Summary of Ph.D. thesis

Primarily this work is focused on design and synthesis of novel LMWGs, and to probe the supramolecular assemblies and their gelation capabilities in various polar and non-polar solvents using solid state analysis, and *in-situ* gel phase analysis like SANS. This work aims to contribute to produce the structure-property corelation and decrease the serendipitous discovery of gelling systems.

- We synthesised a variety of thiazole-based amides (Tz-9 to Tz-12, Tz-15, and Tz-16) with various aliphatic chain lengths and investigated the packing of molecules from crystalline state to semi-solid gel.
- A dimeric zero-dimensional packing of the molecule with an extended aliphatic chain was visible in the single crystal structure of the Tz-9 packing. This packing was subsequently extended to a 2D network by weak noncovalent interactions like the C-H···O and van der Waals interactions.
- Further testing of the compound Tz-9's gelation capabilities revealed that it was a superb polar solvent gelator with a low MGC for acetonitrile gel (2.78 (% w/v)).
- Even in their crystallised condition, Tz-9 molecules showed clearly defined cylindrical packing. The three-dimensional network of gel is predominantly composed of monodisperse cylindrical fibres with almost a double molecular diameter than the cylindrical fibres in the solid state, according to a SANS analysis of Tz-9 gel in ACN.
- Based on multiple physical-chemical analyses, a likely mechanism for packing Tz-9 molecules inside the gelator fibre, starting from solid state to supramolecular assembly, is provided.
- Tz-9 may be used in fluoride ion detection with high selectivity and sensitivity, which could pave the way for the development of sensors.
- We also created a sequence of compounds with a thiazole moiety, a hydrogen bonding site (urea functional group), and a lengthy alkyl chain (compounds 1-7). The aliphatic long chain was gradually increased from decyl to heptadecyl [(CH2) or methylene functional group of aliphatic chain varying from 9 to 16, except hexadecyl n = 13] to investigate the role of van der Waals interaction (or

hydrophobic effect) on gelation process along with reliable 1D hydrogen bonding urea functional group.

- Seven newly synthesised compounds (Utz 1–7) demonstrated outstanding gelation behaviour in the presence of polar solvents and alcohol-water/ACN-water combinations.
- SANS investigation of supramolecular assembly in solid-state compounds revealed the formation of cylindrical assemblies with varied molecular diameters that were substantially reliant on the long aliphatic chain.
- The temperature variation SANS analysis of gel samples revealed a loose assembly of irregular fibres, which was confirmed by SEM micrographs of xerogel.
- Interestingly, the iodide ion sensing ion in the solution and gel phase rather than chloride/fluoride ions (which are commonly sensed by urea-based compounds) led us to conclude the syn-anti conformation of the urea functional group, which was supported further by DFT calculation and NMR titration.
- The addition of iodide salts to the gel and degelation (gel-to-sol) provides an appealing way of selective identification and detection of iodide ions.
- In another interesting work, we created benzimidazole-based compounds with various alkyl chains functionalized with amide and urea to give robust interactions.
- Gelation studies reveals that bisamide compounds (A1, A2, and A3) gelate well in polar solvents (especially alcohols), but Bisurea compounds (U1, U2, and U3) do not gelate well in most solvents.
- The introduction of an extra N-H group does not increase gelation capabilities, but it does, strengthen intermolecular H-bonding, causing the molecule to precipitate out of the solvent quickly rather than forming fibres.
- Amide derivatives whereas has improved balance between crystallization and solvation due to the combine effect of both Hydrogen bonding, Van der waals interaction also solvent effects is the key point to be consider
- The temperature variation SANS was used to investigate gelation morphology and concluded that shape independent morphology in gel state is corroborated by SEM images.
- A2 and B2 are investigated for their potential as chemosensor for the detection of various anions such as I^-, F^-, Br^-, and PF_6^-, Pb^{2+}, Cd^{2+}, Co^{2+}, Hg^{2+} and Mn^{2+}

which are found to interact only with Hg2+ by UV-Visible and Fluorescence spectroscopy.