Electronic Supplementary Information

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

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Experimental Section

Materials. Silicon wafers from Silicon Quest were cut into 2 x 1cm pieces and used as substrate for polymerization. CuBr, ethyl-2-bromoisobutyrate (Et2BrIB), $CuCl_2$, $NiCl_2$, $FeCl_2$, $MgCl_2$, $ZnCl_2$, $CoCl_2$, $HgCl_2$, and ethanol were purchased from either TCI or Alfa Aesar and used as received. Methyl methacrylate (MMA) and tert-butyl acrylate (tBA) were passed through a column of neutral alumina to remove inhibitor before polymerization. Tetrahydrofuran (THF) was distilled over sodium/benzophenone, N, N, N', N'', N''-pentamethyldiethylenetriamine (PMDETA), MMA, and tBA were degassed prior to use.

Initiator Synthesis and Monolayer Self-Assembly. 10-undecen-1-yl 2-bromo-2-methylpropionate and (11-(2-bromo-2-methyl)propionyloxy)undecyltrichlorosilane were synthesized according to published procedure[1]. Silicon wafers were sonicated in acetone, ethanol, and 18.2MΩ deionized water each for 5 minutes. The wafers were then dried in a nitrogen stream and oxidized in a UV/ozone chamber for 5 minutes. The wafers were then transferred to a glove box and placed into a 3mM solution of the trichlorosilane initiator in degassed toluene. The samples were allowed to react for 16 hours, after which they were rinsed with toluene and dried under a stream of nitrogen. The monolayer thickness was 2.5 nm. When not in use, the substrates were stored in toluene.

SPMA Monomer Synthesis. $1^{/}$-(2-Hydroxyethyl)-$3^{/}$-dimethyl-6-nitrospiro(2H-1-benzopyran-2,$2^{/}$-indole (SP alcohol)[2] was subsequently coupled to the methacrylic acid chloride following standard procedures.[3]

General Polymerization Procedure. The monomer copolymerized with SPMA was either methyl methacrylate or tert-butyl acrylate and the monomer ratio between spiropyran and the other monomer was varied. A typical procedure for the synthesis of p(SPMA-co-MMA) where the brush contained 10mol% SP was as follows: SP (0.381g, 0.906mmol), MMA (0.816g, 8.15mmol), and CuBr (0.005g, 0.0349mmol) was added to a schlenk flask under Ar, containing a Si wafer and glass slide with initiator. 5mL of anhydrous THF was then added and the reaction mixture was degassed under Ar for 1h. To this was added PMDETA (0.060g, 0.346mmol) which was also degassed under Ar for 1 hour. The rubber septum on the schlenk flask was then replaced with a glass stopper while the reaction was still under Ar to avoid any possible oxygen poisoning. The reaction was then place in a 65ºC oil bath for 16-18h. Upon removal from the solution, the samples were immediately washed thoroughly with THF and DMF. The samples were stored in the dark when not in use. The Si wafer was used for thickness characterization by ellipsometry, while the glass substrate was used for UV-vis.

Measurements. Null ellipsometry was performed on a Multiskop (Optrel GbR) with a 638.2nm He-Ne laser. Both δ and ψ value thickness data were measured and calculated by integrated specialized software. At least three measurements were taken for each wafer, and the average thickness recorded. This same instrument was used to measure water contact angles by using a white light source and replacing the photodiode with a CCD camera. A contour tracing algorithm that distinguishes the drop from its mirror image was used to evaluate the contour of the drop and fit it to the Young-Laplace equation. At least three drops were measured and the average of these measurements reported. UV-vis spectra of the polymer films were obtained using a Cary 50 spectrophotometer.

Light Source. An OmniCure, series 1000 with 365nm wavelength light was used as the UV light source. The substrates were held 2 cm from the source and irradiated at a power of 30 mW/cm^2. The visible light source was a Fiber-Lite, Model with a 30W quartz halogen fiber optic illuminator.

