Design and Applications of 4-yl-(methyl)coumarins and Their Derivatives

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Surface chemistry is a well-established area of research and is required in many commercial applications. However, most surface modifications are static in nature meaning a single treatment will produce a single, fixed surface state (eg: hydrophobic, hydrophilic, etc.). Dynamic systems, those that respond to stimuli, have become an active area of surface chemistry because they provide a means to vary surface properties.[1] Responsive dynamic systems are classified as either reversible or irreversible. When light is used as a stimulus, the chemical moieties that produce the reversible and irreversible responses are known as photoswitches and photofuses, respectively.

The *o*-nitrobenzyl photofuse, which was initially used as a biological caging group,[2] has been utilized in various surface applications with great success. However, this photofuse can be problematic due to the long exposure times required for full conversion and the reactive byproducts that form upon UV exposure. Another photofuse, known as the 4-yl-(methyl)coumarin, is of particular interest because of its rapid photochemical response,[3] lack of reactive products upon UV exposure,[4] and many different photofuses are readily prepared from inexpensive, commercially available starting materials.

A divergent synthetic scheme was developed that allows access to a variety of coumarin photofuses, via similar synthetic pathways, that enable multiple surface modifications. After establishing this synthetic pathway, various coumarin photofuses were prepared and applied to surfaces to demonstrate the utility of this convenient and efficient photofuse. Prepared photofuses provide transitions including hydrophobic-to-negative, hydrophobic-to-positive, negative-to-positive, positive-to-negative, and hydrophobic-to-neutral transitions.

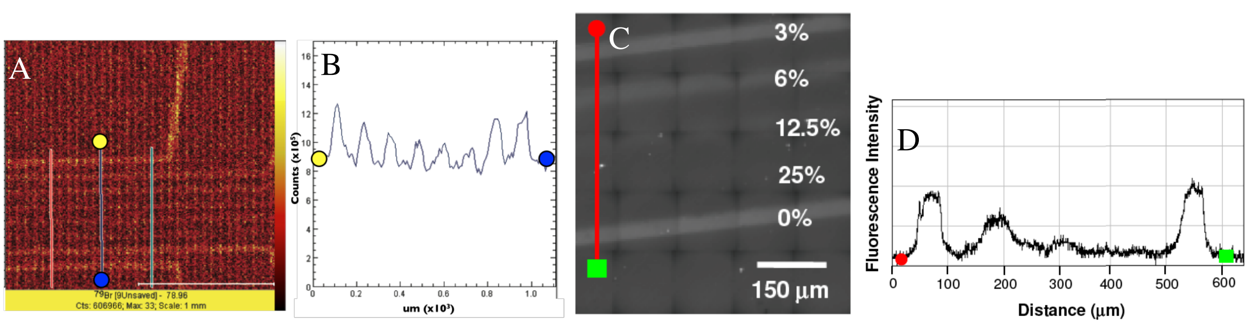

Figure 1: A) ^{79}Br SIMS ion map and B) accompanying linescan of greyscale features patterned within a coumarin monolayer. C) Fluorescence microscopy image of greyscale features modified with dansyl chloride and D) accompanying linescan.

Multiple photofuses were then utilized to probe chemical greyscaling by combining the photoresponsive coumarin monolayer with novel greyscale photolithography masks.[5] The versatility of the coumarin photofuse was demonstrated through simple modifications of the coumarin core to provide access to characterization techniques such as secondary ion mass spectrometry (SIMS) and fluorescence microscopy (Figure 1). The patterned gradients were then used to produce pressure sensitive microfluidic gates based on the variation in surface hydrophobicity. Correlation of mask transparency to resulting surface hydrophobicity provided a predictive curve of gating pressures that were in excellent agreement with theoretically predicted values.

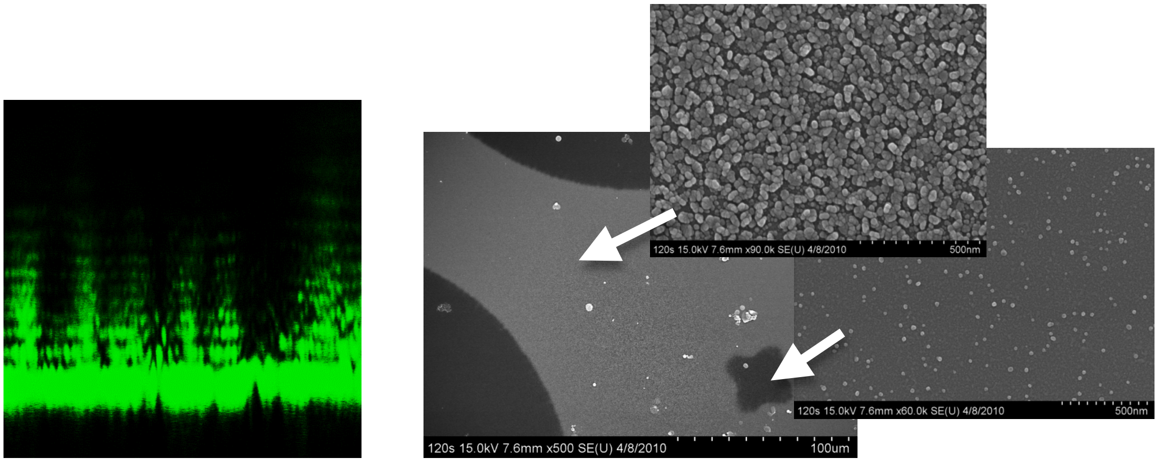

Figure 2: A) Confocal fluorescence image of dansyl chloride labeled inverse opal. Features appear due to defects in the inverse opal or localization of light within the inverse opal structure. B) SEM images of a silicon substrate photochemically templated with a photoresponsive coumarin and then subjected to Ag electroless deposition.

The coumarin photofuse was then utilized to pattern substrates based on the changes in surface composition. Monolayer templating has been reported previously, but the photoresponsive nature of the coumarin monolayers reported herein provides unique patterning capabilities within three-dimensional structures such as artificial opals by taking advantage of the photonic properties of these materials. Functionalization, photochemical conversion, and labeling within inverse opals was performed and characterized using confocal fluorescence microscopy (Figure 2a). Alternative labeling and patterning schemes were also successfully performed on planar substrates including atomic layer deposition and selective metallization (Figure 2b).

References

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