

Antiplasticization and Water Uptake of NAFION® Thin Films

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SUPPORTING INFORMATION

The fluorescence of dry films (I_0) was measured for 70 nm and 616 nm films over a range of dye:polymer ratios based on the mass of polymer and dye in the casting solution. It was observed that the fluorescence intensity reached its maxima in the 616 nm film when the concentration of CCVJ was 0.018 wt % in solution (approximately dye:polymer mass ratio of 0.002). Beyond this concentration of CCVJ, the quenching action of highly populated CCVJ in film became dominant as evidenced by the decrease in I_0 (Figure S1).

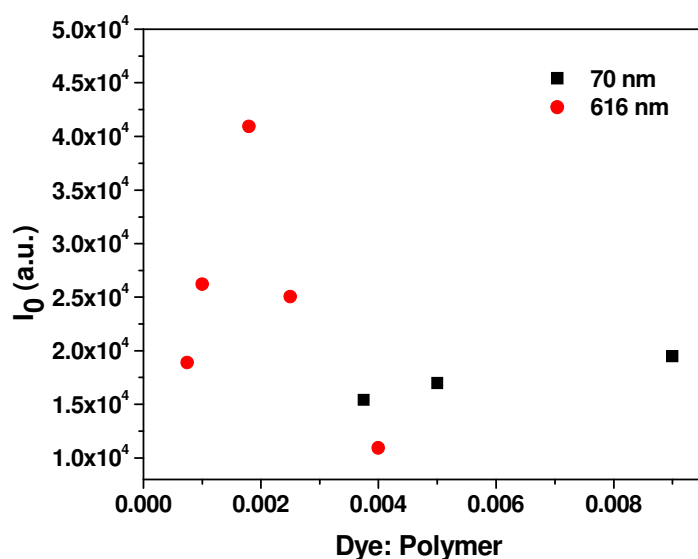


Figure S1. Effect of dye: polymer mass ratio on the fluorescence of dry film (I_0) with different thickness ((■) 70 nm; (●) 616 nm).

On the other hand, the fluorescence was too low to measure when CCVJ: NAFION® was below 0.0038 in the 70 nm film (Figure S1). However, the fluorescence did not change significantly in the 70 nm thick films in the CCVJ concentration range of dye:polymer \approx 0.0038-0.009. Keeping the constraints

in mind from these observations, we choose a single dye concentration in the casting solution for which films of all thicknesses showed their maximum fluorescence among all the dye:polymer ratios investigated. Figure S1 shows that the fluorescence of 70 nm film was slightly increased at ratio of 0.009. Therefore, all the films were spun from solution containing 0.018 % CCVJ (equivalent to dye:polymer ratio of 0.002 for 616 nm film and 0.009 for 70 nm film) to avoid any ambiguity arising from signal-to-noise ratio in the fluorescence emission spectra.

The shape of the emission spectrum of CCVJ did not change significantly as a function of RH (Figure S2), rather only the fluorescence intensity changed with the amount of water in the film. This behavior indicates that the dye CCVJ is not sensitive to polarity of the microenvironment and the rotor probe could be used effectively to measure the dynamics of the thin films.

