible light for several hours in the solid state.

The metal decomplexation reaction is reversible when the films are irradiated with visible light in nonpolar solvents. Using toluene, a better solvent for the nonpolar SP form, the reverse reaction occurs in minutes. The colorimetric response of the films is identical after repeating several cycles of complexation/decomplexation.

The MC absorbance band of the polymer is much more sensitive than free monomer in the presence of the different ions, due to the confined microenvironment of the pendant chromophores present in the film. The free monomer in solution does bind to each metal in 2 : 1 merocyanine–cation complex (see ESI<sup>†</sup>), but the shift in absorbance maximum is not sensitive for metal ions other than  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$ . We are currently investigating the influence of different microenvironments by fabricating copolymer brushes of methacrylates with differing steric bulk.

The metal ion bonding also amplifies the changes in wettability that occur in the system by stabilizing the phenolate tautomer of MC, presumably through a dimeric complex.<sup>13</sup>



**Fig. 2** Reversible contact angle changes. (a) Film irradiated in DMF, (b)  $1 \times 10^{-3} \text{ M Co}^{2+}$ , (c)  $1 \times 10^{-3} \text{ M Fe}^{2+}$ , (d) plot of reversible contact angle changes for SP film irradiated in  $\text{Fe}^{2+}$ .

Fig. 2 shows the reversible switching of wettability changes of a droplet of water on the SP polymer brush (60 nm in thickness). The films were submerged in an ethanolic solution (10 mM) of metal salt and irradiated for two minutes. Static contact angle changes as large as 70° are observed when the films are irradiated in the presence of metal ions. The change in contact angle was completely reversible when the substrates were irradiated with visible light in nonpolar solvents. The reversibility is shown in Fig. 2(d), where several cycles of contact angle changes for UV and visible irradiation are shown with Fe<sup>2+</sup>. These are the largest reversible contact angles reported for flat surfaces based on organic chromophores. The amount of static contact angle change in the presence of different ions correlates with the blue shift in absorbance spectra for the SPMA polymer brushes. Fig. 2(a–c) show the change in wettability when the substrates are irradiated in the presence of DMF, Co<sup>2+</sup>, and Fe<sup>2+</sup> solutions.

In conclusion, we have developed a reversible ion sensor based on spiropyran containing polymer brushes. The confined microenvironment provides a colorimetric response that is sensitive and selective for different metal ion complexation. The sensor response to different chemical microenvironments, detection limits and fluorescence sensitivity are currently under investigation in our laboratory.

The metal ion complexation was also used to create surfaces with drastic changes in wettability. Reversible contact angle changes up to 70° were observed for films grown from flat substrates, which can be amplified further by growing polymers from rough surfaces. Polymer brushes grown from surface bound initiators allow for an increase in sensor stability, high chromophore density, impart a rapid response to analyte, and provide reversible, switchable sensor surfaces with longer lifetimes.

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## Notes and references

‡ For better color contrast, the substrates shown in Fig. 1 were spin coated films (80 nm) of the same polymer synthesized in solution. There was no difference in UV spectrum between polymer–metal complexes of the spin coated film and polymer brush, except the films would delaminate upon rinsing with toluene.

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