Supporting Information

Alkanethiol Molecular Barriers for Controlling Small Molecule Release Kinetics from a Microgel-Based Reservoir Device

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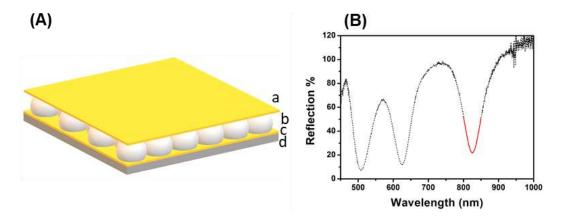


Figure S1. (A) Schematic of a pNIPAm-*co*-AAc microgel based etalon; (a) 20 nm of Au layer with 2 nm of Cr adhesion layer, (b) pNIPAm-*co*-AAc microgel monolayer, (c) 15 nm of Au layer with 2 nm of Cr adhesion layer, and (d) glass substrate. (B) Optical reflection spectrum (black dashed curve) of a representative, unmodified etalon. A Gaussian curve was fit (red solid curve) to a portion of the spectrum to identify the wavelength of the trough.

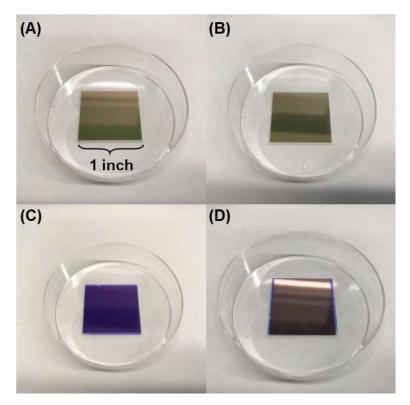


Figure S2. (A) 15 nm of Au with 2 nm of Cr adhesion layer deposited on a microscope glass cover slice; (B) metal-coated substrate with a pNIPAm-*co*-AAc microgel layer; (C) CV-loaded pNIPAm-*co*-AAc microgel monolayer on substrate; (D) fabricated CV-loaded etalon device with 20 nm of Au and 2 nm of Cr adhesion layer deposited on top of microgel layer.

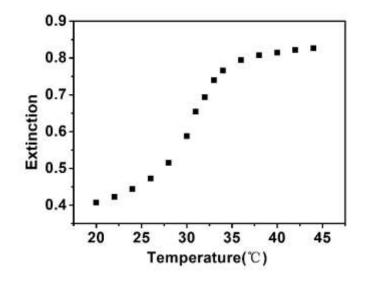


Figure S3. A graph of UV-vis extinction (measure from absorbance) at wavelength 240 nm of the pNIPAm-*co*-AAc microgels as a function of solution temperature. According to these data, the LCST of the microgels is \sim 31 °C.

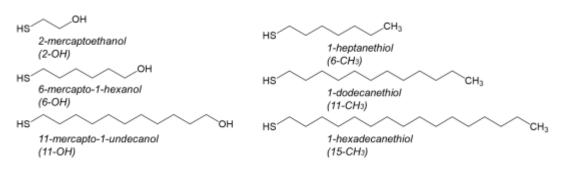


Figure S4. Structures, full names, and abbreviations of alkanethiol molecules used in surface modification.

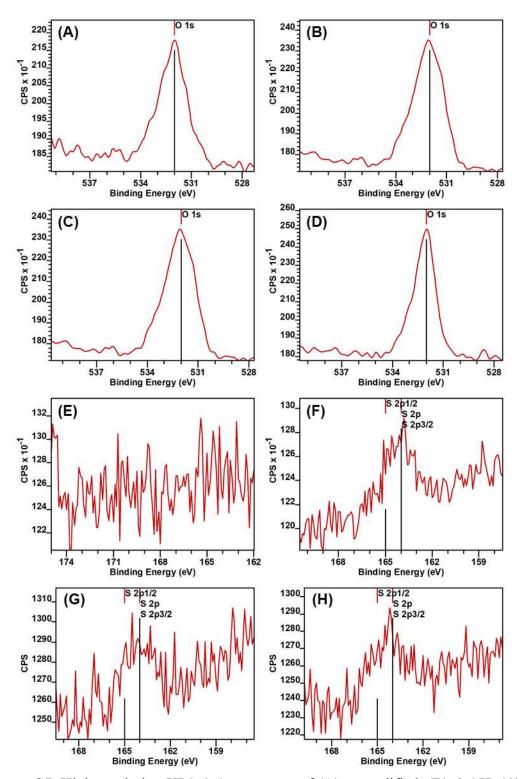


Figure S5. High resolution XPS O 1s spectrum of (A) unmodified, (B) 6-OH, (C) 6-CH₃, (D) 6-O/6-C etalon sample, and high resolution XPS S 2p spectrum of (E) unmodified, (F) 6-OH, (G) 6-CH₃, (H) 6-O/6-C etalon sample.

