

Beads-Based System for Optical Sensing Using Spiropyran Photoswitches

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In science, control of interactions at the molecular scale is the ultimate goal, as this in turn determines all macroscale behaviour. Using molecular-switches based on spiropyran-like molecules, it is possible to produce surfaces whose physico-chemical properties can be controlled under external photonic stimulation [1]. It has been demonstrated that low-power light sources such as UV and green LEDs can switch spiropyran-modified surfaces between an inactive spiro (SP) form and an active merocyanine (MC) form which is highly coloured, and possesses a phenolate binding site for metal guest species such as Cu^{2+} [2], Co^{2+} [1]. Similarly, aminoacids interact with the MC form through complementary zwitterionic charges [3]. The amino acid and metal ion ‘guests’ can be subsequently expelled using a green LED to reform the original inactive SP [4]. These processes have been observed in liquid phase experiments, but recently, in order to generate smart adaptive surfaces based on spiropyran photochromic moieties, we have covalently bound spiropyran derivatives to the surface of polystyrene microspheres.

Beads-based systems are of considerable interest as they provide a particular kind of bi-phase system in which solid particles in suspension can be moved as a fluid but easily separated from the liquid-phase. Hence, micro-beads are an attractive alternative to the traditional solid-phase and liquid-phase approaches used to carry out reactions for synthesis and analysis [5]. The low density of the polymer matrix allows binding kinetics that can be compared to those of solution based systems and their large surface area and greater density permit rapid and highly efficient binding of target species. The combination of bead-based systems and spiropyran properties opens routes to the generation of photoswitchable, high-surface area, smart adaptive systems with potential applications for controlled separation and retention. In this paper the covalent immobilization of spiropyran on polystyrene microsphere beads is reported together with their characterisation in terms of switching and optical properties. The polymeric beads functionalised with spiropyran can be switched using LEDs between a pink, active form and a white, passive form (Figure 1). The colour change on the microbeads corresponds to the reversible interconversion of the spiropyran between a coloured, planar merocyanine form upon irradiation with 370 nm UV-LEDs, and a colorless spiro form by exposure to white or 525 nm green LEDs (Figure 2). The photochromic behaviour of the coated beads has been characterised using different LEDs, reflectance measurements and as a reference, a sample of polystyrene microspheres where the spiropyran derivatives have been simply physically absorbed. Future studies will be focused on the photoswitchable retention of coated microbeads, used as a stationary phase for photocontrolled separations of guest species, such as metals cations or amino acids.

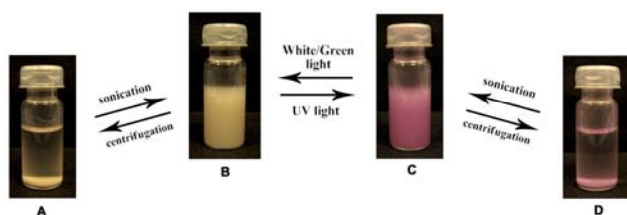


Figure 1: From the left: (A) Sedimented white beads layer after centrifugation; (B) Beads suspension exposed to one minutes of white light; (C); Beads suspension exposed to one minute of UV light; (E) Sedimented pink beads layer after centrifugation (All the samples are in ethanol).

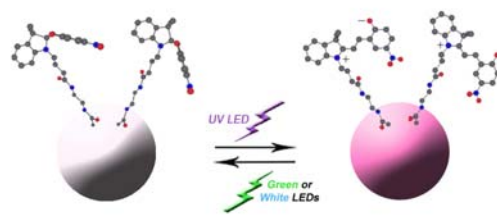


Figure 2: Spiropyran covalently immobilised on the beads switching between the closed, uncharged, colorless form and the open, zwitterionic pink form; the conversion explicates through a color change from white to pink.

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