1.1 Introduction to Nanoscience and Nanotechnology:

Nanoscience and Technology is an important discipline of 21st century. Nanoscience is the understanding of behavior and phenomena of the nanoscale world and nanotechnology deals with the capability to manipulate, control, assemble, produce and manufacture things at atomic precision. Nanoscience and technology is inherently interdisciplinary in nature involving many major disciplines such as chemistry, physics, biology, engineering, computation, and medicine. A comparison of the size domains of various naturally existing and manmade systems is presented in Fig. 1.1. The word ‘nano’ is originated from the Greek “νανοσ”, meaning ‘dwarf.’ Lohmann used the prefix ‘nano’ for the first time in 1908, to address small organisms having size in the order of ~200 nm scale.¹ The visionary idea of controlling matter in the nanoscale regime was proposed by Nobel laureate Richard P. Feynman, in his famous lecture entitled “There’s Plenty of Room at the Bottom”, delivered at California Institute of Technology, in 1959.² In his talk, he outlined the theoretical concept of manipulating matter in the atomic/molecular level and the potential applications of nanoscale systems. In the famous talk he told…

“The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom. It is not an attempt to violate any laws; it is something, in principle, that can be done; but in practice, it has not been done because we are too big”

1.2 Historical Perspective of Nanoscience:

The first nano sized gold in colloidal state was prepared by Michael Faraday in 1857.³ In nature a lot of biological processes are accompanied by nanoparticles. It was the
German bacteriologist Robert Koch, who found that compounds made with gold inhibited the growth of bacteria in 1890, which brought him the Nobel Prize for medicine in 1905. The use of gold in medicine is not new, Indian medical system Ayurveda used gold in several preparations. In 3150 BC the Egyptians used gold in dentistry. Colloidal gold has been incorporated in glasses and vases to furnish them colour, which has been found in many European cathedrals. The use of gold and silver nanoparticles in dichroic glass is found in the Lycurgus cup made by the Romans in 4 A.D. (Fig. 1.2). If light source is kept inside the cup it appears red from the outside (transmitted light) and green from the inside (reflected light). Modern study shows it contains very small amounts of gold (about 40 ppm) and silver (about 300 ppm) in the form of nanoparticles. *Magnetosperillum magnetotacticum*, a bacterium is known to produce Magnetite (Fe₃O₄) particles of nanometer size. It is also established that the bacteria make nanoparticles of specific morphology. The magnetism caused by the particles helps in finding a direction favorable for its growth. The familiar bacterium called lactobacillus, which grows in curd can uptake metal ions from the curd and reduce them in nanoparticles inside the cell. The formation of nanoparticles are not only restricted to bacteria, but also has been found in fungi and viruses.

Although nanomaterials have existed for a long time, systematic scientific discussion about them was initiated only in 1959, after Richard Feynman prophetic lecture at the annual meeting of the American Physical Society. At the beginning of 1900 the development of nanoscience and technology was crippled by the resolution. Because according to Abbe’s theory the ability to resolve detail in an object was limited approximately by the wavelength of the light used in imaging, which limits the resolution of an optical microscope to a few hundred nanometers ~ 250 nm.

\[
d = \frac{\lambda}{2NA} \tag{1.1}
\]

\(\lambda\) = Wavelength of light used for imaging

\(NA\) = Numerical apperture of the objective
The development of Transmission Electron Microscopy (TEM) in 1928, Atomic Force Microscopy (AFM) in 1980 and Scanning Tunneling Microscopy (STM) in 1981 paved a way to characterize nano objects down to atomic resolution. Now it is not only possible to see atoms/molecules but also to manipulate them in a desired pattern. For example positioning of CO molecules in a “C” shaped arrangement has been done by using a STM tip (Fig. 1.3). Later development of fullerene, carbon nanotubes, semiconducting quantum dots, and graphene revolutionized the era of science and technology. Nano science and nanotechnology mainly focuses in the size region 1-100 nm. As the quantum confinement effect arises in the size domain 1-50 nm, nonmaterials show a very different physical and chemical properties compared to their bulk counterparts or from their atomic/molecular constituents in terms of color, solubility, reactivity, magnetic, optical, mechanical and electrical properties. Recently the interfaces of nanoscience have been extended to nanobiology, nanosensors, nanomedicines, molecular nanomachines and nanotribology.

1.3 Classification of Nanomaterials:

Nanomaterials can be classified based on their chemical nature, properties and also applications in areas such as metals, ceramics, semiconductors, composites and polymers. These can be further subdivided into biomaterials, catalytic materials, coatings, glasses, magnetic and electronic materials; another way to visualize families of nanomaterials is based on their building blocks–atoms, ions, small molecules or macromolecules. If the nanomaterial is made of small molecules or macromolecules they are often called molecular nanomaterial. The molecular nanomaterials shows completely different properties compared to the nanomaterials made of atoms and ions. As the field of nanostructure materials has evolved, many names and labels have been used. For e.g. a cluster is a collection of atoms or reactive units of up to around 50 units. A colloid is a stable solution of particles ~ 1-1000 nm. Nanoparticles are solid particles in the range of a few tens of nanometers that could be amorphous, aggregates of crystallites or single
crystalline. Quantum dot (or Q-particles) is a particle that shows a size quantization effect and emits different colour light depending upon its sizes in at least one of the dimension.

Based on dimension, nanomaterials can be classified as zero-dimensional (0-D), one-dimensional (1-D), two-dimensional (2-D), and three-dimensional (3-D) materials. 0-D nanomaterials are those where all the dimensions are measured within the nanoscale. The most common representation of zero-dimensional nanomaterial is nanoparticles. In case of 1-D material one of the dimensions is outside the nanoscale (even up to several microns). This includes nanotubes, nanorods, and nanowires. 2-D materials are those where two of the dimensions are not confined to the nanoscale viz. nanofilms, nanolayers, and nanocoatings. Three dimensional materials are not confined to the nanoscale in any dimension. These materials are thus characterized by having three arbitrarily dimensions above 100 nm.

Nanomaterials can be fabricated by two major approaches called the top-down and bottom-up methods. In the former method essentially a structure or pattern is imposed on the substrate being processed. e.g., lithography, writing, stamping, etc. The latter method guides the assembly of atomic and molecular constituents into organized surface structures through processes inherent in the manipulated system.

1.4 Assembly of Nanomaterials:

In order to realize the integration of nanoscale materials into devices that have practical significance, nanoscale patterning techniques that are scalable, massively parallel, low-cost, and high throughput must be developed. Although 1-D nanowires/tubes are of great interest for applications, their disordered structures seem to be problematic for use in device fabrication (for example, microelectronics and photonics) that often requires well-aligned and highly ordered architectures. Recently, the group of Yang have studied and reviewed nanocrystal and nanowire assembly of metallic and inorganic nanostructures by the Langmuir–Blodgett (LB) method; they have shown the optical responses of a silver nanoparticle film, which can be tuned using LB assembly. Müllen and co-workers have used Zone casting to produce large area anisotropic uniaxial alignment of the HBC film, which they have successfully integrated into an organic field-effect transistor device. Assembly of nanoparticles in desired fashions can be made by designing molecular nano-architectures by fine tuning of molecular building blocks and engaging them in programmable/ predefined interactions,
which can lead to directed self-assembly. Self-assembled nanofibers of a phthalocyanine derivative are oriented by applying electric field under photoexcitation. Murphy et al. have self assembled gold nano rods in a stacked fashion in presence of adipic acid. The assembly and disassembly of gold nano rods can be triggered by varying the pH of the solution. They have also shown a preferentially end-to-end assembly of gold nanorods by biotin streptavidin connectors. L. M. Liz-Marzán and coworkers have used carbon nanotube as a template to align gold nano rods. Paul Malvaney and coworkers have used electric field to direct the growth of gold nanorods in aqueous solution containing cetyltrimethylammonium bromide (CTAB) as surfactant. M. A. El-Sayed and coworkers have presented a simple method through vertical dipping of TEM grid into a nanoparticle solution. They have anticipated the packing of nanoparticles on the substrate could be a result of the hydrodynamic pressure of water stream and the lateral capillary forces. Carsten Sönnichsen et al. have presented a general strategy to stabilize gold nanorod suspensions with mono- and bifunctional polyethylene glycol (PEG) and to attach a controlled number of nanoparticles or biomolecules. Yan reported a feasible approach for the linear assembly of Au nanorods using glutathione and cysteine in aqueous solutions without the addition of organic solvents. Thomas and co workers have studied the longitudinal surface plasmon resonance (SPR) of end-to-end coupled Au nanorods and observed a red-shift as the number of rods in the chain increased.

