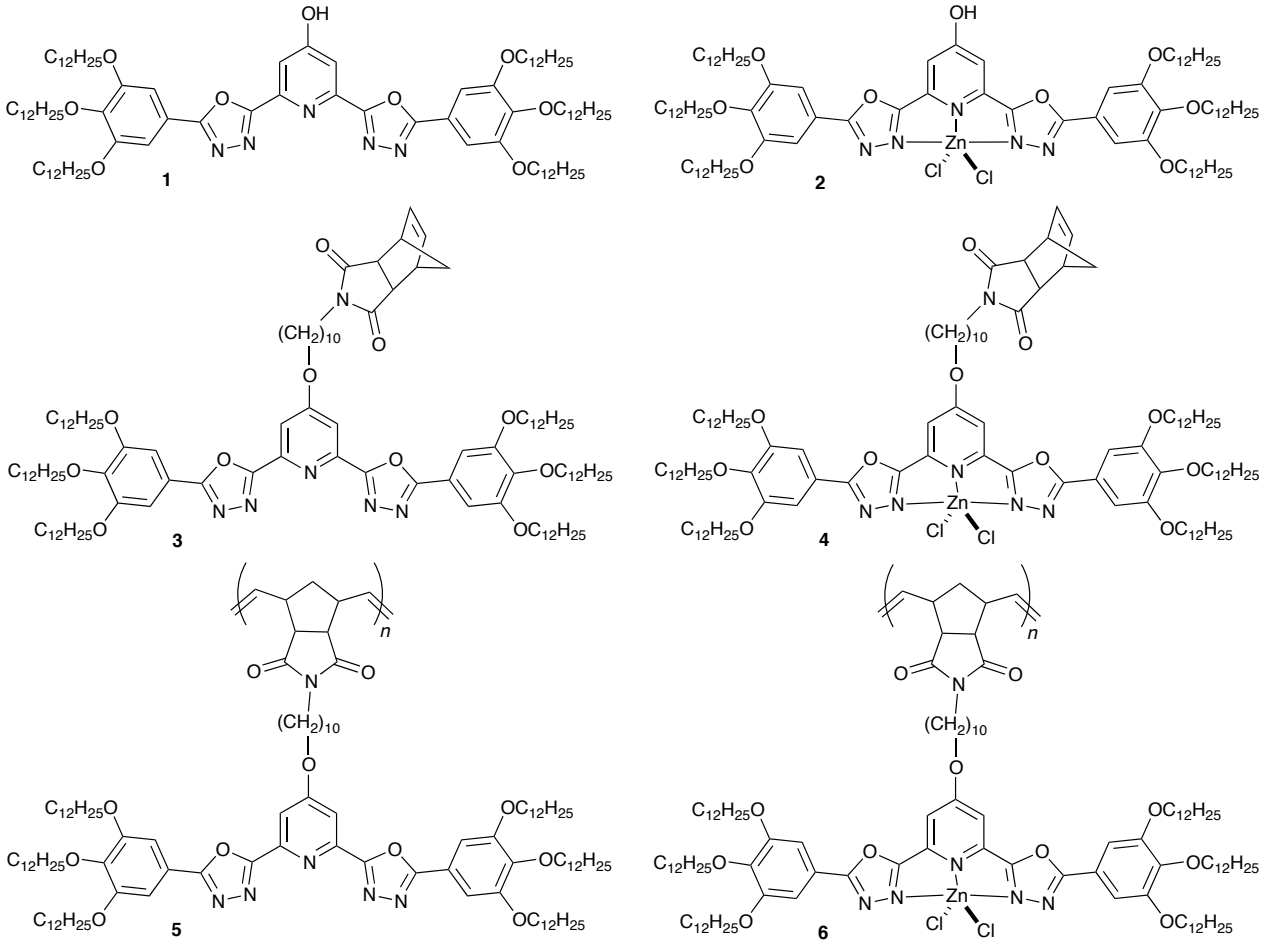
REPORT

1. 1,3,4-Bis(oxadiazole)-anchored, side-chain liquid crystal polymer: an investigation of the synthesis, photophysical and mesogenic properties