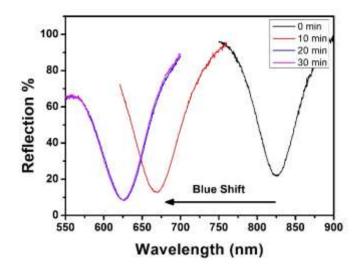


Figure S6. Collection of partial reflectance spectrum of an unmodified etalon sample at different times after the solution pH changed from 6.5 to 3.

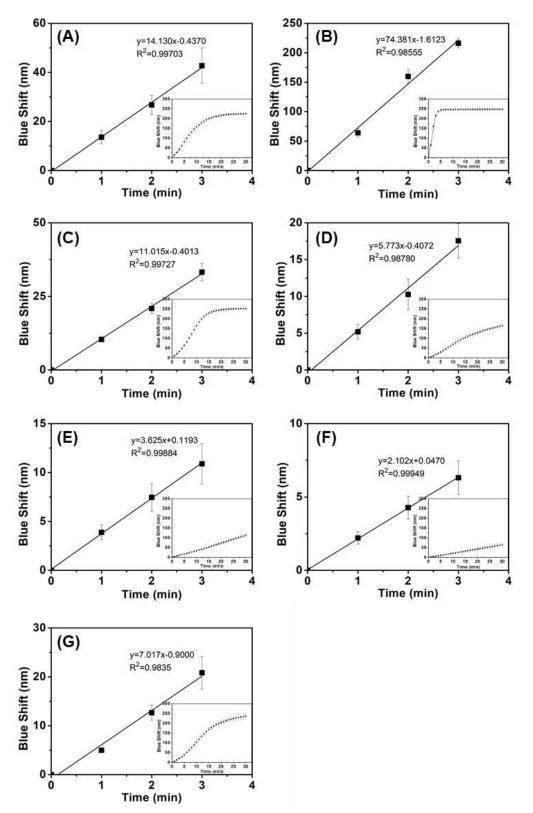


Figure S7. Defining initial slope of blue shift kinetics curves of (A) unmodified, (B) 2-OH, (C) 6-OH, (D) 6-CH₃, (E) 11-CH₃, (F) 15-CH₃ and (G) 6-O/6-C etalon samples with linear fitting on initial four data points. The subfigure is the full blue shift kinetics curve of each modified sample.

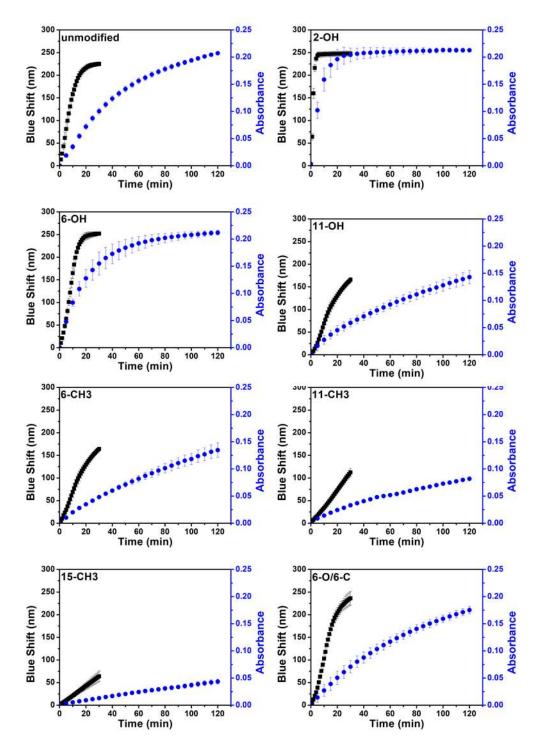


Figure S8. Comparison between CV release kinetics and optical reflectance spectrum trough shift kinetics of each kind of modified etalon samples.