

CHEMICAL SCIENCES CLUSTER

Scientific Excellence

Synthesis and Characterization of Furanoid Amino Acids

CSIR-NCL has documented an interesting observation that has many applications in the area of constrained β -amino acids design. In order to provide a missing link between the β -FAAs (beta-furanoidamino acids) and β -ACPC (2-aminocyclopentane-carboxylic acid) homooligomers (a missing link corresponding to the question: what is the role of the heteroatom?), CSIR-NCL had developed methods for the synthesis of parent *cis*-/*trans*- β -furanoidamino acids and synthesized their homooligomers. The detailed NMR/CD assisted secondary structural analysis revealed that the homo-oligomers of two diastereomeric furanoid-beta amino acids (FAA) showed distinct left-handed helicity. The *trans*- β -FAA homooligomers displayed a 12-helical secondary structure like the *trans*- β -ACPC peptides. On the other hand, the *cis*-FAA oligomers adopted a 14-helix structure, which is in contrast to the homooligomers derived from *cis*-ACPC, which adopt a sheet-like structure. This is an important observation, as earlier reports, dealing with the homooligomers derived from a fused bicyclic *cis*-FAA, revealed that a rigid conformation in the monomer is the decisive factor for the observed 14-helical conformation in their homo-oligomers. However, the studies at CSIR-NCL have clearly demonstrated that the rigid conformation may not be a sufficient explanation. By comparing the structural features of *cis*-ACPC and *cis*-FAA hexamers, no marked change was observed in the hydrogen bond strength, but the overall conformation of the *cis*-FAA was seen to be more compact, favoring close dispersion contacts. This is evidenced in comparing DFT with DFT-MP2 results (in association with the researchers at the University of Göttingen, Germany) in which the former lack the description of van der Waals forces. The more compact packing of the *cis*-FAA hexapeptide should be due to a more favorable interaction between the ring and the backbone fold, primarily in the amide hydrogen pointing towards the ring. The replacement of CH_2 with oxygen removes steric repulsion and introduces an electrostatic interaction which allows for a tighter fold.

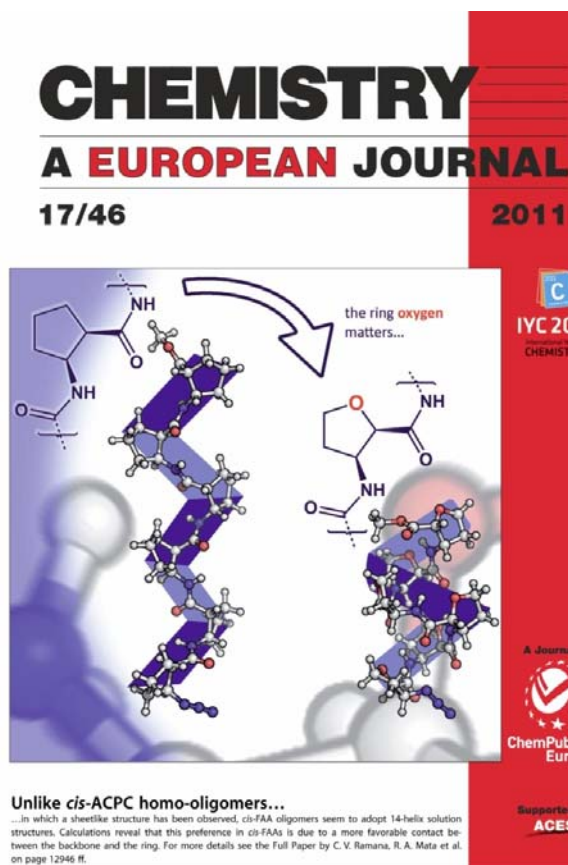


Fig. 1.38 Research work on cover page of the Journal

Synthesis of Benzodiazepinyl Phosphonates as Clostripain Inhibitors

CSIR-NCL has synthesised benzodiazepinyl phosphonates (BDPs). Ferric chloride efficiently catalyzed four-component condensation of diamines, acetone and phosphites in the presence of molecular sieves to furnish BDPs as novel chemical entities with good yield. The synthesized BDPs have shown significant protease inhibition activity against clostripain, a disease model for gas gangrene. Compound derived from 2,3-diamino toluene and diethyl phosphite inhibited the clostripain enzyme with an IC₅₀ value of 32 μ M suggesting that these novel chemical entities could be further explored as cysteine protease inhibitors.

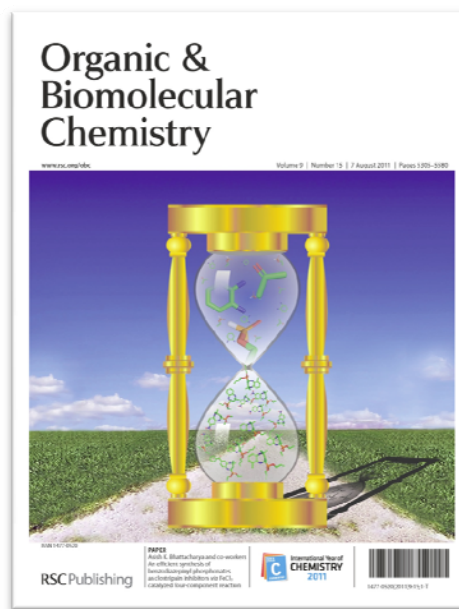


Fig. 1.39 Research work on cover page of the Journal

Highly efficient (R-X-R)-type Carbamates as Molecular Transporters for Cellular Delivery

The backbone of one of the most-effective cell-penetrating peptides, the (R-X-R)-motif, arginine-rich peptides has been engineered to increase the efficacy of these oligomers for mammalian cell penetration several fold. CSIR-NCL has achieved this by replacing the amide linkages by carbamate linkages, which leads to an increase in flexibility and hydrophobicity, and reduces the possibility of hydrogen-bonded secondary structures and to optimize the effect of guanidinium display.

