Engineering and Innovation Research Studentship 2023/2024

Project title:	**Photoactive Functional Materials for Antipathogenic and Antifouling Applications**
Discipline	Organic Synthesis, Materials Formation, Polymer Science
Key words:	Chromophores, aggregation effects, polymer formation, functional materials
Supervisory team:	Dr Daniel Payne, Dr James Bruce
URL for lead supervisor's OU profile	https://www.open.ac.uk/research/node/5838

Project Highlights:

- Investigate the application of photoactive functional materials in life (antipathogenic) and environmental (antifouling) and sciences.
- Synthetic modification of organic chromophores to design low molecular weight aggregable and polymerizable building blocks for smart materials.
- Measurement, analysis and optimisation of physical and photophysical properties of chromophore polymers towards the desired applications.

Overview:

Molecules that can absorb visible light (i.e. photons) are called chromophores and are the species responsible for a chemicals colour. These absorbed photons cause the molecule to enter an electronic excited state, which returns to the ground state by several relaxation processes including radiative decay (fluorescence or phosphorescence) and non-radiative energy transfer. The relaxation processes of chromophores can be used for a plethora of applications including sensing reporters, photocatalysts and photosensitizers for the formation of *in situ* reactive species.[1-3]

Chromophores have proven to be useful tool in the design of functional molecules, however when incorporated into functional materials their photophysical properties can be affected and can undergo deactivation due to aggregation. The common way to incorporate chromophores into materials is to design multi-component systems that utilise a scaffold to disperse the chromophores and overcome these detrimental aggregation-based deactivation pathways.[4] A method for the incorporation of chromophores into aggregated single component functional nanomaterials using 'chromophore encryption' has recently been reported.[5] The method uses synthetic modification to introduce a protective sphere around the chromophore with functionality capable of hindering close spatial contact between the chromophore moieties. The ability to aggregate these chromophores without change to the photophysical properties allows for the formation of nanoparticles capable of promoting the formation of a reactive oxygen species called singlet oxygen ($^1O_2$). These particles have been demonstrated to pass through cell membranes and cause cell death upon irradiation with light, under a nanomolar dosing regime, by $^1O_2$ mediated degradation of internal cell structure. This demonstrates proof of principle for the formation of functional materials from singlet component chromophores and their application as anticancer agents.

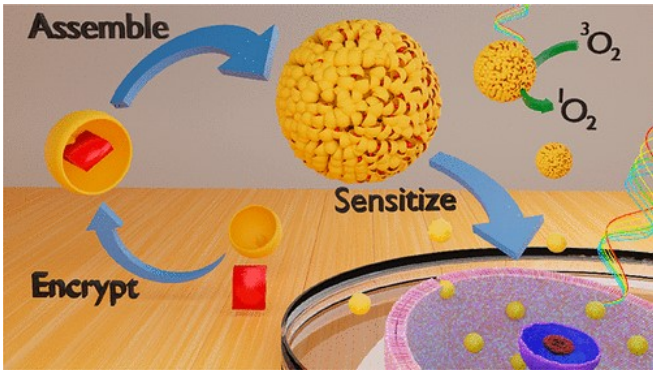

Figure 1. Formation of functional nanoparticles by the aggregation of encrypted chromophores.[5]

Methodology:

This project will study the synthetic modification of various organic chromophores to incorporate functionality to limit the detrimental effects of aggregation on the photophysical properties of the chromophore and to facilitate polymerisation. Synthesised building blocks will be aggregated and polymerised to produce stable materials with tailored properties based on the chemical structure of the monomers. The physical and photophysical properties of these materials will be investigated and engineered through modification of the building block structures. The applications of synthesised polymers in environmental (antifouling) and life (antipathogenic) sciences will be investigated and properties will be optimised towards identified applications.

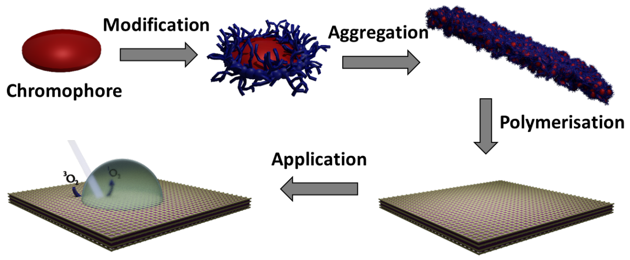

Figure 2. Schematic representation of the proposed project workflow to produce functional polymeric materials.

The successful applicant will be given the opportunity to develop their skills in organic synthesis methods, materials production and in identified application-based studies. Training in the acquisition and analysis of various molecule and material characterisation techniques will be given including multinuclear NMR spectroscopy, mass spectrometry, infrared spectroscopy, absorption and emission spectroscopies and electron microscopy methods (SEM, TEM), amongst others. Opportunities will also be provided throughout the course of the project to develop transferable skills and the applicant will be supported throughout by an experienced team of academic and support staff at the Open University.

References & Further reading:

1. Payne, D. T.; Chahal, M. K.; Brezina, V.; Webre, W. A.; Ariga, K.; D'Souza, F.; Labuta, J.; Hill, J. P., Diporphyrin tweezer for multichannel spectroscopic analysis of enantiomeric excess. *Front. Chem. Sci. Eng.* **2020,** *14* (1), 28-40.
2. Payne, D. T.; Webre, W. A.; Gobeze, H. B.; Seetharaman, S.; Matsushita, Y.; Karr, P. A.; Chahal, M. K.; Labuta, J.; Jevasuwan, W.; Fukata, N.; Fossey, J. S.; Ariga, K.; D'Souza, F.; Hill, J. P., Nanomolecular singlet oxygen photosensitizers based on hemiquinonoid-resorcinarenes, the fuchsonarenes. *Chem Sci* **2020,** *11* (10), 2614-2620.
3. Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C., Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chem. Rev.* **2013,** *113* (7), 5322-5363.
4. Gnanasekar, S.; Kasi, G.; He, X.; Zhang, K.; Xu, L.; Kang, E.-T., Recent advances in engineered polymeric materials for efficient photodynamic inactivation of bacterial pathogens. *Bioactive Materials* **2023,** *21*, 157-174.
5. Bloyet, C.; Sciortino, F.; Matsushita, Y.; Karr, P. A.; Liyanage, A.; Jevasuwan, W.; Fukata, N.; Maji, S.; Hynek, J.; D'Souza, F.; Shrestha, L. K.; Ariga, K.; Yamazaki, T.; Shirahata, N.; Hill, J. P.; Payne, D. T., Photosensitizer Encryption with Aggregation Enhanced Singlet Oxygen Production. *J. Am. Chem. Soc.* **2022,** *144* (24), 10830-10843.

Further details:

Applicants should have (or expect to obtain) at least the equivalent of a UK upper second-class honours degree (and preferably a Masters degree) in organic chemistry, materials science, or other relevant scientific disciplines. Knowledge and/or research experience in synthetic and characterisation techniques for organic compounds and/or materials and a broad interest in applications of functional materials would be an advantage. The student will join a team researching functional materials for various applications including the treatments of cancer and eradication of environmental pathogens.

Please contact Dr Daniel Payne by email (Daniel.Payne@open.ac.uk) for informal enquires related to this project.

Applications should include:

- A 1000 word cover letter outlining why the project is of interest to you and how your skills match those required
- an academic CV containing contact details of three academic references
- an Open University application form, downloadable from: http://www.open.ac.uk/postgraduate/research-degrees/how-to-apply/mphil-and-phd-application-process
- IELTS test scores where English is an additional language

Applications should be sent to **STEM-EI-PhD@open.ac.uk by 15.02.2023**