Chattopadhyay et al. introduce a new lithographic method for the generation of 2-D patterns of composite nanoparticles (NPs) of Ag and Au through galvanic replacement by taking recourse to combine top-down and bottom-up approaches using commercially available compact disks (CDs) and digital versatile disks (DVDs) as templates. They also used top-down and bottom-up approaches to fabricate a fluorescent yellow pattern. In their work they have reported a new form of lithography that involves a reaction between a H2S gas and a Cd2+ ions embedded in a polymer film using a transmission electron microscope grid as a mask. In a separate work they also report the formation of linear assemblies of citrate-stabilized spherical gold nanoparticles in the presence of acetonilide in aqueous medium. In a systematic they have analyzed the dependency of acetonilide concentration on the effective surface areas and catalytic properties of the gold nanoparticles array.

T. Pradeep et al. developed a technique combining the seed mediated growth and the electrochemical deposition in which they formed oriented gold nanotriangles on
indium tin oxide (ITO) coated conducting glass surfaces.\textsuperscript{18} In another work a synthesized fluorescent, porphyrin-anchored, Au\textsubscript{22} cluster was fabricated to form fluorescent patterns by soft lithography technique.\textsuperscript{19} They have also developed a facile and reversible method for assembling and disassembling gold nanorods using a common chelating agent, ethylenediaminetetraacetic acid (EDTA).\textsuperscript{20}

When a lower dimensional structure such as quantum dots or quantum wires forms a periodic structure of layers of two (or more) materials they are called super-lattice. Talapin and co workers have shown that the colloidal inorganic nanoparticles can self-assemble into binary periodic superlattices.\textsuperscript{21}

Although it is very easy to form self assembled nano/micro structures from small organic molecules, dendrimers and polymers, but the assembly of nano/micro structures in a desired pattern is still remains a challenging task. If the nanostructures are susceptible to magnetic field they can be aligned by applying the magnetic field.\textsuperscript{22} This method is mostly applicable for magnetic nano structures and can be extended to prepare aligned single walled carbon nanotube.\textsuperscript{23} Electrical force or dielectrophoresis is another method to assemble electrically charged objects.\textsuperscript{24} But this technique is also restricted to metallic nanowires and can be extended to large-scale directed assembly\textsuperscript{25} of single-walled carbon nanotubes devices.\textsuperscript{26} Another economical and domestic method to align nanowires/tubes

![Figure 1.4 Illustration of blown-bubble film (BBF) process. (a) NW/NT polymer suspension, (b) bubble expansion over a circular die, and (c) films transferred to crystalline wafers, plastics, curved surfaces, and open frames. Nitrogen gas at pressure P flows through the die and expands a bubble from the NW/NT−epoxy suspension (dark-blue color) on the top of the die while a stable vertical force, F is applied by means of a wire-ring connected to a controlled speed motor. Black straight lines represent aligned NWs/NTs embedded in the bubble film. (d−g) Control of aligned NW density in BBFs. (d) Photograph of 0.01, 0.03, and 0.15 wt % (left to right) epoxy suspensions of Si NWs. (e−g) Dark-field optical images recorded from 0.01 (e), 0.03 (f), and 0.15 (g) wt % Si NW-BBFs, respectively. The scale bars in e, f, and g are 50, 20, and 10 mm, respectively. Adapted from ref. 27b.]}
is “Bubble-Blowing Process”. The bubble-blowing assembly strategy is a general and scalable method that has been recently developed for uniformly aligned and controlled-density nanowires and nanotubes films by controlling bubble expansion of homogeneous polymer suspensions containing 1-D nanomaterials. In this method first, the functionalized nanowires were dispersed in a controlled concentration polymer to form a homogeneous and stable suspension. Then expansion of the polymer suspension occurs, using a circular die to form a bubble at controlled pressure, and expansion rate, where stable vertical expansion is achieved by using an external vertical force. Lieber and coworkers have first developed this method and shown the fabrication of flexible plastics sheets of dimensions of at least $225 \times 300 \text{ mm}^2$ over a highly curved surfaces (Fig. 1.4).27

Electrospinning is another method to fabricate highly aligned microstructures. In this method a polymer solution or melt is pumped through a thin nozzle with an inner diameter of the order of 100 μm. The nozzle also serves as an electrode, to which a high electric field of 100–500 kV m$^{-1}$ is applied, and the distance to the counter electrode is 10–25 cm in laboratory systems. Electrospinning mainly makes use of the electrostatic repulsions between surface charges to reduce the diameter of a viscoelastic jet or a glassy filament. Yu and coworkers have used poly(vinylalcohol) (PVA) to fabricate high SERS-active Ag dimers or aligned aggregates, which are assembled within nanofibers with chainlike arrays. In this way they have successfully developed a free-standing and flexible surface-enhanced Raman scattering (SERS) substrate via the electrospinning technique (Fig. 1.5).28

The LB technique which was traditionally used to fabricate amphiphilic molecule monolayers onto a water surface is now has been shown to be a high-throughput, low-cost, and easily integrated method to assemble nanosized building blocks to fabricate both closely packed nano superstructures and well-defined patterns with low density.29 In this method, at first the nanomaterials to be processed was dissolved in an immiscible volatile solvent and spread onto a water-supported surface using a microsyringe. After solvent
evaporation, the sample was compressed slowly while the surface pressure was monitored and a Langmuir thin film consisting of a nanostructure monolayer can be obtained. The monolayers can be repeatedly deposited in a layer-by-layer fashion onto a solid substrate through vertical-dipping (Langmuir–Blodgett) or horizontal-lifting (Langmuir–Schaefer) techniques. Plenty of integrated logic circuits, one-dimensional functional networks and programmable nanowire nanoproprocessors have been fabricated by using this technique. Recently hydrophilic Te nanostructures have also been arranged by using a non aqueous solvent like DMF/CHCl₃.

Assembly by mechanical force is one of the emerging areas. Since Controlled and uniform assembly of nanowire materials with high order and large area can be obtained by this method which is one of the criteria for electronic applications. Contact-printing method, the knocking-down method, strain-release assembly are to name quite a few, which are driven by mechanical force. Lieber et al. have used the contact-printing method, to directly transfer regular arrays of semiconductor NWs from donor to patterned receiver substrates, to assemble both single and highly dense parallel arrays of NWs on substrates and in large scale. Weak interactions between the chemically unmodified NWs and surface chemical modification of the receiver substrate play an important role in the assembly process. Knocking–down method was first developed by Patolsky and co-workers. In this method, at first a typical vertical nanowire array was formed by the simple top-down sculpting of an appropriate substrate. Then followed by manual rolling of the elastomer-based roller, made of poly(dimethylsiloxane) (PDMS), teflon, or other elastomers with different rigidity and surface properties, over the nanowire-array substrate. Compared with the contact-printing method, nanowire elements are directly grown on the final device substrate, which is advantageous over transferring the nano-wires from a “donor” substrate. Lei et al. reported a two-step knock-down method for successful fabrication over large-area and well-aligned arrays of ZnO nanowires and high density along their c-axis on a flexible
substrate. First, a modified chemical vapor deposition (CVD) process is initially used for synthesizing vertical ZnO NW arrays perpendicular to the donor substrate surface. Then, the manual contact-printing method was introduced to knock the nanowires down and transfer them to a receiver substrate with well patterns. Interestingly, nano and micro patterning of functional metal complexes and organic solids are still in its infancy with only a few examples. For example, Cavallini and coworkers used LCW (lithographically controlled wetting) and MIMIC (micro molding in capillaries) techniques to fabricate Mn$_{12}$-based single molecular magnet (Fig 1.6), oligothiophene fibers with enhanced functional properties, and spin state switchable Fe(II) spin crossover arrays.