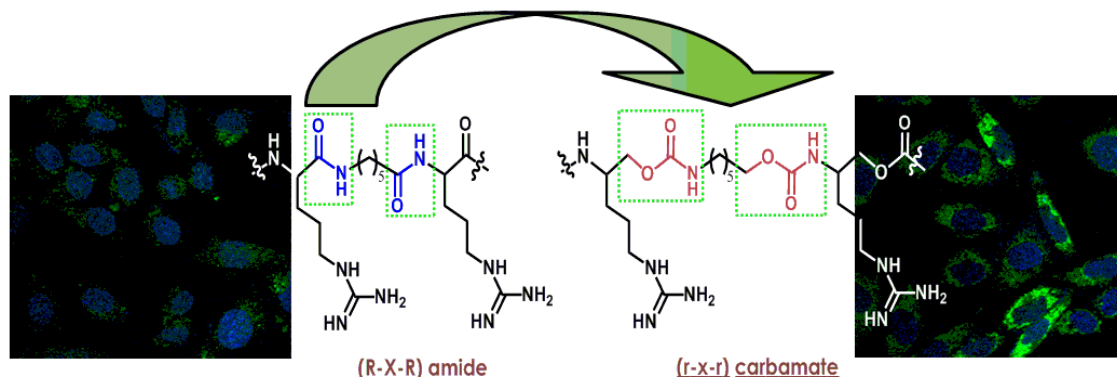


Fig. 1.40 Schematic for oligocarbamate-DNA complexes

These oligocarbamates were not only more efficient at cell penetration than the oligoamide controls, but also carried the cargo such as siRNA (siGLO), a tripeptide (Tyrosinerleutide) and also, much larger plasmid DNA (pMIR-Report luciferase) into the cell interior. The transported plasmid DNA expressed its biological activity, as evident from the expression of the reporter gene without the use of endosmolytic agents such as chloroquine. Moreover, oligocarbamate-DNA complexes were nontoxic compared to Lipofectamine2000, making these designed oligocarbamates extremely attractive for further development as transporters

for cargo ranging from small molecules to peptides and oligonucleotides for therapeutic applications.

Conformationally rigid aromatic amino acids as potential building blocks for abiotic foldamers

Structural frameworks - called scaffolds, which help achieve a specific conformation (architecture) for the biopolymers are of considerable importance in dictating their material and biological function. Nature uses small alpha-amino acids as building blocks for the construction of functional biopolymers. CSIR-NCL has described the development of conformationally constrained unnatural aromatic amino acids, constructed on rigid backbone wherein the carboxyl and amino groups project in two dimensions (planes) on the aromatic framework. Such a feature offers the possibility of design and development of conformationally ordered synthetic oligomers with intriguing structural architectures distinct from those classically observed. Furthermore, such amino acids will have the potential to extend the conformational space available for foldamer design (synthetic oligomers) with diverse backbone conformation and structural architectures.



Fig.1.41 Research work on cover page of the Journal

Concise Enantioselective Synthesis of Reboxetine and (+)-epi-Cytosazone

Reboxetine and (+)-epi-Cytosazone are biologically active important drug molecules. Reboxetine is a norepinephrine reuptake inhibitor (NRI) and an antidepressant drug used in the treatment of clinical depression and panic disorder whereas (+)-epi-Cytosazone is a microbial metabolite isolated from *Streptomyces* sp., which has been identified as a potent cytokine modulator. The hydrolytic kinetic resolution (HKR) of racemic syn- or anti- alkoxy- and azido epoxides catalyzed by Co(salen) complex affords a practical access to a series of enantioenriched syn- or anti- alkoxy- and azido epoxides and their corresponding 1,2-diols in single step. The adopted synthetic route herein this methodology is very convenient and can be carried out under mild conditions with the readily available catalysts in both the enantiomeric forms. This strategy has been successfully employed in the concise enantioselective synthesis of bioactive molecules such as (S,S)-reboxitene and (+)-epi-cytosazone at CSIR-NCL.

Assembly of nanoparticles in H1 Phase

CSIR-NCL has demonstrated that dynamic phase separation of nonionic surfactant hexagonal domains is a generic technique for assembly of three-dimensional nanoparticulate networks. Inorganic, organic, and protein particles can be assembled into networks. The large surfactant content in solution renders the matrix amphiphilic, and therefore, hydrophobic nanoparticles can also be dispersed in such matrices. Dynamic templating of H1 mesophases involves mild conditions—near ambient temperatures and a facile water wash for template removal. Thus, it is possible to employ this technique to

prepare networks of even relatively delicate bionanoparticles, such as ferritin protein, that would aggregate irreversibly on freezing. Materials prepared using this technique have potential for application in a wide variety of technologically important areas.

Self-regulation of photovoltaic module temperature

CSIR-CSMCRI has carried out a study to take advantage of the enhanced solar insolation in V-trough while limiting the temperature of the photovoltaic (PV) module at around the maximum (ca. 65°C) observed for conventional usage without any concentration. Paraffin wax of 56–58°C melting range was chosen as phase change material (PCM) and incorporated at the rear of the module to absorb the excess heat. The problem of low thermal conductivity of the wax was solved with the help of packed metal turnings wherein the wax resided. Two sets of experiments were performed one indoor and another outdoor. Employing a 0.06 m thick bed of the PCM matrix, the module temperature in the indoor experiment could be maintained at 65–68°C for 3 hours whereas in its absence the temperature rose beyond 90°C within 15 min. In outdoor studies, the module temperature in V-trough could be reduced from 78°C to 62°C with the PCM assembly and operation could be sustained throughout the day. Using the V-trough PV-PCM system, the output power over the day could be enhanced 1.55 times with self-regulation of temperature. The molten wax formed during operation re-solidified during the evening and night and could be re-used. A significant finding was the safe operation of the module even under low wind velocity conditions without sacrificing operational simplicity.

Characterization of polydimethylsiloxane pervaporation membranes using small-angle neutron scattering

CSIR-CSMCRI has reported characterization of polydimethylsiloxane (PDMS) pervaporation membranes prepared under various conditions using the small-angle neutron scattering (SANS). The PDMS membranes were prepared by cross-linking reactions between hydroxyl terminated polydimethylsiloxane (HPDMS) and polymethylhydrosiloxane (PHMS) with pendant hydride. The radius of gyration (R_g) of HPDMS and PHMS polymer chains determined from the SANS data analysis is found to be similar with the size of about 12 Å. Upon the initial cross-linking reaction at 25°C, the R_g of the polymer was increased to 31 Å. The final membrane structure obtained after the completion of reaction is comprised of interacted polymer chains of the R_g values in the 55–61 Å range. With increasing the reaction temperature to 40°C, about a two-fold increase in the chain length of polymer and polymer chain clustering was observed in the membrane structure. Such membrane exhibited high separation factor (α), of about 100–140 for hydrophobic organics over water. Similar high separation factor was observed for the membrane obtained by curing at 150°C, which also has longer polymer chain and a larger polymer chain clusters. Thin film membranes coated over a porous support have loose membrane structures and show poor organic selectivity.

