The Role of Inorganic Photosensitisers in Radiation Sensitive Films for Cancer Treatment

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The commercially important diacetylenes are used to provide a colourimetric change in practical chemosensors, biosensors, and dosimeters. Of particular importance are radiology and radiotherapy films such as Gafchromic which are used, for example, to monitor radiation targeting and dosage during cancer radiotherapy. Gafchromic films can also be utilized in non-destructive testing (NDT) applications where rapid X-ray inspection of articles (*e.g.* pipes, boxes *etc.*) can be essential. Gafchromic films are based on radiation-induced photopolymerization of a lipophilic diacetylene as part of a complex photoactive layer coated on a polyester base. Tuning of the photoresponse of the active ingredient and its dosage dependent conversion is of considerable interest for radiation dosimetry applications. In particular, the role of inorganic photosensitizers within the film is poorly understood both in terms of mode of action and chemical speciation. Existing film components such as bismuth and aluminium oxides seem to play a key role in activating and controlling film response but the way in which they interact with the diacetylene is unknown.

This project aims to derive a bottom-up understanding of the in-film coordination chemistry of bismuth and aluminium oxides and the role these inorganic additives have in organizing the solid state structure of diacetylenes in order to promote radiation absorption and result in controlled, well-understood topotactic photopolymerization. The project will involve the synthesis and structural characterization of diacetylene carboxylate complexes of bismuth and aluminium, study of the chemical speciation of this system in films, dependence on factors such as local pH and derivation of structure-sensitivity relationships guided by the topochemical parameters governing solid state dialkyne photopolymerization. The project will also explore new photosensitisers such as bismuth vanadium oxides and chart the structure-property relationships arising from vanadium coordination. The project will rely heavily on single crystal and powder X-ray diffraction methods and in previous work it has been surprisingly possible to undertake detailed X-ray structural work on these types of diacetylenes despite their surfactant-like nature. the student will be exposed to synthetic coordination chemistry as well as multiple crystallization approaches. The student will learn to use a broad range of analytical techniques such as X-ray powder diffraction, single crystal diffraction, thermal analysis of crystalline & amorphous materials, NMR spectroscopy (particularly solid state NMR), and approaches to understand crystal packing and structure-property relationships. The student will also use hot stage polarized optical microscopy, SEM and TEM in analysing particle shape and thermal behaviour.

The student will benefit from monthly meetings and presentations with the industrial supervisory team led by Dr. Osama Musa (Chief Technology Officer) and Dr. David Hood at Ashland. They will be exposed to product development workflows and approaches taken in industry to understand solid forms, complex formulations and photoreactivity. They will prepare regular technical reports and slide packs to present and so will learn softer communication skills, presenting with impact and reaching out to a wider audience beyond chemical scientists to demonstrate the value of their research. They will take part in national training courses such as the BCA Crystallography and Powder Diffraction Schools and will present their work at Conferences such as the RSC MASC.