1.5 1-D Organic Materials:

After the discovery of carbon nano-tubes by Iijima in 1991, various kinds of 1-D semi-conducting nanomaterials, including nanorods, nanowires, nanotubes and nanobelts, have been attracted considerable attention among scientist, because their two-dimensional quantum confinement effect. 1-D nanomaterials are promising building blocks for miniaturized devices, and used as chemical sensors, light emitting diodes, field-effect transistors, solar cells, and so on. Most of the reported literatures focused mainly on inorganic based 1-D materials, whereas organic materials are not much studied although the organic functional molecules have been playing important roles in various optoelectronic applications. Organic macromolecules such as polymers, biomolecules, dendrimers, etc., have been under active investigation during the past couple of years. For instance, conductive polymers, such as polyaniline and polypyrrole, have been fabricated into 1-D nanostructure owing to their good electrical conductivity, redox properties, environmental stability, and potential applications in sensors, biomedicine, actuators, etc. Polymers can be fabricated into 1-D nanostructures via electrochemical deposition, electrospinning, and the template method. 1-D organic nanomaterials can be fabricated by liquid and vapor phase based bottom-up methods. In this method, the tendency to form 1-D material is inherent in the molecular system. It is a facile and reliable strategy, using mild conditions. More importantly, composite nanostructures of organic materials can be readily achieved with this method, by physical vapor deposition (PVD) organic 1-D nanomaterials with high crystallinity can be achieved. Doped organic materials using highly efficient organic or
inorganic light emitting materials as dopant to generate multicolor emission\textsuperscript{58} and white light emission have also been realized recently by using physical vapor deposition (PVD) techniques.\textsuperscript{59} There is another universal method to fabricate 1-D nano structure which called template method. It is a \textit{top-down} method. This method can be applied in most of the organic molecular materials that cannot form 1-D structure through liquid-phase or vapor-phase methods described before. The idea behind the template method is to fill organic molecules into 1-D nanosized vacancies, which are often referred as “templates” in nano fabrication techniques. If the template induce the 1-D growth of organic aggregates by the hydrophilic and hydrophobic interactions with solvents and molecules they are called soft template. Soft templates are often made up with surfactant solutions. Various shapes, like spherical or rod-like soft templates can be made depending on the surfactants. Scientist has also realized the formation of nano structures of various shape from a single organic molecule by only changing the reactant/surfactant ratio.\textsuperscript{60} As a hard template ordered porous membranes like anodized aluminum oxide (AAO), silica, nanochannel glass, and iontrack-etched polymers are often used. After filling the pores with organic molecules the templates are often treated thermally to increase the crystallinity of the nanostructure.\textsuperscript{61}

One dimensional nano and micro scale organic solid structures are potential components for miniaturized devices. The most fascinating aspect of 1-D organic nanomaterial is their opto-electronic and photonic properties, which are fundamentally different from their inorganic counterparts. The luminescence efficiency, energy levels can also be fine tuned by rational design of small organic building block. The weak intermolecular interactions between the molecules can also be manifested into the photo-physical and photo-chemical processes, including energy transfer, charge transfer, exciton coupling and diffusion.

1-D organic solids are promising candidates to manipulate and guide optical waves in the nano/submicro/micro domains, because the refractive index ($n$) of the organic solid is usually higher than the surrounding medium.\textsuperscript{62} Based on the type of light a 1-D solid propagates, organic optical wave guides are classified into \textit{active} and

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Passive optical wave guiding behavior of a bent organic submicro tube illuminated with 488 nm laser source. Adapted from ref. 64.}
\end{figure}
passive-waveguides. In active wave guides,\textsuperscript{63} the molecular building block of the organic solid is electronically excited and the coupled exciton-polariton propagates to the opposite end of the elongated wave guide. Here, the wave length of the output light is longer than the input light due to electronic excitation of molecular building blocks and resultant fluorescence. There are quite a few excellent examples reported for this type of exciton-polariton based wave guides.\textsuperscript{63} On the other hand, passive organic wave guides function almost similar to commercial optical fibers, i.e., here the input light directly propagates along the organic medium to the output end.\textsuperscript{64} Most of the \(\pi\)-conjugated organic molecules have absorbance window in the range of ultra-violet (UV) light. The use of laser light energy in the range of the absorbance window of the molecule leads to electronic excitation and subsequent fluorescence. Hence to create passive organic wave guides, Chandrasekar and coworkers have used visible lasers (Ar\(^+\) 488; Nd:YAG 532 and He:Ne 633) to avoid the unwanted fluorescence light generation in their light-organic tube interaction studies (Fig. 1.7). For their surprise, orthogonal illumination of laser light at one of the open end (input) of a linear tube showed propagation of the laser to the opposite exit end of the tube. They have also observed similar results for the bent tubes and \textit{directional coupling} behavior in X-crossed tubes. Chandrasekar et al. have also confirmed the weak interaction of the propagating laser light with the organic tube building block molecules by Raman spectroscopy/mapping technique. Organic optical wave guide also exploited to electronically excite a meso-tetratolylporphyrin molecular nano-sheet kept ca. 20 \(\mu\)m away from the main 488 nm laser source (Fig. 1.8).

Other than the organic optical wave guiding property the 1-D nanowires can be used for optically pumped laser with the increase of the excitation power,\textsuperscript{65} and multicolour emission.\textsuperscript{66} Yao and co workers used the organic 1-D structures extensively for tunable emission from a nanowire containing two components through FRET,\textsuperscript{67} waveguide modulators,\textsuperscript{68} electroluminescent device,\textsuperscript{69} heterojunction solar
cells,\textsuperscript{70} and also as chemical sensors.\textsuperscript{71}

1.6 Historical Perspective of a Building Block Molecule: Bispyrazolyl Pyridine (BPP):

After the first synthesis of 2,6-bispyrazolyl pyridine (BPP) by Goldsby et al. in 1990, BPP has attracted a great attention among the inorganic chemist due to its structural resemblance to a well-known terpyridine (terpy) ligand. Recently, 2,6-bistriazolyl pyridine (btp) and 2,6-triazolylpyrazolylpyridines (tpp) were also added into the club of tridentate ligands (Fig. 1.10). Due to its moderate ligand field strength BPP shows unique magnetic phenomenon such as spin crossover (SCO) effect with Fe(II) ion.\textsuperscript{74} Eleven years after the discovery of BPP, Halcrow et al. have shown its coordinating ability as a tridentate ligand with Ni(II), Co(II) and Cu(II) metal ions.\textsuperscript{72} As the chemistry of tridentate ligand like terpyridine reached its saturation level, more and more scientists turned towards BPP. In 2002 Brunet and co-workers have first synthesized water soluble macrocyclic chelates by connecting diethylenetriaminepentaacetic acid to 2,6-bis-pyrazolylpyridine. The chelates shows high luminescence properties upon binding with Eu(III) and Tb(III) metal ions. They also proposed the energy transfer from ligand (BPP) to lanthanide metal centre.\textsuperscript{73} In the same year Halcrow et al. have reported the temperature dependent reversible spin crossover property (High-spin; $S=2 \leftrightarrow$ Low-spin; $S=0$) of an octahedral

![Figure 1.10](image)
[Fe^{II}(BPP)_{2}(BF_{4})_{2}] complex displaying $T_{1/2}$ at 260 K (Fig. 1.10).^{74} BPP ligand also form redox active metal complex Ru(II) ion.^{75} BPP and its derivative 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine (Me_{4}BPP) also form coordination complexes with Ni(II)^{76} Ru(II) ions.^{75}

In 2005 Giorgio et al. have developed a one-pot synthetic route that allows functionalization of the BPP backbone in the 4- and 4''-pyrazole carbons by direct H(4)-pyrazole halogen exchange. The symmetrically substituted di-iodo derivative provides easy access to additional functionalities through both Sonogashira and Grignard exchange reactions. In 2006 Chandrasekar and co workers have synthesized a 1-D supramolecular head-to-tail N^{+}-H···N hydrogen-bonded chain of the complex [Fe^{II}(L)_{2}H](ClO_{4})_{3} MeOH [where, $L = 4''$-(4'''-pyridyl)-1,2':6'1''-bis(pyrazolyl)pyridine] which exhibits a reversible, thermally driven spin transition at $T_{1/2} = 286$ K with a hysteresis loop ($\Delta T_{1/2}$) of ca. 2 K (Fig. 1.11). In the same year Halcrow and coworkers functionalized the 4-pyridyl carbon of BPP with nucleobase substituents, and also first time synthesized the back-to-back coupled BPP having a CH_{2}-CH_{2} spacer.^{77} In 2007, Chandrasekar and coworkers have reported the synthesis of a back-to-back coupled BPP ligand bridged by a phenyl spacer and its 1-D metallo-supramolecular polymer with Fe(II) ions exhibiting $T_{1/2}$ at 323 K with a ca. 10 K wide hysteresis loop. Several SCO complexes and their $T_{1/2}$ dependency on lattice solvent,^{78} guest desorption have also been studied.^{79} Oshio et al. have synthesized an Fe(II) complex using a BPP ligands carrying...
doublet state nitronyl nitroxide radicals, to study the interplay between bulk magnetism (exchange coupling) and SCO effect.\textsuperscript{80} In 2008, BPP attached to thiol anchoring groups and its SCO Fe(II) compound was synthesized for single molecule conductivity studies (Fig. 1.12).\textsuperscript{81} From 2009 onwards a lot of chemistry developed towards the functionalization of BPP unit. Kadjane and coworkers synthesized a nona-coordinating precursor using a regioselective strategy for nucleophilic aromatic substitution on polyfluoropyridines. The noncoordinating BPP ligand upon coordinating with rare earth metals like Tb, Eu, Yb afforded numerous applications for near-IR emission, two-photon absorption spectroscopy, or the formation of luminescent gels.\textsuperscript{82} Light induced excited state spin trapping (LIESST) property of BPP based Fe(II) complexes displaying SCO effect has also been demonstrated.\textsuperscript{83}