Microbial synthesis of Green Plastic- Polyhydroxyalkanoates (PHA) using Jatropha Biodiesel Waste Residues

Recognizing that cost is a key deterrent in the large scale promotion of green plastics Polyhydroxyalkanoates (PHAs), CSIR-CSMCRI has used the crude glycerol stream from Jatropha biodiesel production as a low cost carbon source. It was further recognized that other useful nutrients required in the fermentation process can also be met from the above

crude stream and other by-product streams such as deoiled cake. Critical to the success was the discovery of a potent marine bacteria, *Halomonas hydrothermalis* (Accession No. MTCC 5345), which converts the carbon from the feed into PHA with 18-20% carbon conversion efficiency and with PHA content of 70-75% with respect to cell dry weight. Analytical measurements conducted in the Institute as well as at CIPET, Ahmedabad. Solvay Advanced Polymers indicated similar properties to that of standard PHA (obtained from Sigma Aldrich). Further, biodegradability in moist soil was evident after 50 days. The process is being scaled from gram scale to kilogram scale.

Biofuel from Marine Microalgae

CSIR-CSMCRI has identified two coastal lagoons on the west coast having naturally occurring floating marine microalgal mats which are easy to harvest. The mats were predominantly *Microspora sp.* (ATCC Accession No. PTA - 12197) & *Cladophora sp.* (ATCC Accession No. PTA - 12199). Hexane extracted non-polar lipids from the biomass of the microalgal mats were converted to Biodiesel (B20) to run an unmodified Tavera car.

Institute could raise 300 kg of auto-settling sundried biomass with an average biomass productivity of 32.45 g/m²/d (dry basis) and a maximum biomass productivity of 45 g/m²/d (dry basis) in open solar salt pans at CSIR-CSMCRI's experimental salt farm. The biomass was used for preparing 30 litres of B100 microalgal biodiesel (CvME). The test run using the biodiesel was flagged off by the Shri Vilasrao Deshmukh, the Hon'ble Minister for Science & Technology & Earth Sciences at CSIR Headquarters, New Delhi on 30th March, 2012.



Fig. 1.42a. Solar ponds where micro algae is cultivated; 1.42b. Biomass of microalgae and 1.42c. Biodiesel from microalgal

Cationic lipid-conjugated haloperidol derivatives as a new class of anticancer therapeutics Pal

Haloperidol (HP), a neuroleptic drug, shows high affinity toward sigma receptors (SR). HP and reduced-HP at higher concentrations are known to induce apoptosis in SR-overexpressing carcinomas and melanomas. CSIR-IICT has developed cationic lipid-conjugated HP as a new class of anticancer therapeutics. It was demonstrated that in comparison to HP, the C-8 carbon chain analogue (HP-8) shows significantly high, SR-assisted antiproliferative activity against cancer cells presumably mediated through up regulation of caspase-3 and down regulation of pAkt. Importantly, it has been shown that melanoma tumor aggressiveness in HP-C-8-treated mice is significantly lower than that in HP-treated mice. HP-C8 simultaneously reduced Akt-protein level and increased Bax/Bcl-2 ratio in vascular endothelial cells thereby indicating a possible protein kinase down-regulatory and apoptosis inducing role in tumor endothelial cells. CSIR-IICT has

demonstrated for the first time that sigma receptor-targeting cationic lipid-modified HP derivatives are a promising new class of anticancer therapeutics.

Inhibiting Tubulin polymerization to treat cancer: 2-Anilinonicotinyl linked 1,3,4-oxadiazole derivatives

A series of 2-anilinonicotinyl linked 1,3,4-oxadiazoles has been synthesized and evaluated by CSIR-IICT for their antitumour activity against various cancer cell lines, inhibition of tubulin polymerization and cell cycle effects. Some of these compounds showed good antiproliferative activity with GI50 values ranging from 4.57 to 97.09 mM in the human cancer cell lines and one of the compounds 5m showed potent antitumour efficacy in all the cell lines tested. This compound also inhibited tubulin polymerization under both *in vitro* and *in vivo* conditions. Analysis of tubulin by Western blot experiments demonstrated that 5m depolymerizes microtubules by causing disturbances in the ratio of soluble *versus* polymerized tubulin in cells, leading to the cell cycle arrest at G2/M phase of the cell cycle followed by activation of caspase-3 activity and apoptotic cell death .



Fig. 1.43 Research work on cover page of the Journal

Dehydrogenase activity in association with poised potential during biohydrogen production in single chamber microbial electrolysis cell

CSIR-IICT is working on the production of biohydrogen using Microbial electrolysis cell, which can overcome the problems encountered during dark-fermentative hydrogen production process by giving a small input of the electric current. Variation in the dehydrogenase activity and its simultaneous influence on hydrogen production, substrate degradation rate and volatile fatty acid generation has been investigated with respect to varying poised potential in single chambered membrane-less microbial electrolysis cell using anaerobic consortia as biocatalyst. Poised potential showed significant influence on H₂ production and DH activity. Maximum H₂ production was observed at 1.0 V.



Fig.1.44 Research work on cover page of the Journal

Benefits of benzothiazoles

A series of substituted benzothiazoles were designed, synthesized, and evaluated by CSIR-IICT for their anticancer activity and their capacity to block tubulin polymerization. Three such compounds have promising anticancer activity, while one effects cell-cycle arrest and

inhibition of tubulin polymerization on par with combretastatin A-4. Modeling studies with the colchicine binding site gave insight into the SARs of these and other benzothiazole derivatives.

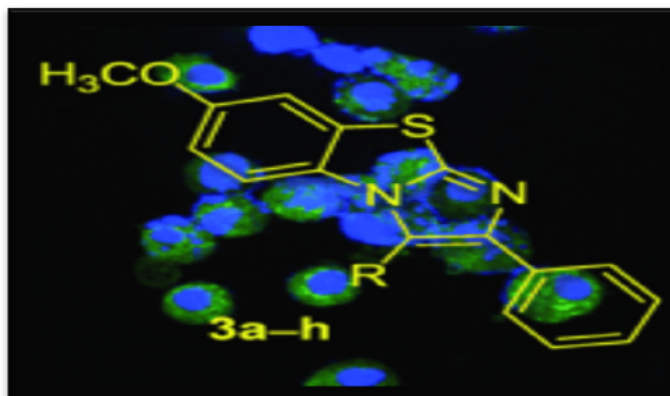


Fig. 1.45 Substituted benzothiazoles

Potential allergens of green gram (*Vigna radiata* L. Millsp) identified as members of cupin superfamily and seed albumin

