Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Electronic Supporting Information

Sequential and Controlled Release of Small Molecules from Poly (N-isopropylacrylamide) Microgel-Based Reservoir Devices

*Yongfeng Gao, Ka Yee Wong, Andrews Ahiabu, Michael J. Serpe**

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

*Corresponding Author: Michael J. Serpe (michael.serpe@ualberta.ca)

1. Absorbance spectrum for methylene blue (MB) in solution

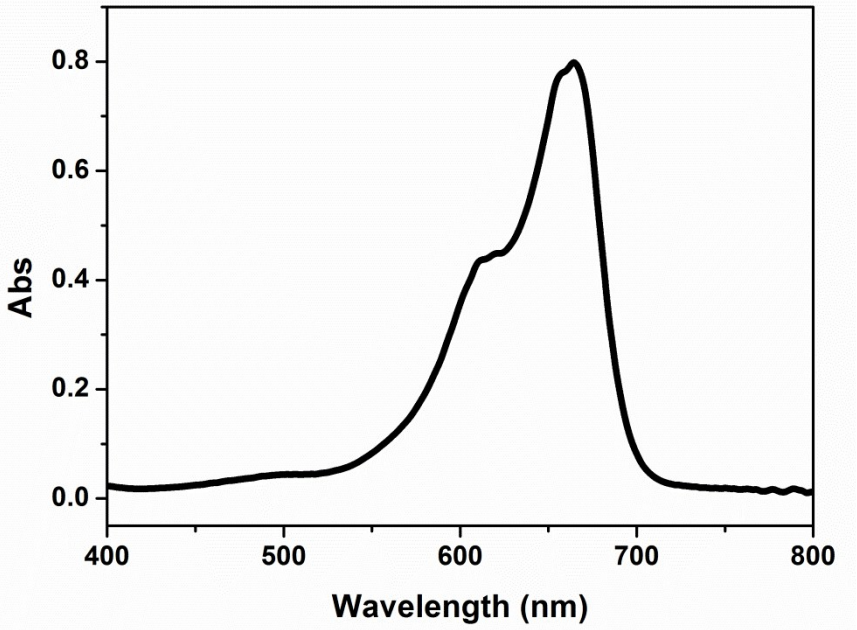

Figure S1. UV-Vis absorption spectrum for MB.

2. Photographs of MB-loaded slides

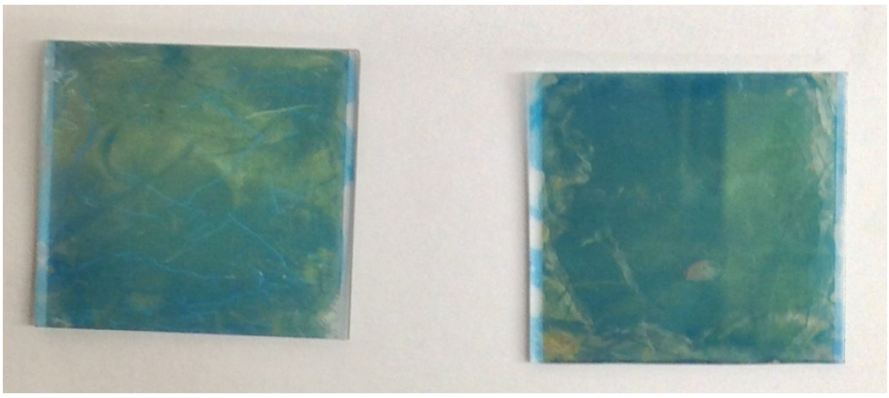

Figure S2. Photographs of reservoir devices after MB loading.

