# CHAPTER 7

## Summary

In this chapter, we summarize some of the important results and conclusions derived from this thesis work, which deals with the synthesis, characterization and self-assembly of functionalized soft nanomaterials. We briefly discuss the possibilities and scope for future work based on the results obtained from our experimental work. Broadly, the research work that has been reported in this thesis can be classified as follows:

Chapter 1 is an introductory chapter and mainly deals with the physical properties of discotic liquid crystals, making them ideal candidates for various optical and electronic devices such as photocopiers, laser printers, photovoltaic cells, light-emitting diodes, field effect transistors, and holographic data storage. Beginning with an overview of liquid crystals, this chapter mainly focuses the major classes of columnar mesogens formed by discotic liquid crystals, their efficient synthetic procedures, relevant mesomorphic and physical properties and finally, some applications and perspectives in materials science and molecular electronics.

Chapter 2 describes the synthesis and characterization of mesogens-decorated gold nanoparticles. It has been divided into two sections. In the first portion of the chapter we describe the preparation of novel thiol functionalized alkoxycyanobiphenyls which have been used for the preparation of self-assembled monolayers on gold and gold nanoparticles. The second portion focuses mainly inclusion of gold nanoparticles in the supramolecular order of discotic liquid crystals. This has been achieved via following three ways.

1. Mixing monolayer protected gold nanoparticles and discotic liquid crystals

2. Mixed monolayer: attaching thiol-functionalized discotic liquid crystals to gold nanoparticles using exchange reaction

3. Discotic liquid crystals protected gold nanoparticles

Chapter 3 presents phase transitions in novel disulfide-bridged alkoxycyanobiphenyl dimers. All the chemical structures of the disulfide-bridged alkoxycyanobiphenyl dimers were confirmed by $^{1}H$ NMR, $^{13}C$ NMR, IR, UV spectroscopy and elemental analysis. The thermal behaviour of these mesogens was investigated by polarizing optical microscopy, differential scanning calorimetry and X-ray diffractometry. The dimers with a shorter spacer exhibit only the nematic phase while dimers with a longer spacer display nematic as well as smectic phases. X-ray diffraction experiments reveal the intercalated structure of the SmA phase of these dimers and the presence of short range SmA-like order in the N phase (cybotactic nematic) of all the compounds, except the one with the shortest spacer.

Chapter 4 focused the synthesis, characterization and mesomorphic properties of novel triphenylene-based ionic discotic liquid crystals. A series of ionic pyridinium and imidazolium salts have been synthesized and characterized from their spectral studies. These are the first known thermotropic ionic liquid crystals based on triphenylene. These salts are not only important for a new possibility of organic molten salts in materials science, but also contribute to the development of novel anisotropic soft materials for directional ion conductivity and charge transport.

Chapter 5 addresses the chemistry of novel triphenylene based ionic discotic liquid crystalline dimers and polymers. This chapter has been divided into two sections. The first portion deals with microwave-assisted synthesis of imidazolium-based ionic liquid crystalline

dimers based on calamitic-calamitic, calamitic-discotic, discotic-discotic moieties. The second portion describes novel imidazolium-based ionic discotic liquid crystalline polymers. Ionic discotic polymers, having processable properties of polymers and electronic properties of discotic liquid crystals, might be very useful for unidirectional transport of ion and energy at nanoscale.

Chapter 6 discusses microwave-assisted synthesis of novel rufigallol-based rod-disc mesogens. Here we report the synthesis and characterization of a series of molecules in which one, two, four, five and six rod-like cyanobiphenyl moieties are attached to a central rufigallol discotic core *via* flexible alkyl spacers. Classical reactions failed to produce these mesogens. We see that single rod-like cyanobiphenyl mesogen attached to the rufigallol moieties show a critical balance of mesomorphism. All the rod-disc-rod trimers were found to be non-liquid crystalline. Between, tetramer and pentamer, the former shows only the N phase, whereas the later one shows both N and SmA phases. Interestingly, hexamers with a shorter spacer show nematic phases and SmA phases with the longer spacer. Hexamers with medium alkyl spacers show both N and SmA phases at higher temperature and a reentrant N phase at lower temperature which could be a biaxial N phase.