No systematic study on allergenicity of green gram seed proteins have been performed so far, although incidences of IgE-mediated reaction to green gram seedlings have been reported. CSIR-IITR has investigated the allergenic potential of green gram, followed by identification and characterization of its relevant allergens using proteomic approaches. Methods BALB/c mice were sensitized intraperitoneally with green gram proteins, and levels of specific Igs, Th2 cytokines, histamine, anaphylactic symptoms and histopathological responses were studied. Twelve naso-bronchial allergic patients with a history of sensitization to green gram were selected on the basis of positive skin prick test and elevated specific IgE levels. Green gram allergens were identified and characterized by their ability to endure pepsin, by IgE immunoblot of two-dimensional (2D) gels in combination with mass spectrometry and by bioinformatics approaches. Increased specific IgE, IgG1, Th2 cytokine and histamine levels, high anaphylactic scores and histological changes in lungs and spleen of green gram crude protein extract treated mice are indicative of its sensitization ability. Four proteins (molecular weights: 52, 50, 30 and 18 kDa) showed pepsin resistance and IgE-binding capability with sensitized human and mice sera. The four proteins tentatively named as Vig r2 (52 kDa, pI 5.7), Vig r3 (50 kDa, pI 5.8), Vig r4 (30 kDa, pI 6.6) and Vig r5 (18 kDa, pI 5.5) showed significant sequence similarity with known allergens of soybean, lentil, pea, lupin, etc. Mass spectrometric analysis identified Vig r2 as 8S globulin b-isoform precursor, Vig r3 as 8S globulin a-isoform precursor and Vig r4 as seed albumin. Green gram seeds contain at least four clinically relevant allergenic

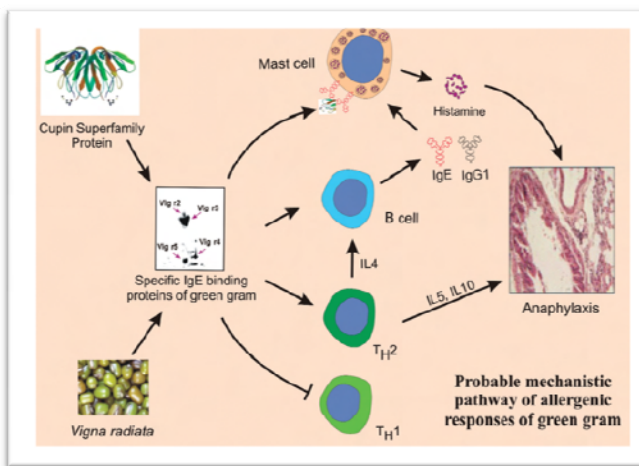


Fig. 1.46 Probable mechanistic pathway of allergenic responses of green gram

proteins, namely Vig r2, Vig r3, Vig r4 and Vig r5 that were capable of inducing strong IgE-mediated reactions. One of the most important steps towards diagnostic and therapeutic approaches to deal effectively with food allergy is continued identification of newer food allergens and their characterization. The significance of this study can be enormous as the data generated may work as basic biology data in developing a green gram species modified genetically that may have reduced allergenicity.

A mesoporous WN co-doped titania nanomaterial with enhanced photocatalytic aqueous nitrate removal activity under visible light

The work of CSIR-NML on the increased and selective nitrate reduction under visible light over a WN co-doped titania photocatalyst attracted the attention of well-known web-writer Giorgio De Faveri and agriculture experts. He commented that the study carried out by scientists of CSIR-NML proposed a preliminary but encouraging process to photocatalytically convert nitrate in nitrogen gas with minimal production of side-products.

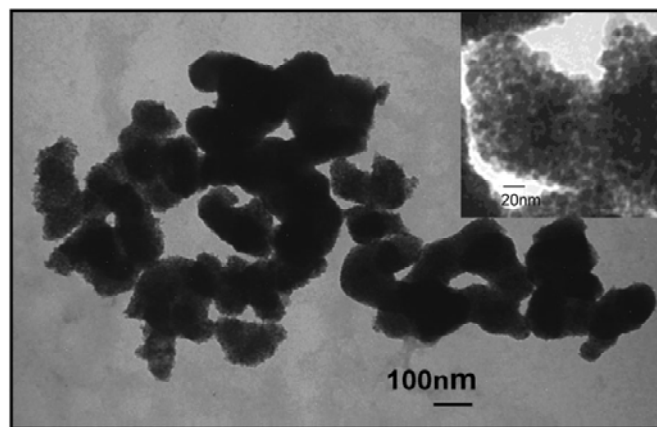


Fig. 1.47 TEM image of 2-WTiN material

A series of WN co-doped titania nanomaterials were synthesized with varying tungsten content and were characterized by TEM, XRD, UV-vis and nitrogen adsorption–desorption studies. Tungsten doped materials are found to be noodle shaped and mesoporous with a stable anatase phase after 500°C calcination. Peak shifting in the XRD pattern indicates the tungsten doping in the crystal lattice. Visible light absorption increases with the increasing tungsten amount. The hole scavengers, formic acid was found to be the best for nitrate reduction with more than 94% nitrogen gas selectivity. The amount of hole scavenger also controls the reaction efficiency and product selectivity. Both nitrate reduction and nitrogen gas selectivity increases with WN co-doping in comparison to only N doped titania. High nitrate reduction with formic acid is attributed to the formation of (CO_2^-) species having high reduction potential. The material with 2% tungsten shows the highest surface area and the best photocatalytic activity under visible light. Presence of anion like chloride increases the nitrate photoreduction. Overall high nitrate reduction can be attributed to the synergistic effect of tungsten and nitrogen co-doping, optimum surface hydroxyl group, mesoporosity and appreciable visible light absorption of the materials.

Stereoselective multi-component organometallic reactions and synthesis of bioactive molecules using green methodologies

CSIR-NEIST has developed a new strategy to synthesize optically active aminohydroxyl acid derivatives bearing two stereogenic centers via chiral Bronsted acid $\text{Rh}_2(\text{OAc})_4$ cocatalyzed three component reactions of diazo acetates with alcohols and imines. A matched reaction system was identified to give the products in moderated diastereoselectivity and good enantioselectivity. The desired product aminoalkoxy ester was isolated with 58% yield with

a dr of 46:54 and the enantioselectivity is 20%. In order to enhance the enantioselectivity, the reaction was studied using alcohol, a racemic Bronsted acid (BH) to activate the imine and tert-butyl diazoacetate. The reaction gave a slightly better result. The ratio to the desired syn diastereomer slightly improved from 37:73 (syn:anti) to 45:55 with a higher ee (49% vs 35%) of the syn isomer. The application of this methodology was demonstrated in the efficient synthesis of a taxol side chain and (-)-epi-cytoxazone. This is the first time that the highly efficient ylide-trapping process is applied for the synthesis of pharmaceutically interesting molecules. Institute has also performed the pseudo four-component Biginelli-type condensation of barbituric acid, urea/thiourea and aldehyde in presence of 1 mol% of iodine under microwave irradiations. The corresponding symmetrical spiroheterocyclic compounds were obtained with excellent yields. This molecular iodine-catalysed one-pot synthesis of spiro heterocycles is therefore simple, high yielding, time-saving and environment friendly process. Moreover, CSIR-NEIST is not using expensive rare earths or strong Bronsted acids or costly metal salts like indium rather it employs inexpensive catalyst like iodine.