3. MB release from microgels in solution

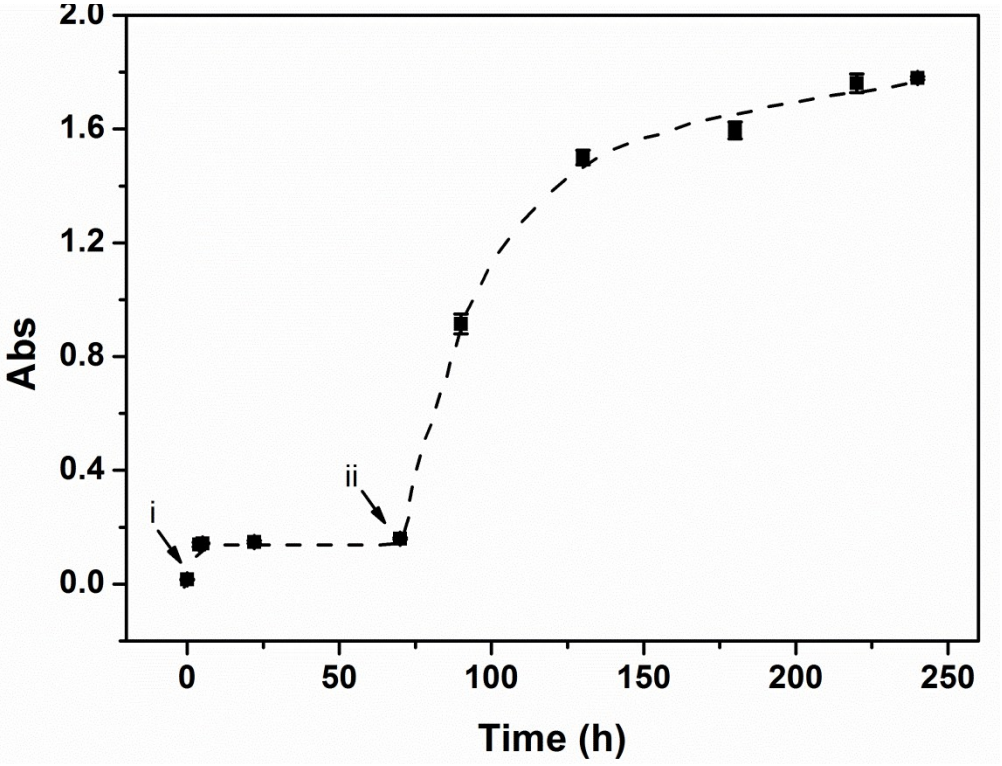

Figure S3. MB release from a solution composed of 1:1 (v/v) APBA-MG:AAc-MG. The solution pH was changed from 10.0 to (arrow i) 7.0 and (arrow ii) 3.0.

4. pH responsivity of microgels

Etalons composed of APBA-MG were assembled, and showed their characteristic multipeak reflectance spectra.[1, 2] The position of the reflectance peaks depends on a number of variables, according to Equation 1:

$$m\lambda = 2ndcos\theta \qquad (1)$$

where λ is the wavelength maximum of the peak(s), m the peak order, n the refractive index of the dielectric, d the spacing between the devices Au layers, and θ the angle of incidence. Therefore, since the microgel solvation state can be modulated with pH variations via ionization, and the microgels define the distance between the etalon's Au layers, the position of the reflectance peaks (and the etalon color) should depend on solution pH. That is, when the solution pH is above the pKa of APBA, the boronic acid groups become negatively charged, which results in microgel swelling and a concomitant increase in the distance between two Au layers. However, when the solution pH is again lowered to below the pKa value of APBA, the microgels decrease in diameter, because of the APBA neutralization; this results in a decrease in the distance between the Au layers of the etalon. Etalons were fabricated,[3] and their reflectance spectra recorded using a Red Tide USB650 spectrometer, a LS-1 tungsten light source, and a reflectance probe from Ocean Optics (Dunedin, FL). The spectra were record using Ocean Optics Spectra Suite Spectroscopy Software at room temperature over a wavelength range of 400-1000 nm. Measurements were conducted by placing the device in a Petri dish with water at room temperature. The pH response of the devices can be seen in Figure S4.

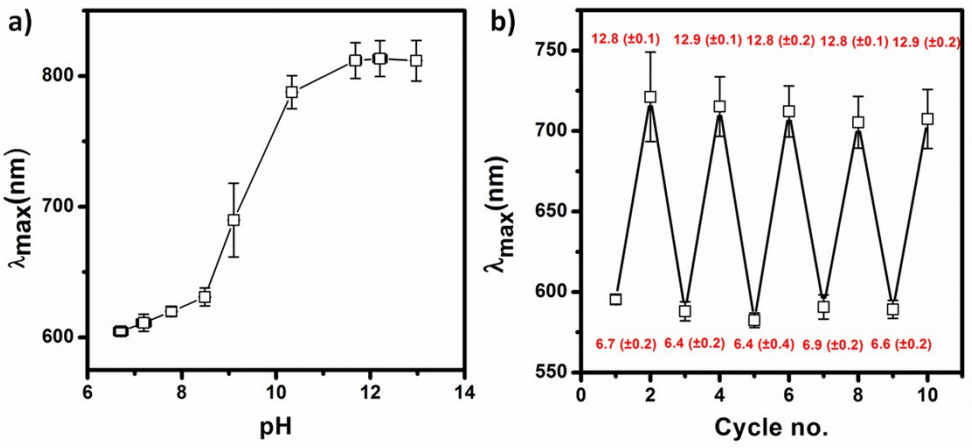

Figure S4. pH responsivity of etalons composed of APBA-MG. a) Reflectance peak position as a function of pH, and b) the reversibility of the pH response. As can be seen, at high pH, the reflectance peaks shift to higher wavelengths, which is indicative of microgel swelling due to pH-induced ionization. Data were obtained from three individual etalons.

References:

1. C. D. Sorrell and M. J. Serpe, *Advanced Materials*, 2011, **23**, 4088-4092.
2. C. D. Sorrell, M. C. Carter and M. J. Serpe, *Advanced Functional Materials*, 2011, **21**, 425-433.
3. C. D. Sorrell, M. C. Carter and M. J. Serpe, *ACS Applied Materials & Interfaces*, 2011, **3**, 1140-1147.