In 2010 for the first time Chandrasekar et al. have exploited the BPP derivatives to fabricate fluorescent nanotapes and nearly monodispersed submicrotubes in a controlled manner via a supramolecular bottom-up self-assembly approach.\textsuperscript{84} Holliday et al. have developed a conductive metallopolymer from thiophene appended bispyrazolyl pyridine coordinated to Ru(II) ion by electropolymerisation method (Fig. 1.13).\textsuperscript{85} His group further reported on the synthesis of a red luminescent nine-coordinated Eu(III) complex of BPP and its photo-physical properties. The solid-state structure of complex has been determined by single-crystal X-ray crystallography and shows the geometry of the local coordination environment around the Eu(III) ion to be a slightly distorted tricapped trigonal prism (see chapter 4).\textsuperscript{86} Ye and co workers have developed a dual-BPP based chelating ligand. The ligand shows weak luminescence on chelating with Tb(III) ion, but can be selectively and strongly enhanced upon reaction with Zn(II) ions. The Tb(III) chelate-based luminescent chemosensor is highly selective and sensitive towards the detection of Zn(II) ions in living cells.\textsuperscript{87} In 2011 Nishihara and co workers have designed and synthesized bispyrazolyl pyridine decorated with stilbene and its Fe(II) complex exhibiting a visible light photoisomerization from Z-2 to E-2, both in solution and in solid phases. The Z- isomer remains in the high-spin state in temperature range between 2-300K, whereas E-2 displayed a SCO phenomenon between

\textbf{Figure 1.13} BPP based electropolymer, synthesized by Holliday et al. Figure adapted from ref. 85.
100 K and 300 K.\textsuperscript{88} Oshio et al. have prepared Fe(II) complexes with neutral and oxidized tetrathiafulvalene (TTF). X-ray crystallographic analyses, magnetic and electrical resistivity measurements of this complex suggested the influence of SCO effect on electrical conductivity.\textsuperscript{89} Ruben and co workers have synthesized two BPP functionalized with pyrene moieties through linkers of different lengths. In one of the ligand the pyrene group is directly connected to the BPP moiety via a C–C single bond, while in the other ligand it is separated by a benzyl ester group involving a flexible butanoic chain. The flexible chain of ligand in Fe(II) complexes prevents structural constraints allowing for reversible spin transitions, but in other one where pyrene is directly attached with BPP is blocked in its high spin state due to constraints caused by a strong intermolecular $\pi$-$\pi$ stacking in its structure.\textsuperscript{90} In 2012 Chandrasekar and co workers synthesized a series of nitronyl-nitroxide (NN), oxoverdazyl (OVZ) based mono-, and bi-radicals attached to 4-phenyl-2,6-bispyrazolylpyridine coupling unit and studied their intramolecular spin-spin coupling behavior by cryogenic electron spin resonance (ESR) spectroscopy and by computational analysis.\textsuperscript{91} At the same time Ziessel and coworkers have prepared lanthanide complexes of ligands constructed from a BPP core bearing various chelating arms with anionic mixed carboxylate/phosphonate substituents. They reported these ligands to form particularly stable complexes with Eu(III) and Tb(III) which display outstanding spectroscopic properties suitable for bio-labeling.\textsuperscript{92}

1.7 Metallo-Supramolecular Polymers (MSP):

Supramolecular materials\textsuperscript{93} have attracted attention and grown tremendously over the last two decades after the Nobel Prize winning work of Lehn, Pederson, and Cram in 1987 on “molecular structure specific interactions studies”.\textsuperscript{94} Now it is well known that hydrogen bonding (5–30 kJ/mol),\textsuperscript{95} $\pi$-$\pi$ interactions (8–12 kJ/mol),\textsuperscript{96} and metal coordination (29–46 kJ/mol)\textsuperscript{97} offer supramolecular interactions. The weak interactions among the supramolecular polymers differ from conventional polymers as the noncovalent interactions can be reversible in nature which has led to their use as stimuli-responsive materials. The stimuli-responsive materials are susceptible to various environmental factors such as temperature, pressure light, chemical interactions and so on.

If the supramolecular polymer contains a metal which is held by coordination bond the resulting polymer is called metallo-supramolecular (MSP) polymer. MSPs are
attractive because they combine the mechanical properties and processability of polymers with the inherent functionalities of metal ions. Depending upon the position of metal-ligand complex in the polymer chain the MSP can be classified as main-chain, side-chain, branched, crosslinked, star-shaped, dendritic, or helical polymer.

1.7.1 Main-Chain Metallosupramolecular Polymers: Main chain MSPs contains directly incorporated metal-ligand moiety into the polymer chain. This type of polymers can be obtained by addition of the appropriate metal-ions to a ditopic ligand end-capped monomer in a 1:1 ratio resulting a MSP with many metal-ligand complexes along the polymer backbone. Rehahn and coworkers have first prepared a main-chain MSP by adding Ag(I) or Cu(I) to a solution of ditopic phenanthroline ligand derivatives (Fig 1.1).

Figure 1.14 Main Chain metallo-supramolecular polymers synthesized by Rehahn et al. Figure adapted from ref. 105.

Schubert and coworkers have reported the synthesis and characterization of a series of main-chain MSPs by combining a ditopic terpyridine end-capped poly(ethylene glycol) with a variety of

Figure 1.15 (a) Ditopic terpyridine end-capped poly(ethylene glycol) metallo-supramolecular polymer prepared by Schubert et al. (b) Water-Soluble reversible Nd(III) branched coordination polymers synthesized by Stuart et al. Figures adapted from ref. 106 and 107.
transition metal-ions to achieve high molecular weight polymers (Fig 1.15a).\textsuperscript{106} Cohen Stuart and coworkers have prepared multiple examples of water-soluble and highly branched or cross-linked Nd\textsuperscript{3+} containing MSPs by using a short poly(ethylene glycol) chains end-capped with pyridine-2,6-dicarboxylate ligands (Fig. 1.15b).\textsuperscript{107}

Currently, much attention has been directed towards the creation and exploitation of MSPs as functional materials. Swager and coworkers have reported the use of an Co(II) based electropolymerizable MSPs as a sensor for nitric oxide (NO) monitored by polymer conductivity.\textsuperscript{108} Terech and coworkers have prepared a small molecular weight gelator comprised of two different types of metal-ion receptor sites terpyridine end-groups with a cyclam core. The gel formed by complexation of Co(II) or Ni(II) show stimuli-responsive property including mechanically-induced gel-sol transitions (thixotropic) and electrical stimulus.\textsuperscript{109} Rowan and coworkers developed benzimidazol based MSP exhibiting diverse properties such as, multi-responsive gels,\textsuperscript{110} thermo-, photo-, and chemo-responsive shape-memory functions,\textsuperscript{111,112} coupling\textsuperscript{113} and decoupling\textsuperscript{114} of optical properties, in situ formation of metal nanoparticle in polymer films,\textsuperscript{115} MSP gels having rheological behavior\textsuperscript{116} and optically healable polymers\textsuperscript{117} (Fig. 1.16).

\textbf{Figure 1.16} Multi-responsive and multi-stimuli metallo-supramolecular polymers prepared by Rowan et al. Figures adapted from ref. 110, 115 and 117.