Synthesis of novel pyrimidine derivatives biological significance based on inter and intramolecular cycloaddition strategy

5,8-dihydropyrido[2,3-d]pyrimidine **9** formed directly without the formation of any intermediate. CSIR-NEIST has got a breakthrough when uracil amidine **1** was reacted with 2-amino-substituted acrylonitriles **8** in PEG-400 and in presence of 10 mol% of K_2CO_3 at room temperature. The reaction was generalized by taking different amine substituents in **8** and observed that cyclic secondary amines like morpholine, piperidine and pyrrolidine leads to generation of the same product after elimination of the amine moiety. However, when N,N-diphenyl amine was taken as the substituent, the reaction did not proceed at all despite long reaction time and the reactants were quantitatively recovered. This could be due to the large steric hindrance offered by the phenyl groups that renders the initial step sterically unfavorable. Institute carried out a three component reaction also between uracil amidine **1**, an aldehyde and acetyl acetone **10** in acetic acid and refluxed for appropriate time to get the products. The structure of the compound **12a** was assigned from its spectral analysis and finally by X-ray crystallography.

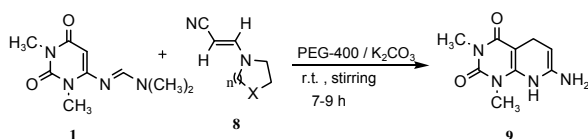


Fig. 1.48a

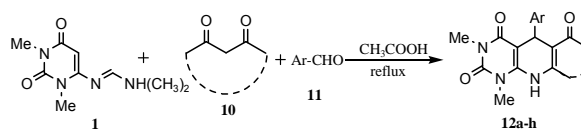


Fig. 1.48b

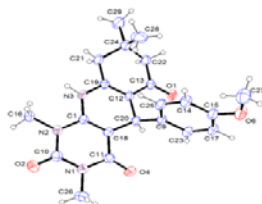


Fig. 1.48c

Fig. 1.48 Schematic for Synthesis of novel pyrimidine derivatives

New analogues of Drugs & Intermediates

Indium catalyzed tandem hydroamination/hydroalkylation of terminal alkynes: The first direct intermolecular hydroamination/ hydroalkylation of terminal alkynes catalyzed by $In(OTf)_3$

under one-pot conditions leading to the formation of conjugated ketimines in good yields and in absence of any other additive and/or co-catalyst has been investigated by CSIR-NEIST. A range of arylamines and alkynes were studied and good yields of the products were obtained. This methodology offers a new approach for the synthesis of conjugated ketimines from simple starting materials with excellent atom-economy.

Molecular Understanding on the Enhancement of Thermal Conductivity by Carbon Nanotube Based Nanofluids

Classical molecular dynamics (MD) simulation has been carried out by CSIR-CLRI on model systems composed of ethylene glycol (EG) and carbon nanotube (CNT) in water medium to gain insight into the interaction between them. The analysis of the MD results reveals that the EG molecules aggregates around CNT expelling water molecules due to the hydrophobic-hydrophobic interaction. Hydrogen bonding (H-bonding) interaction between two EG molecules increases in the presence of CNT. Further, the presence of CNT decreases the solubility of EG in water. The analysis of dihedral angle of EG reveals that the CNT induces conformational changes in EG. Specifically, a fraction of the gauche form of EG is converted into trans. In addition, electronic structure calculations have also been carried out on model systems which coerce that the trans form of EG has a more favorable interaction with CNT than its gauche counterpart. These findings on the distribution of EG and WAT in the presence of CNT and the conformational change in the EG due to the addition of CNT has important implication in understanding the application of nanofluid composed of CNT as an excellent candidate for preparing thermally conductive cooling fluids.

An unusual oxidation of imidazolyl ring in a cobalt terpyridyl complex Inorganic Cool Colorants

CSIR-CLRI has synthesized inorganic cool colorants of cobalt oxide and chromium oxide. Cobalt oxide nanoparticles were synthesized on starch template in the size range of 15-30nm. The formation mechanism involves complexation with starch, Co^{2+} ions have been preferentially bound to starch, resulting in clathrate cages. A controlled preparative methodology which involves initial drying at a temperature of 80–90°C, removed a large number of water molecules to provide for a solid rigid network, in which the metal ions remained segregated. Subsequent calcination and sacrifice of the template resulted in mono-dispersed nanoparticles of around 20 nm.



Fig. 1.49a. Research work appeared on page of the Journal

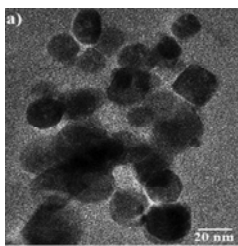


Fig.1.49b. TEM images of the synthesized CoO nanoparticles in the size range of 15-30nm

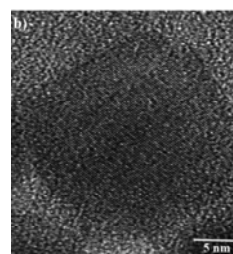


Fig. 1.49c HRTEM image of a CoO nanoparticle

Design of acid-responsive microcapsules for targeted drug delivery application

CSIR-CLRI has prepared acid responsive microcapsules using functionalized carbon nanotubes and ytterbium triflate. FESEM pictures showed that packing of the carbon nanotubes and formation of holes in the microcapsules are acid dependent. While filming the action of acid on microcapsules under microscope, an interesting phenomenon was observed, where the microcapsule can be opened up for certain time using an acid that can close after some time spontaneously (“zip-unzip” phenomenon?). Several model compounds were loaded in the microcapsules and released later by the addition of aqueous acid. The methodology can be applied for pH-driven targeted drug delivery at the specific site of the body.