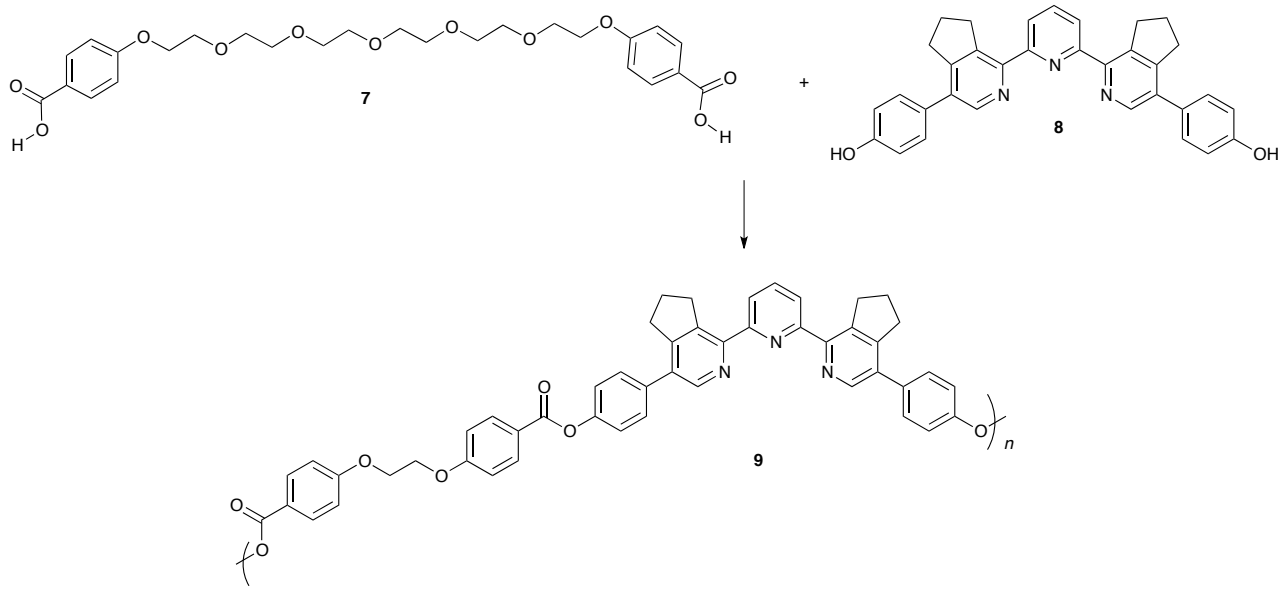
The first part of the proposal was to design, synthesise and study luminescent liquid-crystalline polymers and their metal complexes to obtain materials for optoelectronic applications. We chose the 1,3,4-oxadiazole chromophore as a core incorporated with a polymerisable unit (*cis*-5-norbornene-*endo*-2,3-dicarboxylic imide) *via* a decyl chain. Preparation involved a multi-step synthesis in which the final step requires the conversion of a tetrazole to 1,3,4-oxadiazole. While carrying out the synthesis, it was observed that the chelating molecule (1) showed liquid-crystalline behaviour as did the monomer (3) and polymer (5) once synthesised. The homo polymer (10-mer) was synthesised *via* ROMP using the Grubbs' 3 catalyst. The polymer obtained was finally purified by passing through a bio bead column yielded a 10-mer with polydispersity (M_w/M_n) 1.146. The synthesis of luminescent bis(oxadiazole)-based liquid crystalline metallomesogens *via* this methodology has not been attempted before. We also succeed in synthesising Zn^{II} complexes of chelating molecule (**2**), monomer (4) and polymer (6) and altogether six molecules studied in detail after a good deal of synthesis. Polymers **5** and **6** showed a Col_h mesophase slightly above room temperature, thus realising the main goal of obtaining luminescent, polymeric metallomesogens. Thus, all molecules cited here (**1**-**6**) (Scheme 1) are luminescent in both solutions as well as spin-coated films and detailed photophysical characterisation was carried out. The ease of processability associated with **5** and **6** along with reasonably good emission in the thin films make them promising materials for the future optoelectronic applications and devices.



Scheme 1 The structure of synthesised materials.

2. Design, synthesis and liquid crystalline properties of terpyridine-based main-chain liquid-crystalline polymer

A new terpyridine-based main-chain liquid-crystalline polymer was synthesised and characterized in collaboration with UG student Yang Wu. The polymer was obtained from esterification of a functionalised terpyridine and 4,4'-hexa(ethyleneoxy)dibenzoic acid (Scheme 2). Preliminary IR analysis of the polymer showed a characteristic stretching frequency of carbonyl group of ester at 1730 cm^{-1} and further confirmation was obtained from the comparative NMR analyses of monomers and polymer. GPC analysis gave M_n of 2396 Da (PDI = 1.17), indicating that a dimer or trimer was obtained. MALDI analysis supported the formation of dimer and trimer, with $[M + H]^+$ values 1985.8205 and 2969.2163 Da respectively. The birefringence textures obtained from polarised optical microscopy showed that the polymer obtained is a nematic liquid crystal between 40 and 90 °C). The transition temperatures obtained from POM were confirmed by DSC analysis. UV spectroscopy indicated that the polymer has a strong absorption in a range of 200 nm to 400 nm with λ_{max} = 269 nm.



Scheme 2. The general scheme adopted for the synthesis of polymer.

Outreach Activities

I have completed the following outreach activities:

a) An article is published in Chemistry Review (targeted at student aged 16-18) entitled '*Lyotropic Liquid Crystals – Essential for Life*'.

b) I was involved in mentoring four students of senior level (16-18) from different schools of UK as a part of their work experience during the last one year.

c) I also participated on 'YORNIGHT' EUROPEAN RESEARCHER'S NIGHT and the purpose of the event in this group was to talk to public about our research interests and make them aware of the theory behind our research topic. http://yornight.com/ http://yornight.com/researchers/smart-and-green/saleesh-sivaraman/

d) I completed a YouTube video (https://www.youtube.com/user/CIECPromotingScience) based on fundamentals of liquid crystals for primary school children and teachers in collaboration with Joy Parvin, the Director of CIEC in York. This video forms part of an extension experiment that is being trialled in local schools aimed at students aged 10-11 to introduce them to liquid crystals. A series of experiments and a workbook have been created and some commercial sponsorship by Merck Ltd in the form of devices, has been secured. Initial training of school teachers has already taken place.