\textbf{1.7.2 Side-Chain Metallo-Supramolecular Polymers:}

An important property of metal-containing polymers is that they can display interesting optical and electronic characteristics depending on the metal ions. In this
regard the metal ions from the lanthanide series are particularly interesting because of their characteristic intense emissions with distinctive colors depending on the choice of metal. Tew and coworkers\textsuperscript{118,119} investigated the optical properties of poly(methyl methacrylates) (PMMA) functionalized with terpyridine groups on the side-chains coordinated with different lanthanides (Eu(III) and Tb(III)). Films prepared by coordination with Eu(III) displayed a characteristic red metal-based emission while those prepared with Tb(III) show green emission. They generated a unique yellow luminescence when these two different metal ions were incorporated into the same molecular backbone at a 1:1 ratio, producing an alloy which generates a selective thermochromism, from yellow to orange/pink, when the film was heated above 50 °C (Fig. 1.17). They also reported a novel white-light emitting terpyridine based MSPs, comprises of two-emitter system, a blue-emitting dysprosium-chelated polymer and a red-emitting ruthenium complex.\textsuperscript{120}

Tieke and coworkers prepared several terpyridine based side chain MSPs,\textsuperscript{121,122} where they varied the main chain by phenyliminofluorene,\textsuperscript{121} polyaniline derivatives.\textsuperscript{123} They have also synthesized conjugated copolymer with poly(phenylene-alt-fluorene) main chain and 2,6-bis(10-methylbenzimidazolyl)pyridine (bip) ligands attached to the main chain via flexible spacer groups through Pd-catalyzed Suzuki coupling of the 2,7-bispinacolatoboron ester of 9,9-dihexyfluorene and a 1,4-dibromobenzene derivative carrying two o-bip-substituted alkoxy groups in the 2- and 5-positions.\textsuperscript{124} Coupled with Layer-by-layer assembled films from metal ion complexes they have found the reversible ionochromism upon anodic oxidation. They also proposed

\textbf{Figure 1.17} a) Structures of PMMA functionalized with either one type of terpyridine:Ln\textsuperscript{3+} complexes in the side-chain (Ln\textsuperscript{3+} = Eu\textsuperscript{3+} or Tb\textsuperscript{3+}) (1.9) or a combination of lanthanides in a 1:1 ratio. b) Images (\(\lambda_{ex} = 350\) nm) of an irreversible thermo-responsive change in emission by heating two homo polymers to give a new blend and c) new thermo-reversible emission change of the new mixed metal system resulting from quenching of the green Tb\textsuperscript{3+} emission at elevated temperatures. Figures adapted from ref. 118.
the films might be useful as active materials in electrochromic devices, metal ion sensing and for preparation of fluorescent coatings (Fig. 1.18).

Figure 1.18 Structures of side-chain metallopolymers synthesized by Tieke et al.

1.7.3 Metallo-Supramolecular Polymers - Characterization and Difficulties:

Since the first development of terpyridine by Morgan and Burstall,\textsuperscript{125} it has been widely used as building blocks in various MSPs.\textsuperscript{126} Terpyridine is known to form kinetically inert bonds with Ru(II), Ni(II), Os(II), and Fe(II) and they form stable MSPs, which can be characterized by standard techniques, including gel permeation chromatography (GPC), viscosity and analytical ultra-centrifugation.\textsuperscript{127} Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) is not useful since the polymer assemblies tend to fragment during the experiment.\textsuperscript{127a} On the other hand terpyridine forms much weaker bonds (low binding constant) with other metal ions such as Zn(II), Cu(II) and lanthanides. As the resulting MSPs exist in equilibrium with free ligand and metal ions, the polymer properties becomes sensitive towards external stimuli like temperature, solvent, concentration and the nature of the counter ions. These types of labile stimuli responsive polymers are not stable during the GPC run. They can be only characterized by solution based techniques like NMR, UV-Vis spectroscopy and viscosity measurements.

1.8 White Light-Emitting Polymer Materials:

White light-emitting devices based on small organic molecules, oligomers or polymers (WOLEDs/WPLEDs) have attracted much attention among both the scientific and the
industrial communities due to their potential applications in areas such as full-colour flat-panel electroluminescent (EL) displays, back-lighting sources for liquid-crystal displays and next-generation solid-state lighting sources (Fig. 1.19).\textsuperscript{128} Recently, the WOLEDs attracted particular interests because they have advantages over a fluorescent lamp which contains significant amounts of toxic mercury in the tube and incandescent lighting bulb which converts 90% of consumed power into heat. Indeed several laboratories have achieved power efficiency of WPLEDs exceeding 20 lm W\textsuperscript{−1} which outperforms incandescent light bulbs in efficiency,\textsuperscript{129} suggesting WPLEDs can find practical applications as large area lighting sources in the near future.

In 1931, Commission Internationale d’Eclairage (CIE) set up a set of standard colorimetric system, referred to as CIE 1931, which is the most widely used colorimetric system so far. CIE 1931 regulates that the color coordinates of equal energy point of white light are (0.33, 0.33) (Fig. 1.20). According to optical principles, all the colors can be achieved by mixing the three primary colors (red, green, and blue), so white light can also be obtained in this way. The white light emitting polymer can be generated by many ways some of them are discussed here.

1.8.1 Small-Molecule-Doped Polymer Type:

In this method the host polymer materials are doped with a little amount of narrow band-gap small light-emitting molecules, and then the incomplete energy transfer can be used to achieve white light emission. The host polymer is generally blue or sky blue light-emitting materials and can be mixed with one, two, or multiple kinds of guest materials,
whose doped contents are about 1000 to 1%. Weight percentage is more often used than mole percentage in lots of reported papers. The thermodynamic compatibility for most of the material systems has not been investigated so far. So if the system of guest and host has no enough thermodynamic stability, there is a potential phase separation, which will leads to decreasing the efficiency and color stability. Since the existence of excimer, the emission spectrum of the material itself will be widened, this provides conditions to prepare PWLED. However, up to now, the thermodynamics and kinetics of excimer formation for conjugated polymer are not very clear and need further investigation. Tsai et al. synthesized a light-emitting polymer through ring-opening metathesis polymerization, which shows excimer based emission, formed due to anthracene chromophore between side chains (Fig. 1.21).

### 1.8.2 Polymer Blend Type:

The principle of fabricating white emission device using polymer blend is similar to that of a small-molecule-doped white emission polymer. The wide-band-gap host materials are also doped with a small amount of guest light-emitting polymers, using incomplete energy transfer to obtain white emission. The amount of doped-chromophore is very small (generally one-thousandth magnitude, mass content). The light color can also be changed by adjusting the primary colors and doping content. Compared with small-molecules-doped polymer, this method is generally considered to possess the advantage against phase separation and thereby improving the device stability.

### 1.8.3 Fluorescent Molecule-Dispersed Polymer Type:

Doping method and polymer blend method in fabricating PWLED are generally discouraged due to phase separation problem, which leads to declined device efficiency and poor reproducibility. One solution is chemically embedding the low-band-gap dye in the conjugated polymer main chain. Stable white emission can be achieved by adjusting the ratio of chromophores and controlling the energy transfer. Additionally, as the doped chromophores disperse at the molecular level, a homogeneous system with high energy transfer efficiency can be obtained. The low-band-gap chromophore can be embedded into the polymer host chain.
and also can be suspended in the polymer side chain, during the materials design and synthesis, this approach has great control space (Fig. 1.22). In 2005, Wang et al. for the first time reported the construction of a single polymer displaying white light emission by embedding a red chromophore along the blue chromophore polymer’s main chain, and suspending a green chromophore in the polymer’s side chain. As a result red, green, and blue chromophores were successfully incorporated in a single polymer chain. Subsequently, by adjusting the ratio of chromophores, they obtained highly efficient PWLED.

**1.8.4 Phosphorescent Molecule-Dispersed Polymer:** Phosphorescence dye molecule can also be chemically dispersed into the polymer. Because of its high efficiency the doping amount is extremely small, which could effectively avoid phase separation problem. Additionally, the use of triplet and singlet excitons, further improved the efficiency. Cao and coworkers have first introduced the triplet phosphorescent material into the molecule-dispersed (EL) material and developed a new type of single molecule white EL material (Fig 1.23). The host polymer was blue polyfluorene, where the main chain was doped with a little yellow green benzothiazole chromophore. The side chain was grafted with the red triplet iridium complexes. Adjusting the ratio of copolymerizing chromophores gave a pure white EL with a color coordinates (0.32, 0.33) very close to
white light. There are many fluorine based polymer system are reported by grafting triplet state Ir based complex onto the side chain,\textsuperscript{134,135} or the main chain of the polymer.\textsuperscript{136}

1.9 A Brief Overview of Spin Cross-Over Effect:

The spin cross-Over (SCO) phenomenon was first discovered more that 60 years ago by Cambi et al. in 1930s, on the observation of unusual magnetic properties of dithiocarbamato complexes of Fe(III).\textsuperscript{137} They interpreted, erroneously, the observation of temperature-dependent moments as arising from equilibria between two magnetic isomers. However after development of ligand field theory (LFT),\textsuperscript{138} and the principle of the SCO phenomenon, and the thermal condition to be fulfilled in order to observe it, are now well understood.\textsuperscript{139}

![Figure 1.24](image)

\textbf{Figure 1.24} Schematic representation of the spin cross-over phenomenon for octahedrally coordinated Fe(II) ions (\(\Delta_{\text{O}}\): ligand field splitting parameter; EP: spin pairing energy; \(k_B\): Boltzmann constant; \(T\): temperature).