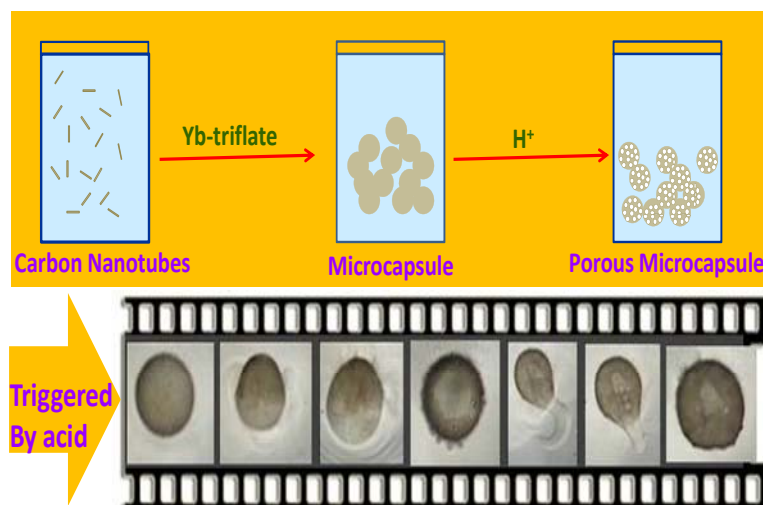


Fig. 1.50 Schematic presentation of the synthesis of microcapsules followed by introduction of porosity with acid. Pictures on filmy strip show the sequential states of microcapsules after controlled acid addition, viewed by microscope

Solid waste for the treatment of liquid waste

CSIR-CLRI has used solid waste for the removal of pollutants from liquid waste wherein, the fleshing, a solid waste (biopolymer) emanating from leather industry has been used as an adsorbent for removal of dyes from wastewater. Fleshing has been cross-linked with glutaraldehyde to stabilize it against degradation. About 90% dye removal has been achieved by treating 100 mg/L dye solution with 12 g/L of glutaraldehyde-cross-linked fleshing. It gives the possibility of reusing the dye loaded fleshing as a reductant in the manufacture of a tanning salt, which is used in leather industry for tanning of leathers.

Mineral Free Eco-Benign Tanning

Conventionally most of the skins and hides are stabilized through mineral tanning agents predominantly using chromium salts. However, due to the ecological and safety concerns associated with chromium salts and other mineral tanning systems a need was felt for an alternative tanning system. Disposal of used leather products has also come under surveillance for their eco-compatibility posing challenges to choice and designing of novel tanning systems. Emerging criteria for such new tanning systems are environmental safety and easy biodegradability of leather products after use. Vegetable tanning agents based on poly phenols of plant materials which were in vogue prior to advent of mineral tanning are re-

emerging as principal tanning materials to offset the perceived concerns of mineral tanning. In order to overcome short comings of vegetable tanning, use of multifunctional material(s) of plant origin has been developed by CSIR-CLRI. *Jatropha curcas* seed oil provides a possibility for its use in tanning as an adjunct along with poly phenols. This oil when used as a co-tanning agent along with vegetable tannins eliminates most of the drawbacks associated with conventional tanning. The novel tanning process using *Jatropha curcas* seed oil along with vegetable tanning agents can emerge as a viable tanning system based on replenishable resources.

Properties of Apparel Leathers and Natural Fabrics

In the area of leather product research, sewability of sheep nappa leathers was measured in terms of seam efficiency and was correlated with related mechanical properties. Seam efficiency was found to be between 44 and 99% for the sheep nappa leathers employed in the study carried out by CSIR-CLRI. Among the various mechanical properties studied, elongation at break seems to influence the seam efficiency significantly as evidenced from the correlation coefficient value of 0.99. In another study, non-mulberry silks such as eri, muga and a blend of eri and muga fabrics were combined with goat suede leather for apparel application. The results of this study suggest that the selected silk fabrics can be used for making apparel as well as other variety of products in combination with leather.

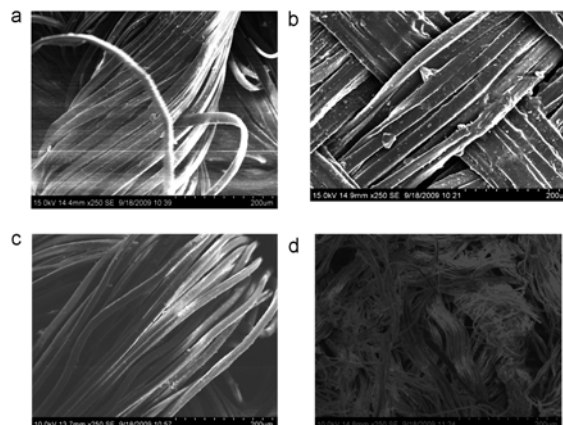


Fig.1.51 Scanning Electron Micrographs of silk based fabrics and goat suede leather showing the grain surface at a magnification of 250x. (a) Eri fabric; (b) Muga fabric; (c) EM blend fabric; (d) Goat suede leather

Preparation and application of Ice Cool Biomaterial

To avoid zero hour inflammation and burning sensation, a new biomaterial with ice cool property has been prepared by CSIR-CLRI based on collagen and alginic acid. Ice cool biomaterial displayed fast healing and significant reduction in IL1 and IL6.

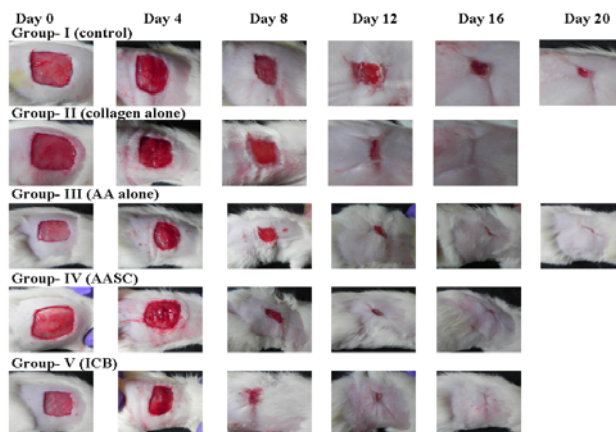


Fig.1.52 Sequence of healing

Duplex DNA binding of photoactive Rull-polypyridyl complexes

The duplex-DNA binding properties of a non-intercalating polypyridyl ruthenium(II) complex that incorporates a linear extended ligand with a catechol moiety has been probed by CSIR-CSMCRI with a variety of photo and biophysical techniques. These studies reveal that the complex groove binds to DNA sequences biphasically, and displays binding constants equivalent to those of high-affinity metallointercalators. The complex also displays preferential binding to AT-rich sequences. Changes in the structure of the coordinated catechol ligand and the incorporation of intercalating ancillary ligands into the complex were found to modulate both the optical-binding response and binding parameters of the system, which indicates that the catechol moiety plays a crucial role in the observed enhancement to binding affinities.

Effect of fuel choice on nanoparticle emission factors in LPG-gasoline bi-fuel vehicles

Nanoparticle and gas-phase emission factors are presented by CSIR-IIP in collaboration with University of Alberta for a liquefied petroleum gas (LPG) passenger vehicle and are compared to gasoline operation. A bi-fuel LPG-gasoline vehicle certified for use on either fuel was used as the test vehicle so that a direct comparison of the emissions could be made based on fuel choice. These values were considered along with previous studies to determine the relative change in particulate emissions due to fuel choice over a wide range of vehicles and operating conditions. The vehicle examined in this study was tested on a chassis dynamometer for both steady-state and transient conditions. Transient test cycles included the US FTP72 driving cycle, Japanese driving cycle and modified Indian driving cycle while steady-state tests were done at vehicle speeds ranging from 10-90 km/hr in various transmission gears. Exhaust particle size distributions were measured in real-time using a differential mobility spectrometer (DMS50), and particle number and particle mass emission factors were calculated.



