Light Switchable Optical Materials from Azobenzene Crosslinked Poly (N-Isopropylacrylamide)-Based Microgels

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Electronic Supplementary Information
**4,4’-di(methacrylamido)-azobenzene synthesis**

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\text{Scheme S1 4,4’-di(methacrylamido)-azobenzene synthesis.}
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To a solution of 4,4’-diamino-diazobenzene (5 grams) in CH\_2Cl\_2 (200 mL) is added 14.1 mL of diisopropylethylamine and 25 mg of 4-dimethylaminopyridine. The solution is cooled to 0°C and methacryloyl chloride (5.75 mL) is added over 30 minutes. The reaction is warmed to RT and stirred for 24 h. The resulting precipitate is filtered off, washed with water (3 × 50 mL) and then with methanol (3 × 75 mL). Purification by flash chromatography using silica with hexane as the eluent. The solid is dried overnight in a vacuum oven at RT. The yield was 70%.

**Microgel synthesis.**

A 3-neck round bottom flask was fitted with a reflux condenser, nitrogen inlet, and temperature probe, and charged with a solution of N-isopropylacrylamide (11.9 mmol), 4,4’-di(acrylamido)-azobenzene, and BIS (amounts of both crosslinkers varied depending on desired mole ratio) in 99 mL deionized water, previously filtered through a 0.2 mm filter. The solution was purged with N\_2 and allowed to heat to 70 °C over ~1 hour. The reaction was then initiated with a solution of ammonium persulfate (0.2 mmol) in 1 mL of deionized water. The reaction proceeded at 70 °C for 4 hours under a blanket of nitrogen. The resulting suspension was allowed to cool overnight, and then it was filtered through a Whatman #1 paper filter to remove any large aggregates. The microgel solution was then distributed into centrifuge tubes and purified via centrifugation at ~8300 rcf to form a pellet, followed by removal of the supernatant.
and resuspension with deionized water, 6 times. The cleaned microgels were recombined and stored in a brown glass jar.

**Preparation of etalon devices.**

To fabricate the Au coated coverslips (etalon underlayer), 2 nm Cr and 15 nm of Au was added to a 25 x 25 mm ethanol rinsed and N₂ gas dried glass coverslip (Fisher’s Finest, Ottawa, ON) at a rate of 1 Å s⁻¹, and 0.1 Å s⁻¹, respectively (Torr International Inc., thermal evaporation system, Model THEUPG, New Windsor, NY). The Cr/Au substrates were annealed at 250 °C for 3 h (Thermolyne muffle furnace, Ottawa, ON) and cooled to room temperature prior to microgel film deposition.

Approximately 5-10 mL of microgel solution was centrifuged at ~8300 rcf to form a pellet. The supernatant was removed and discarded, and the pellet was vortexed to loosen and homogenize the particles in the remaining solvent. A 40 μL aliquot of concentrated microgels were spread onto an annealed 25 mm x 25 mm Au-coated glass coverslip. The film was allowed to dry on a 30 °C hotplate for 30 minutes before the excess microgels were rinsed with deionized water. The samples were soaked overnight at 30 °C in a deionized water bath. The samples were then rinsed with deionized water, dried with N₂, and another Au overlayer (2 nm Cr for adhesion, followed by 15 nm Au) was added. The completed device was soaked overnight in deionized water at 30 °C before spectral analysis.
Figure S1. $^1$H NMR spectra of (black) 4,4$'$-diamo-diazobenzene and (red) DAAB.
Figure S2. $^{13}$C NMR spectra of (black) 4,4'-diamino-diazobenzene and (red) DAAB.
Figure S3. Microgel sizes at 25 °C, 30 °C and 35 °C tested by dynamic light scattering (DLS).

(a) MG-1%

(b) MG-0.5%

(c) MG-1% at 30 °C.
Figure S4. DLS measured microgel diameters as a function of temperature.
Figure S5. SEM image of microgel-based etalon (microgel-1%).
Figure S6. Reflectance spectra for MG etalon after UV exposure.
Figure S7. Reflectance spectra for MG-1% etalon at the indicated conditions.