Room-Temperature Solid-State Solvents for Molecular Photonics

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Introduction: The optical properties of amyloid staining dyes, such as Thioflavin T (ThT) and 3,3'-diethylthiacyanine iodide (THIA), make them immensely attractive for fluorescence-based applications. THIA and ThT are rotamer dyes, dissipating energy via multiple non-radiative pathways. It results in parallel excited-state transient conformational changes, most of which do not undergo radiative deactivation, i.e. they do not fluoresce.[1] These dyes have a strong affinity for β-sheet proteins, such as amyloids and bacterial surface proteins.[3] Binding to proteins suppresses the degrees of torsional freedom of such rotameric dyes and prevents their non-radiative deactivation, increasing their fluorescence quantum yiled. That is, binding to bacteria causes emission enhancement of ThT and THIA, which is immensely promising for imaging, sensing and bioanalysis.[2] The discovery of such photoprobes that undergo emission enhancement, however, is serendipitous. Therefore, we develop glassy materials as novel room-temperature solid solvents for characterization of optical properties of photoprobes that are sensitive to binding and viscosity of the microenvironment.

Materials and Methods: Fluorescence spectroscopy and imaging were conducted as previously descirbed.[1-3] We compare the optical properties of ThT and THIA for liquid solvents, with those for solid solvents, such as polydimethylsiloxane (PDMS) and sucrose octaacetate (SOA). Bacterial staining tests, we used *E.coli*, *B. subtilis*, *B. megaterium*, and *E. aerogenes*.

Results and Discussion: Traditionally, flash-frozen organic solvents at liquid-nitrogen temperatures are used as solid-state glass media for spectroscopy tests. Molten SOA forms solid glass when cooled to room temperature and it has been our choice for testing solid-state optical medium. Loading the samples at elevated temperature, however, presents challenges. Recently, we discovered a means for loading molecular samples in a solid elastomer, PDMS, at room temperature. Interestingly, PDMS not only reproduces the emission enhancement that SOA induces, but also discourages ground state aggregates. Our studies reveal that suppression of the non-radiative decay processes are the reason for the PDMS-induced emission enhancement. Comparison between the results from the PDMS studies with our bacterial staining results validates our discovery that this elastomer can provide testing ground for biologically relevant microenvironment.

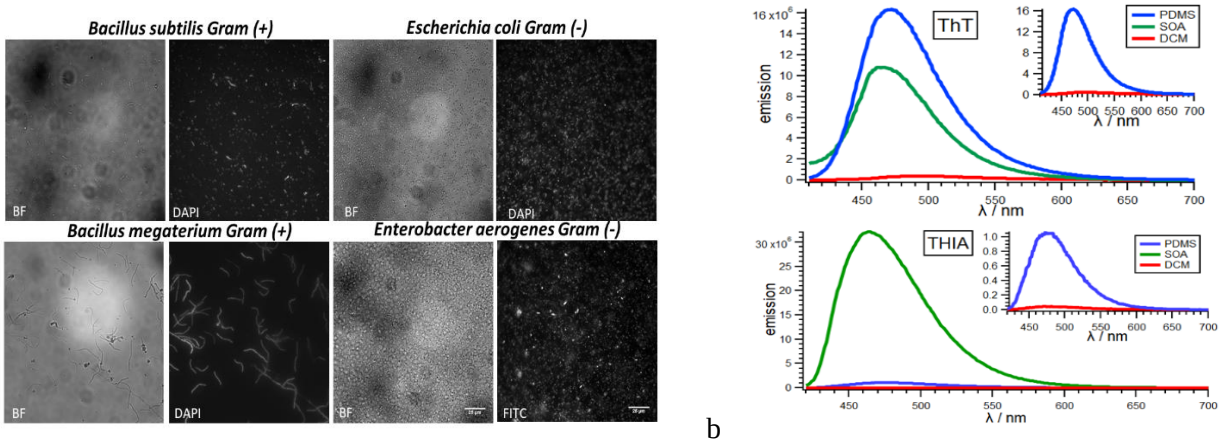

Figure 1. Optical features of ThT and THIA. a) Brightfield (BF) and fluorescence images of Gram (+) bacteria strained with ThT and Gram (-) species stained with THIA. b) Emission spectra of ThT and THIA for liquid and solid media (λ_{ex} (ThT) = 400 nm, λ_{ex} (THIA) = 410 nm).

Conclusions: By far, PDMS proves to be the best optically clear solid-state solvent for biological photoprobes. This discovery is a promising development for molecular spectroscopy and photonics.

References: 1) Upadhyayula, *et al.*, *Chem. Sci.* **2015**, *6*, 2237 2) Thomas et al *Langmuir* **2010**, *26* (12), 9756-9765 3) Xia, B et al, *J. Clinical Microbiol*, **2011**, *49* (8), 2966-2975