Fig.1.53 DMS is the only available equipment which can be used for on-road particle size distribution measurement

For both fuels, the majority of the particles ranged from 5 to 160 nm in terms of particle diameter, with typically more than 85% of the particles in the nucleation mode (between 5-50 nm). In most cases, the vehicle produced a greater number of larger (accumulation mode) particles when fuelled on LPG. Using the data in the literature as well as the data in the current study, gasoline fuel produces 4.6 times more particles in terms of number and 2.1 times more particles in terms of mass.

Organic Synthesis

Synthesis of organic chemicals is major part of chemical industries. CSIR-IICT has, over the years, created a niche in the domain. Following paragraphs present synthesis of some of the significant organic chemicals.

Iodocyclization and Prins-Type Macrocyclization: An Efficient Formal Synthesis of Leucascandrolide

The formal total synthesis of leucascandrolide A has been 20 steps from a known epoxide with overall yield of 11.5% following a recently developed strategy for the construction of trans-2,6-disubstituted-3,4-dihydropyrans and a Lewis acid catalyzed intramolecular Prins-cyclization of aldehydic homoallylic alcohol to generate the tetrahydropyran ring with three stereogenic centers and macrocycle concomitantly.

Total synthesis of Z-isomer of phomolide B

Z-isomer of phomolide B has been synthesized during its investigation towards the effect of protecting group on the outcome of ring-closing metathesis reaction. The other key reactions involved are cis-selective partial hydrogenation, Sharpless asymmetric epoxidation, Yamaguchi esterification and following 12 longest linear sequence with 18.5% overall yield starting from a known intermediate 20.

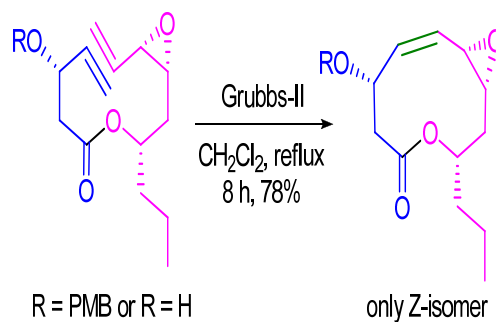


Fig.1.54 synthesis of Z-isomer of phomolide B

Formal Total Synthesis of Cyanolide A

Formal total synthesis of cyanolide A, aglycosidic dimeric macrolide has been accomplished. The compound was found to be an efficient molluscicidal agent. The key reactions involved are asymmetric acetate aldol reaction, CBS reduction and Shiina's lactonization.

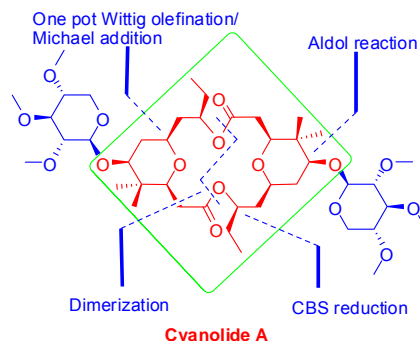


Fig.1.55 Synthesis of Cyanolide A

Iodocyclizations: Novel Strategy for the Total Syntheses of Polyrhacitide A and epi-Cryptocaryolone

Highly stereoselective total syntheses of polyrhacitide A and epi-cryptocaryolone have been achieved in 11 steps with high overall yield of 24% and 28%, respectively, following a recently developed strategy for the construction of trans-2,6-disubstituted-3,4-dihydropyrans. The versatility of iodo-cyclization for the total syntheses of polyrhacitide A and epi-cryptocaryolone is demonstrated.

A facile synthesis of substituted dibenzoxepines using an acid-catalyzed tandem reaction

Dibenzoxepine is an important structural motif in various pharmaceuticals with remarkable diverse biological activities. Synthesis of 11-substituted dibenzoxepine derivatives has been demonstrated by CSIR-IICT via an acid-catalyzed tandem nucleophile addition/ Friedel-crafts cyclization reaction. The reaction of O-benzyloxy salicylaldehyde with various

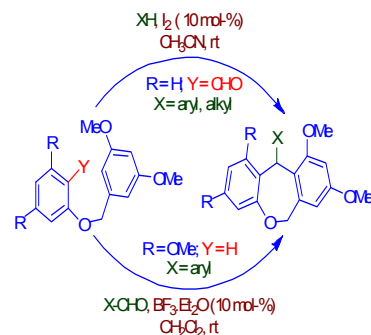


Fig.1.56 Synthesis of substituted dibenzoxepines

nucleophiles (10 mol-% I_2) or O-benzyloxy phenol with aromatic aldehydes (10 mol-% $BF_3 \cdot Et_2O$) has provided the desired products in good yields.

Derivatives of Embelin, a Natural Product with Proapoptotic and Anticancer Properties

CSIR-IICT has synthesized new derivatives of embelin, a natural of X-linked inhibitor of apoptosis protein (XIAP). The design of these new molecules involved introduction of aromatic groups directly linked to the benzoquinone core. A new strategy to provide greater flexibility in the nature and the length of the added chain was developed. The strategy involves first a Suzuki–Miyaura reaction with functionalized aromatics, yielding a first generation of molecules. Then, by appropriate use of the functional groups, a second generation of representative embelin derivatives is prepared.

Towards chemical libraries based on heterocyclic scaffolds with monofluorinated and difluoroalkyl side chainscarbohydrates

Focused chemical libraries, based on five and six-membered heteroaromatic systems with mono and gem difluoro alkyl sidechains, has been developed by CSIR-IICT. Four heterocyclic scaffolds with a p-bromophenyl group have been prepared from readily available propargylic fluorides. Starting with these scaffolds, palladium-catalyzed reactions have been performed by automated procedures, to prepare libraries of molecules designed for biological applications.

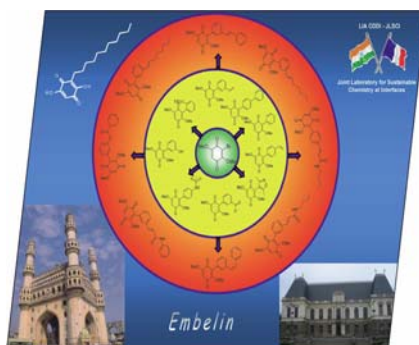


Fig. 1.57 Chemical Library based on heteroaromatic systems

Solid phase microbial fuel cell (SMFC) for harnessing bioelectricity from composite food waste fermentation

CSIR-IICT has designed and evaluated a single chambered solid phase microbial fuel cell for production of bioelectricity

Fig. 1.58 Research work on cover page of the Journal



through solid state fermentation of composite waste.