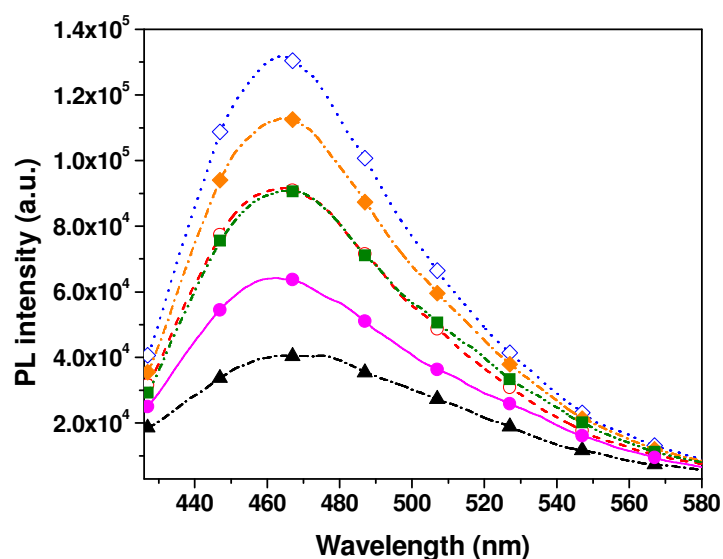


Figure S2. Fluorescence spectra as a function of RH for film with thickness 616 nm ((▲) 0%; (○) 25%; (◇) 30%; (◇) 50%; (■) 75% and (●) 95% RH). Spectra recorded at 2 nm instrument resolution. Symbols spaced periodically to denote the different curves.

Antiplasticization at 25 % and 30 % RH was observed for a range of dye concentrations (Figure S3). In both cases, the antiplasticization (I_{RH}/I_0) of 616 nm film at dye-polymer ratio of 0.002 was significantly higher than the one obtained for the closest possible dye-polymer ratio (~ 0.0038) for thinner film (~ 70 nm). Moreover, the I_{RH}/I_0 showed weak dependence on dye-polymer ratio. Thus it was revealed that choosing a single wt % of CCVJ in spinning solution did not affect our comparisons based on antiplasticization.

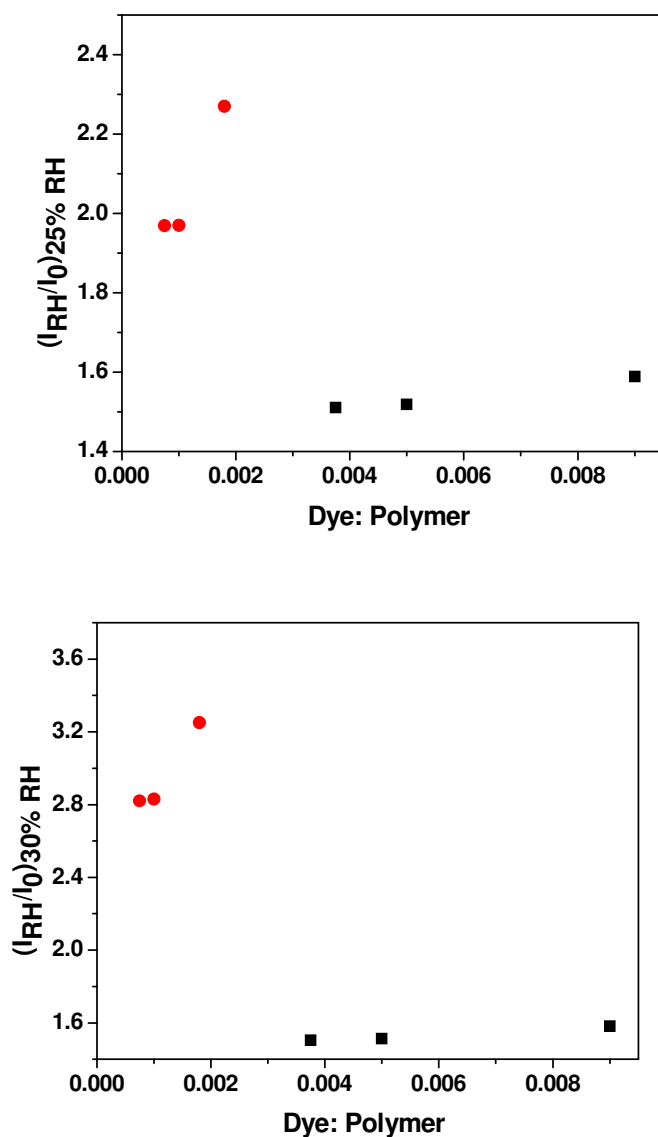


Figure S3. Antiplasticization (I_{RH}/I_0) of films with different thickness ((■) 70 nm; (●) 616 nm) composed of different dye: NAFION[®] ratio at 25% (top) and 30% RH (bottom).