The SCO phenomenon is only occurred in octahedral complexes of first-row transition metal ions with 4–7 3-D valence electrons. The spin state (LS\textrightarrow HS) interconversion can be achieved by applying external perturbations such as temperature (T), pressure (p) and electromagnetic radiation (h\(\nu\)). There are no SCO examples known with 4d and 5d transition elements. Because the ligand field strength increases by roughly 50% on going from 3-D to 4d and from 4d to 5d elements, whereas the spin-pairing energy does not change much in this order. Thus, octahedral 4d and 5d complexes show a strong tendency to adopt LS behavior. When all other factor retains unchanged increase of oxidation number increases the ligand field strength about 40–80%, for e.g., the ligand field strength of Fe\(^{2+}\) complexes increases by about 40% upon oxidation to the corresponding Fe\(^{3+}\) complexes, while the spin-pairing energy does not increase that much.
Thus, one can hardly expect that a SCO complex of Fe(II) will still exhibit SCO behavior after oxidation to the corresponding Fe(III) complex. Tetrahedral SCO complexes of 3-D elements are not known, because the ligand field strength is only about half than that of octahedral complexes, thus favoring HS behavior. Till now most SCO complexes known are of Fe(II), Fe (III), and Co(II). Only a few SCO complexes of Mn(II), Mn(III), Cr(II), and Co(III) have also been reported. The first SCO phenomena of Fe(II) was reported in the literature are [Fe(phen)$_2$X$_2$] (where, phen = 1,10-phenanthroline; X = NCS, NCSe), frequently called the “classical” Fe(II) SCO complex. This Fe(II) SCO complexes also show difference in the Fe-N bond distances of about 0.2 Å between HS ($S=2$) and LS ($S=0$) states (Fig. 1.24). 

The SCO phenomenon is much less frequently observed for Co(II) than for iron(II) complexes. The first spin transition in a six-coordinate cobalt(II) compound was reported by Stoufer et al. The Co(II) six-coordinate compounds undergoes spin transition with the change of electron configuration $t_{2g}^6e_g^1(\text{E}_g; \text{LS}) \leftrightarrow t_{2g}^5e_g^2(\text{T}_1g; \text{HS})$. Some changes have also observed for four-coordinate and some five coordinate complexes of Co(II). But the phenomenon is believed to be configurational equilibria between the complexes. Ni(II) complexes are known to show spin state equilibria in solution. However, in all these cases, changes of spin states arise from configurational changes such as tetrahedral, HS ↔ square planar, LS.

### Effect of Chemical Moieties in SCO:

In the early stage of SCO research, it was recognized that SCO behavior can vary considerably with the nature of the coordinated ligands. The changes of the chemical composition influence the ligand field strength acting at the central metal ion in several ways: viz. σ-interaction between metal and donor atom, steric hindrance by rotating substituent close to the donor atom influences the distance, r, between the metal and the donor atom and thereby the ligand field strength according to $Dq \approx 1/r^5$ equation; Hydrogen bonding; π–π stacking of ligands, formation of 1-D, 2-D, and 3-D polymer through weak supramolecular interaction is also known to influence spin transition. As these influences operate in a concerted manner it is almost impossible to make reliable predictions of the effectiveness of the various contributions. Counter anions and trapped solvent molecules also have known to affect the spin crossover behavior. Scientists have also studied the isotope-effect with H/D- and $^{14}$N/$^{15}$N-labeled SCO compounds to explore hydrogen bonding networks and stepwise spin transitions.
1.9.2 Physical Influences on SCO Behavior: The influence of pressure on SCO behavior is very well known and studied. With the increase of pressure the distance between metal and donor atom decreases resulting HS to the LS state. The low spin state of a SCO compound is generally stabilized and the $\chi T$ vs $T$ curve tends to be shifted upwards on the temperature scale.

1.9.2.1 Light-Induced Excited Spin State Trapping (LIESST): It is a method of changing the electronic spin state of a compound by means of irradiation with laser light at low temperatures. The phenomenon was first discovered on a single crystal of the SCO compound [Fe(ptz)$_6$](BF$_4$)$_2$ (ptz =1-propyltetrazole), when it was irradiated with green laser light. The green light converts the LS state to a long-lived metastable HS state with a lifetime of hours at cryogenic temperatures. Later it was also found that the metastable HS state can revert back to the LS state by irradiating the crystal with near infrared light. Light-induced SCO and HS$\leftrightarrow$LS relaxation have been well examined experimentally and theoretically by Hauser. When the green light was irradiated into the polymer embedded single-crystal or polycrystalline [Fe(ptz)$_6$](BF$_4$)$_2$ complex, it undergoes transition from $^1A_1$ to $^1T_1$ state, followed by two successive intersystem crossing (ISC) processes $^1T_{1,2} \rightarrow ^3T_{1,2} \rightarrow ^5T_{1,2}$ and populate the HS state $^5T_2$. Radiative decay from $^5T_2 \rightarrow ^1A_1$ is spin and parity forbidden, and due to the considerably larger M-L bond distance in the HS state as compared to the LS state, which builds up an energy barrier between the potential wells of the two states (Fig. 1.25), the lifetime of the metastable HS state can be very long. Recently many light induced phenomena such as light-induced thermal hysteresis (LITH), light-induced optical hysteresis (LIOH), hard-X-ray-induced excited spin state trapping (HAXIESST), hard-X-ray-induced thermal hysteresis (HAXITH), nuclear de-cay-induced excited spin state trapping (NIESST), electron-induced excited spin state trapping (ELIESST), ligand-driven light-induced spin change (LD-LISC),...
light-induced cis/trans-isomerization\textsuperscript{88} have also been investigated.

In 2011, keeping future molecule based spintronic devices in mind, Ruben and van der Zant et al. have demonstrated the electric field control of the SCO effect, which allows a local, fast, and direct manipulation of single molecular spins, as an important prerequisite for molecular spintronics.\textsuperscript{161}

1.9.3 Overview and Future Perspective: Kahn first proposed that spin transition polymers bear the potential for applications in memory devices. Recently in all publications dealing with SCO studies the authors emphasize this aspect.\textsuperscript{162} In view of application of SCO, thin films,\textsuperscript{163} gels,\textsuperscript{164} nanoparticles,\textsuperscript{165} cages,\textsuperscript{166} micro/nanoporous materials,\textsuperscript{167} and multifunctional SCO systems\textsuperscript{168} are currently under extensive exploration. To use the spin crossover complexes as multifunctional materials, scientists also have combined the SCO behavior with other physical phenomena such as liquid crystalline properties,\textsuperscript{169} electrical conductivity,\textsuperscript{170} fluorescence,\textsuperscript{171} etc.

1.10 A Brief Overview of Soft Lithographic Techniques:

1.10.1 Micro- and Nanotechnologies Lithography:

Lithography serves a tool to fabricate microelectronics and optoelectronic circuits there by position itself as a central contributor to information technology (IT). An advance in lithography is directly related to the increase in the integration density of silicon chips in modern technology and it is almost in accordance with Moore's Law. The progress in lithographic techniques has lead to an increase in chip yield and a reduction in the chip cost, subsequently steep fall in electronic device price. The past two decades have seen an exorbitant growth in the microelectronics production and associated technologies. Usage of microelectronics impacts on technologies such as communications, computer science, medicine, energy, and more recently, home entertainment and thereby affects our \textit{day-to-day} life. Lithography not only serves in the area of microelectronics but also in the fabrication of sensors, microreactor, combinatorial arrays, microelectromechanical systems (MEMS), microanalytical systems, micro-optical systems, OLEDs and so on.
1.10.2 Conventional Lithography Approaches:

There are two approaches commonly used to fabricate nano/micro structures on various substrates known as “top-down” and “bottom-up” approaches. The top-down approach essentially impose a structure or pattern on the substrate being processed e.g., lithography, writing, stamping, etc. On the other hand the bottom up approach uses interactions between molecules or colloidal particles to assemble discrete nanoscale structures in two and three dimensions. Top-down techniques mainly include photolithography and scanning beam lithography (e.g. electron beam and focused ion beam lithography). The limitations of these conventional approaches are their high capital, large processing time and operating costs, the difficulty in accessing the facilities necessary to use them motivate the exploration and development of new, or “unconventional nanofabrication techniques.