As a final conclusion it may be stated that using classical and modern synthetic chemistry, we have synthesized a variety of novel discotic and calamitic liquid crystals. We have shown that metal nanoparticles can be incorporated in the supramolecular order of discotic liquid crystals. These materials are extremely important for various physical studies and to prepare many electro-optical devices.

Some of the findings made in the thesis have been published/communicated in following international journals.

[1] Synthesis and Characterization of novel imidazolium-based ionic discotic liquid crystals with a triphenylene moiety

Sandeep Kumar, Santanu Kumar Pal, *Tetrahedron Letters*, 2005, 46, 2607-2610.

[2] Ionic discotic liquid crystals: synthesis and characterization of pyridinium bromides containing a triphenylene core

Sandeep Kumar, Santanu Kumar Pal, *Tetrahedron Letters*, 2005, 46, 4127-4130.

[3] The first examples of terminally thiol-functionalized alkoxycyanobiphenyls

Sandeep Kumar, Santanu Kumar Pal, *Liquid Crystals*, 2005, 32, 659-661.

[4] Discotic-decorated gold nanoparticles

Sandeep Kumar, Santanu Kumar Pal, V. Lakshminarayanan, *Mol. Cryst. Liq. Cryst.*, 2005, 434, 251-258.

[5] Microwave-assisted synthesis of novel imidazolium-based ionic liquid crystalline dimers

Santanu Kumar Pal, Sandeep Kumar, *Tetrahedron Letters*, 2006, 47, 8993-8997.

[6] Self-assembled monolayers (SAMs) of alkoxycyanobiphenyl thiols on gold-A study of electron transfer reaction using cyclic voltammetry and electrochemical impedance spectroscopy

V. Ganesh, Santanu Kumar Pal, Sandeep Kumar, V. Lakshminarayanan, *J. Colloid and Int. Sci.*, 2006, 296, 195-203.

[7] Novel conducting nanocomposites: synthesis of triphenylene-covered gold nanoparticles and their insertion into a columnar matrix

Sandeep Kumar, Santanu Kumar Pal, P. Suresh Kumar, V. Lakshminarayanan, *Soft Matter*, 2007, 3, 896-900.

[8] Synthesis of monohydroxy-functionalized triphenylene discotics: green chemistry approach

Santanu Kumar pal, Hari Krishna Bisoyi, Sandeep Kumar, *Tetrahedron*, 2007, 63, 6874-6878.

[9] Phase transitions in novel disulphide-bridged alkoxycyanobiphenyl dimers

Santanu Kumar Pal, V. A. Raghunathan, Sandeep Kumar, *Liquid Crystals*, 2007, 34, 135-141.

(This work has been featured on the *cover page* of the journal)

[10] Dispersion of thiol stabilized gold nanoparticles in lyotropic liquid crystalline systems

P. Suresh Kumar, Santanu kumar pal, Sandeep Kumar, V. Lakshminarayanan, *Langmuir*, 2007, 23, 3445-3449.

[11] Self-assembled monolayers (SAMs) of alkoxycyanobiphenyl thiols on gold surface using a lyotropic liquid crystalline medium

V. Ganesh, Santanu Kumar Pal, Sandeep Kumar, V. Lakshminarayanan, *Electrochimica Acta*, 2007, 52, 2987-2997.

[12] Twist Viscoelastic coefficient of novel thiol terminated alkoxycyanobiphenyl nematic liquid crystals

Amit K. Agarwal, K. A. Suresh, Santanu Kumar Pal, Sandeep Kumar, *The Journal of Chemical Physics*, 2007, 126, 164901-1.

[13] Films of novel mesogenic molecules at air-water and air-solid interfaces

Alpana Nayak, K. A. Suresh, Santanu Kumar Pal, Sandeep Kumar, *J. Phys. Chem B*, 2007, 111, 11157-11161.

[14] Green chemistry approach to the synthesis of liquid crystalline materials
Sandeep Kumar, Hari Krishna Bisoyi, Santanu Kumar Pal, *Mol. Cryst. Liq. Cryst*., 2007 (in press).

[15] Microwave-assisted synthesis of novel rufigallol-based rod-disc mesogens (Communicated).

[16] Novel triphenylene-based ionic discotic liquid crystalline polymers (Communicated).