Merocyanine-metal complexation experiments. An initial UV-vis spectrum was recorded of the polymer brush before UV irradiation. The sample was then irradiated with 365nm light for 2 minutes and a UV-vis spectrum of the MC form was recorded. The sample was then immersed in a 25mM solution of metal salt in ethanol for 3 minutes, blown dried with air for 15 seconds, and a UV-vis spectrum recorded. To reverse the complexation, the sample was washed with ethanol and then irradiated with white light for 10 minutes while immersed in toluene.

Water contact angle experiments. Contact angle measurements were taken on the sample before irradiating with UV light. The sample was then irradiated with 365nm light while immersed in a 10mM solution of metal salt in ethanol for 2 minutes. The sample was blown dry with air and contact angle measurements were taken. To show reversibility, the sample was irradiated for 10 minutes with visible light while immersed in toluene. For samples irradiated in DMF, the same procedure was followed with the exception that the sample was irradiated with UV light while immersed in DMF instead of the metal salt solution.

Experiment	Brush Thickness (nm)
p($SPMA_{0.10}$-*co*-$MMA_{0.90}$)	40 ± 1.9
p($SPMA_{0.20}$-*co*-$MMA_{0.80}$)	28 ± 1.1
p($SPMA_{0.25}$-*co*-$MMA_{0.75}$)	22 ± 1.7
p($SPMA_{0.08}$-*co*-$tBA_{0.92}$)	17 ± 0.5
p($SPMA_{0.15}$-*co*-$tBA_{0.85}$)	12 ± 1.0
p($SPMA_{0.20}$-*co*-$tBA_{0.80}$)	9 ± 0.6

Table S1. Ellipsometric brush thickness for different spiropyran concentraions in copolymerizations with methyl methacrylate (MMA) or tert-butylacrylate (tBA).

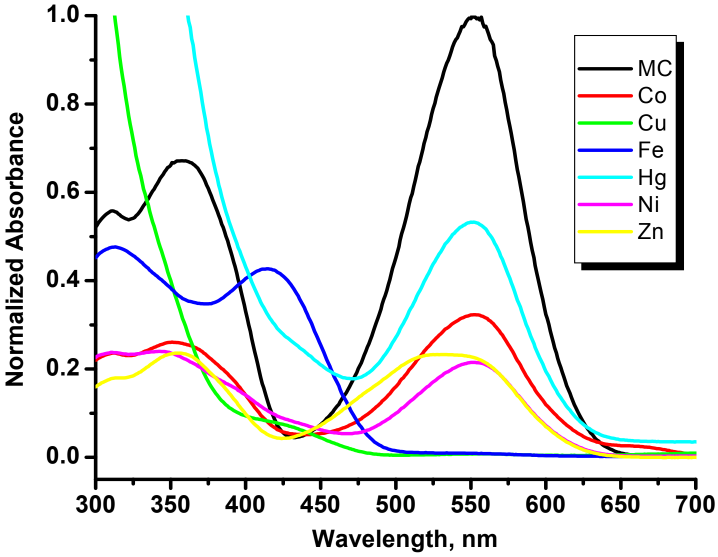

Fig S1 Solution state UV-vis of 2:1 molar equivalent of monomer (merocyanine form) to metal salt solution in the presence of different metal ions. The molar concentration of SPMA in each sample was equivalent, and the MC absorbance has been normalized to 1 for clarity.

References

1. K. Matyjaszewski, P. J. Miller, N. Shukla, B. Immaraporn, A. Gelman, B. B. Luokala, T. M. Siclovan, G. Kickelbick, T. Vallant, H. Hoffmann and T. Pakula, *Macromolecules*, 1999, **32**, 8716-8724.
2. Y. Hirshberg, *J. Am. Chem. Soc.*, 1956, **78**, 2304-2312.
3. J. C. Little, *J. Am. Chem. Soc.*, 1965, **87**, 4020-4022.