1.10.3 Photolithography:

It is a process in which UV light is used to transfer a geometric pattern usually called photomask to a light-sensitive chemical "photoresist", on the substrate (Fig. 1.26). In current semiconductor nanofabrication industry photolithography is an extensively used technique and it can pattern 37 nm wide features with 193 nm wavelength light. Photolithography is usually carried out using one of two different ways: contact (or proximity) printing or projection printing. In contact printing the photomask is kept in contact with the resist film. The maximum resolution of contact mode photolithography is typically 0.5-0.8 µm when UV-visible light (360-460 nm) is used and it is primarily determined by diffraction that occurs as the light passes through the gap between the mask and the resist. The drawback of this technique is that the mechanical contact of photomask with the resist film, which can damage fragile structures on the mask or the sample.
In projection printing, a system of lenses was placed between the mask and the resist film. The features on the resist can be significantly smaller than those on the mask. In recent times all integrated circuits are manufactured by projection photolithography. The theoretical resolution (R) of an optical system for projection printing is limited by Rayleigh diffraction (eq 1.2).\(^{173}\)

\[
R = \frac{k\lambda}{NA}
\]

\(\lambda\) = Wavelength of light
NA = Numerical apperture of the objective
\(k\) = A constant that depends on the imaging technology and process control but typically must be 0.7 for adequate production yield.

State-of-the-art photolithographic techniques are capable to reach the limit as small as ~ 250 nm.\(^{174}\) Photolithography in the regime less than 100 nm include extreme UV (EUV) lithography, soft X-ray lithography, electron-beam writing, focused ion beam (FIB) writing, and proximal-probe lithography.\(^{175}\)

1.10.4 Soft Lithographic Techniques:

Although these photolithography techniques are capable to generate extremely small features (as small as a few nm), but they are not economical, poorly suited for patterning of nonplanar surfaces, specific chemical functionalities on surfaces cannot be generate by this technique and completely dependent on the photoresists. In order to avoid all these drawbacks a new technique called soft-lithography has come up. The soft-lithographic techniques can be subdivided as i) microcontact printing (μCP),\(^{176}\) ii) replica molding (REM),\(^{177}\) iii) microtransfer molding (μTM),\(^{178}\) iv) micro-molding in capillaries (MIMIC),\(^{179}\) v) UV-molding, vi) embossing, vii) nanoinprint lithography, viii) solvent-assisted micromolding (SAMIM),\(^{180}\) ix) microcontact printing, x) nanotransfer printing, xi) microinjection molding,\(^{181}\) and xii) lithographically controlled wetting.\(^{39a}\)

All the soft lithographic techniques share the common feature of using a patterned elastomer as the stamp called mold, which is used to generate micropatterns and microstructures. The fabrication of an elastomeric mold is presented in Fig. 1.27 the elastomeric stamp or mold is prepared by cast molding. A prepolymer of the elastomer is poured over a master having relief structure on its surface, and then cured (Fig. 1.27b)
and peeled off (Fig. 1.27c). The mold replicates the negative features of master, and can be used to fabricate or pattern the next material. The master is, in turn, fabricated using microlithographic techniques such as photolithography, micromachining, e-beam writing, or from available relief structures such as diffraction gratings, TEM grids, polymer beads assembled on solid supports, and relief structures etched in metals or Si.

Soft lithography is not independent of clean room facilities and high-cost equipment in view of master fabrication. The strength of soft-lithography is rather in replication. Once the master is created with the expensive or low-throughput equipment, it can be used more than 50 times. Thus it overcomes the limits of slow throughput compared with scanning beam lithography and makes the soft lithography an attractive alternative in nano scale patterning. Soft lithographic techniques can be divided into major three groups of i) replica molding, ii) UV molding, iii) embossing, and iv) printing, each having sub-groups of techniques.

### 1.10.4.1 Replica Molding:

Replica molding (RM, REM) transfers the pattern of the master into PDMS. First a photo- or thermally curable prepolymer was poured onto the master. The liquid prepolymer takes the shape of the master and exposure to UV radiation or suitable temperature induces the cross linking, making the polymer solid. Peeling off the mold from the master creates an inverse replica. The process described in Fig. 1.28. The polymer mold is often made of poly(dimethylsiloxane) (PDMS). The soft polymer...
mold can be used as a master in the next step, to mold another liquid prepolymer, such as polyurethane (PU)\textsuperscript{186}. This is depicted in Fig. 1.28. A microstructure fabricated by replica molding is shown in Fig. 1.29. Replica molding is able to produce numerous molds, replicas, and patterned surfaces from each master. Replica molding has transferred 30-nm lateral features from a diffraction grating.\textsuperscript{187} The smallest features replicated using PDMS are \~3-nm wide structures\textsuperscript{188} and \~0.5-nm vertical deflections.\textsuperscript{189} Replica molding against a rigid mold with an appropriate material (usually a thermoplastic polymer) has been used for the mass-production of a wide range of structured surfaces such as compact disks (CDs),\textsuperscript{190} diffraction gratings,\textsuperscript{191} holograms,\textsuperscript{192} and micro-tools.\textsuperscript{193} Three techniques related to RM are microtransfer molding (\(\mu\)TM), micromolding in capillaries (MIMIC) and lithographically controlled wetting (LCW).

1.10.4.1.1 Microtransfer Molding:

In microtransfer molding (\(\mu\)TM), a liquid prepolymer, such as polyurethane (PU) or thermally curable epoxy was poured onto the stamp, making sure that the molded PDMS stamp was wetted by the liquid. The excess prepolymer is scraped away using a piece of flat PDMS. Then the stamp is printed manually onto the desired substrates by applying pressure and heat (Fig. 1.30).

The film of polymer that remains between the surface protrusions is called scum, which is around 100 nm in thickness and can be removed using reactive O\(_2\) ion etching (RIE). \(\mu\)TM is capable of generating both isolated and interconnected microstructures. The most significant advantage of \(\mu\)TM over other \(\mu\)-lithographic techniques is the ease with which it can fabricate microstructures on nonplanar surfaces, a characteristic that is essential for building three-dimensional microstructures layer-by-layer. Microtransfer molding is able to produce patterned microstructures of a wide variety of polymers (both pristine and doped with fluorescent dyes such as rhodamine 6G) over relatively large areas (\~3 cm\(^2\)) within a short period of time (\~10 min). Zhao et al. have used this technique to fabricate optical waveguides, couplers, and interferometers from organic...
polymers. Microtransfer molding is capable of generating both interconnected and isolated microstructures. μTM was recently used by Thibault et al. to fabricate homogeneous micropatterns and nanopatterns of SCO nanoparticles of [Fe(NH$_2$trz)](tos)$_2$ over a large area. SCO nanoparticles retain their spin crossover properties (with a transition at around room temperature) after the soft lithography step.

1.10.4.1.2 Micromolding in Capillaries:

During the micromolding in capillaries (MIMIC) technique a soft PDMS master having micro channel structure is used. MIMIC is a simple and versatile soft-lithographic method, introduced by G. Whitesides et al. in 1998. During MIMIC a stamp made of polydimethylsiloxane is placed on a surface to effectively form micro-channels. A low-viscosity prepolymer is then placed at the open ends of the channels, and this liquid instinctively occupies the channels by capillary action. After the complete evaporation of the solvent the stamp is gently
removed and the pattern remains on the surface. The process is shown in Fig. 1.31. The mechanism of this process doesn’t allow creating any scum on the substrate and also it is a single step process. Only micro-channels can be fabricated with this technique. The resulting structures are usually thinner than the height of the channels in the PDMS mold but have approximately the same lateral dimensions. Whitesides et al. used MIMIC to fabricate free-standing microstructures of polyurethane. Recently Ruben et al. used MIMIC to pattern continuous SCO sub-micrometric stripes of Fe(phen)$_2$(NCS)$_2$ on a silicon surface.

**1.10.4.1.3 Lithographically Controlled Wetting:**

In LCW a PDMS stamp is placed in contact with a liquid film of ink spread on a substrate. The menisci form under the stamp protrusions due to the onset of capillary forces. As the solvent evaporates, the solution remains pinned to the protrusions and the contact line between solution and substrate recedes due to faster solvent evaporation in the region between protrusions (Fig. 1.32). This makes the region between the protrusions free of solution. As the critical concentration is reached, the solute precipitates onto the substrate only below the protrusions, giving rise to a structured thin film that replicates the positive pattern on the stamp (Fig. 1.32). LCW is suitable for a large number of soluble materials and can be, in principle, pushed down to the limit where ST molecules are patterned into ordered arrays, being this process ultimately limited only by coarsening of the individual molecules.

**1.10.4.2 UV-Molding:**

Ultraviolet-molding (UV-molding) technique is same as the replica molding except hard rigid master and UV radiation is used to crosslink and hardened a UV-curable prepolymer. A simple
schematic diagram of UV-molding is shown in Fig. 1.33. First the prepolymer is poured on top of a master and a UV transparent substrate is placed on top of it and UV radiation is exposed to pass through the substrate. Once it is cured the master is gently taken off and the pattern remains on the transparent substrate.

1.10.4.3 Embossing (Imprinting):

Conventional embossing uses a rigid master (for example, a master made of nickel or SiO$_2$) to imprint relief structures into a thermoplastic polymer (for example, polycarbonate or PMMA) that has been thermally softened.$^{197}$ It is a simple and cost effective process and is the standard for manufacturing replicas of holograms, diffraction gratings, and compact disks (CDs). This technique can also be used for microelectronic circuitry or information storage.$^{198}$ Embossing techniques can be divided into two categories i) nanoimprint lithography (NIL), which uses a rigid master and ii) solvent assisted micro molding (SAMIM), which uses a soft mold as a master.

1.10.4.3.1 Nanoimprint Lithography:

The principle of nanoimprinting is quite simple. The process is first developed by Chou et al.$^{199}$ Fig. 1.34 shows a schematic of the originally proposed NIL process. In this process usually a hard rigid master is used to physically deform a solid polymer film that is on a rigid substrate surface. In this process a hard mold that contains nanoscale surface-relief features is pressed into a polymeric material casted on a substrate at a controlled temperature [usually at its glass transition temperature ($T_g$)] and pressure, thereby creating a thickness contrast in the polymeric material. A thin residual layer of polymeric material is intentionally left underneath the mold protrusions, which acts as a soft cushioning layer that prevents direct impact of the hard mold on the substrate and effectively protects the delicate nanoscale features on the mold surface. The polymer is allowed to deform by filling the voids in the master. Afterwards it is cooled below $T_g$ of the polymer and the master is removed revealing a pattern that is the inverse of the master. The residual layer then removed by an anisotropic O$_2$ plasma-etching process to complete the pattern. NIL has a tremendous impact over the emerging technologies viz. hybrid plastic electronics,$^{200}$ organic electronics and photonics,$^{201}$ nanoelectronic devices in Si,$^{202}$ and in GaAs,$^{203}$ and nonlinear optical polymer nanostructures,$^{204}$ high-resolution organic light-emitting diode (OLED) pixels,$^{205}$ magnetic devices (e.g., single-domain magnetic structures,$^{206}$ high-
density patterned magnetic media and high-capacity disks, problem with the lifetime of the master, because the heating and cooling cycles and pressures it experiences, causes ageing.

1.1.0.4.3 Solvent Assisted Micromolding:

Solvent assisted micromolding (SAMIM) has same operational principles with NIL except that SAMIM uses a solvent instead of temperature to “soften” the polymeric material and an elastomeric PDMS mold rather than a rigid one to emboss relief structures into the surface of a substrate to be patterned. In SAMIM process (Fig. 1.35), a PDMS mold is wetted with a good solvent for the polymer to be stamped and brought into contact with the surface of that polymer. The solvent is selected such that it can only dissolve (or “soften”) the substrate without affecting/swelling the PDMS mold. After the solvent dissipates and/or evaporates, the mold is removed and a patterned relief structure complementary to that on the surface of the mold remains. A wide variety of organic polymers can be embossed, such as polystyrene, polymethyl metacrylate (PMMA),

![Figure 1.34](image1.png) Nanoimprint lithography technique.

![Figure 1.35](image2.png) Solvent assisted micromolding (SAMIM) process.
poly(vinylchloride), cellulose, acetate, and precursors to conjugated organic polymers.\textsuperscript{180,208} SAMIM is capable of replicating complex quasi 3-D relief structures over relatively large areas in a single step. SAMIM is self-cleaning process so dust particles on the surface of the stamp tend to remain in the molded polymer so the mold is cleaned by each cycle. The drawback is, i) some solvents can swell PDMS and as well as the polymer so we have to choose an opposition between the two, ii) a thin layer, typically 10 nm, of polymer is left between the features as in replica molding. This can be removed by O\textsubscript{2} RIE.

1.10.4.4 Printing:

Printing includes material transfer from the mold onto the substrate either physically or chemically. It can be subdivided in following two categories.

1.10.4.4.1 Microcontact Printing:

By micro contact printing ($\mu$CP) an existing surface features can be patterned onto a substrate. A simple scheme of microcontact printing is presented in Fig. 1.36. At first the stamp is inked with a material that is to be transferred on the desired substrate. Then the inked stamp was kept by a conformal contact between the protruding features of the stamp and the solid substrate. Only the protruding features of the stamp touches the surface, and the ink is transferred only at these areas. After the material is transferred from the stamp to the substrate, the stamp was gently peeled off creating the desired pattern. The stamp material is usually PDMS. As the PDMS has a highly hydrophobic substrate to increase the hydrophilicity, PDMS stamps are generally oxidised by UV/ozone or by oxygen plasma treatment if a hydrophilic solvent is needed to be used. The first $\mu$CP was originally developed by whitesides et al. and used as a method to pattern gold. But later its value in patterning surfaces for other applications
quickly became apparent. Since then, μCP has been widely used by researchers in broadly differing fields to pattern water, organic solvents, metals, polymers, DNA, proteins, and cells. Currently its use is versatile in many fields i.e. for the fabrication of organic light emitting diodes selectively metalized the polymeric substrate usage of μCP can give easy access to organic electronic devices as well as biological microarrays. Stoddart et al. developed click microcontact printing to selectively perform click chemistry on an azide terminated surface. The expediency of micro contact printing is that the same stamp can be used multiple times, and the same master can be used to produce several stamps. To ensure a conformal contact between the substrate and the stamp the material of the stamp needs to be elastomeric.

**1.10.4.2 Nanotransfer Printing:**

Nanotransfer printing (nTP) is conceptually very similar to microcontact printing (μCP). In both the cases high-resolution stamps are used to generate patterns of their relief structure. nTP technique relies on the principle of surface chemistry. Here chemically modified surfaces act as interfacial "release" or "glue" layers to aid in transfer printing nanostructured metal ink from relief features ("stamp") to a surface of interest. For example, nTP prints gold film onto thiol terminated monolayer. In this approach the material is only deposited in locations where it is needed. nTP is capable of generating complex two or three dimensional structures in single or multiple layers with nanometer resolution. The method is first developed by Rogers et al. and similar approach has been followed by other groups (Fig. 1.37, 1.38). This method is quite practical to fabricate complex structures that would be quite difficult to fabricate in conventional ways for e.g. large stacks of nanostructures can be fabricated in this method (Fig. 1.38)
silicon wafer or gold substrates which are restricted to most of the patterning process, nTP substrates containing surface OH groups. For example, Rogers et al. printed Au patterns onto ~250 μm thick sheets of poly(ethylene terephthalate) by first spin casting and curing a thin film of an organosilsesquioxane on the PET.

Figure 1.38 SEM and optical microscope images of gold patterns formed by nanotransfer printing. Adapted from 221, 222a.

1.11 Layout of the Thesis:

In this thesis, an attempt has been made to address several functional nanomaterials aspects related to BPP chemistry, which include synthesis, processing and device fabrication. Our primary goal has been to synthesize soluble and processable functional monomers and metallo supramolecular polymers based on BPP derivatives and to fabricate nano-assemblies and devices possessing magnetic and photonic properties. Some of the mainly focused aspects include (i) synthesis soluble and processable Zn(II) containing 1-D metallo-supramolecular polymer using tetra-octylated back-to-back coupled BPP ligand and exploitation of the polymer in the fabrication of millimeter long fluorescent nano stripes on a glass substrate, (ii) using a magnetically bistable Fe(II) coordinated BPP complex, optically transparent flexible future magnetic memory device comprises of several patterns and arrays has been successfully fabricated, (iii) the self-assembly studies of back-to-back coupled BPP ligand shows the formation of blue emitting parallelepipedic nanotubes. Using the surface selective coordination chemistry with red emitting Eu(III) ions a dual emitting (blue+red) nanotubes has been prepared. (iv) BPP based conjugated polymer has been synthesized and used to incorporate metal ions directly to the conjugated polymer back bone containing ligand. Using the multi-colour emission property of the polymer a white light emitting film has also been
developed. (vi) The parallelepipedic nanotubes exhibit optical wave guiding tendency, further more laser ablation has been performed to cut the tubes thereby control the light propagation distance within the organic nano tube.

References
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Chapter 1

Introduction