Solid phase microbial fuel cells were designed to evaluate potential of bioelectricity production by stabilizing composite canteen based food waste. The performance was evaluated with three variable electrode-membrane assemblies. Experimental data depicted feasibility of bioelectricity generation from solid state fermentation of food waste. Distance between the electrodes and presence of proton exchange membrane (PEM) showed significant influence on the power yields. SMFC-B (anode placed 5 cm from cathode-PEM) depicted good power output (463 mV; 170.81 mW/m²). Sodium carbonate amendment depicted marked improvement in power yields due to improvement in the system buffering capacity. SMFCs operation also depicted good substrate degradation (COD, 76%) along with bio-ethanol production. The operation of SMFC mimicked solid-state fermentation which might lead to sustainable solid waste management practices.

Self-induced bio-potential and graphite electron accepting conditions enhances petroleum sludge degradation in bio-electrochemical system with simultaneous power generation

CSIR-IICT has evaluated the simultaneous removal of soluble [(aliphatics, aromatics and NSO (nitrogen, sulphur and oxygen)] and insoluble (asphaltenes) fractions of petroleum sludge apart from power generation using a specifically designed bio-electrochemical treatment system (BET). BET documented effective degradation of real field petroleum sludge over the conventional anaerobic treatment (AnT). BET operation showed enhanced total petroleum hydrocarbons (TPH) removal over AnT. Aromatic fraction visualized higher removal (75.54%) compared to other TPH fractions viz., aliphatics, asphaltenes and NSO during BET operation. Higher ring aromatics (5–6) documented easy degradation in BET, while AnT was limited to lower ring (2–3) compounds. Voltammetric analysis evidenced simultaneous redox behavior during BET operation due to presence of graphite electrode as electron acceptor, while AnT showed extended



Fig. 1.59 Research work on cover page of the Journal

reduction behavior only. BET documented higher charge/capacitance (2810 mJ/1120 mF) than AnT (450 mJ/180 mF). Power output corroborated well with observed results supporting BET performance as fuel cell.

Indium Tin Oxide films by a Jet Nebulizer Spray Pyrolysis technique

Nanocrystalline Indium Tin Oxide (ITO) thin films were deposited on glass substrates by CSIR-CECRI through a new spray pyrolysis route, Jet nebulizer spray (JNS) pyrolysis technique, for the first time. The substrate temperatures varied from 350°C to 450°C using a precursor containing indium and tin solution with 90:10 at % concentration. The optical band gap values calculated from the transmittance spectra of all the ITO films showed a blue shift of the absorbance edge from 3.60 to 3.76 eV. SEM and TEM results showed the nanocrystalline nature with grain size about 12-15 nm. The electrical parameters like the resistivity, mobility and carrier concentration are found as $1.82 \times 10^{-3} \Omega\text{cm}$, $8.94 \text{ cm}^2/\text{Vs}$ and $4.72 \times 10^{20} \text{ cm}^{-3}$, respectively for the ITO film deposited at 400°C.

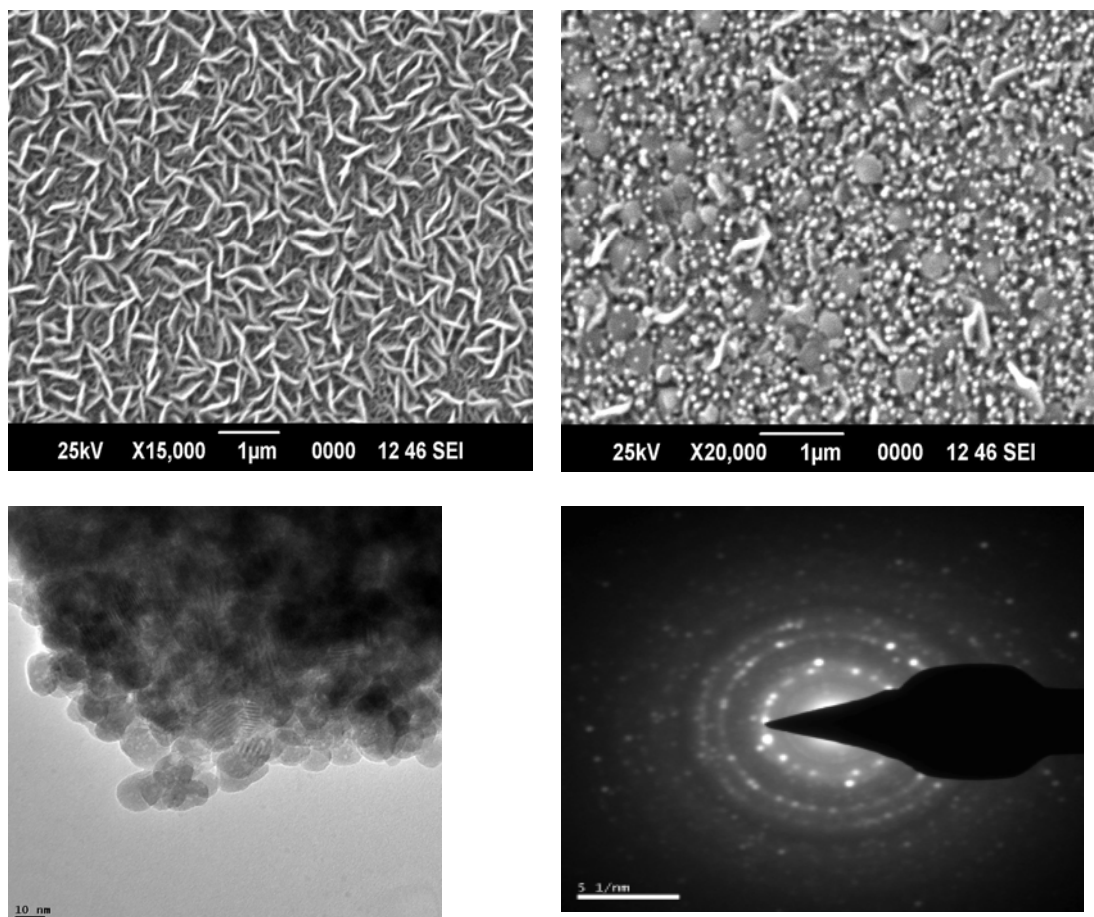


Fig. 1.60 SEM and TEM image and SAED pattern of ITO film deposited at 400°C

Nitride-based Multilayer Coated 316L SS as a Human Body Implant

CSIR-CECRI has prepared and characterized multiple layer of TiN/TiAlN, TiN / NbN, TiN/VN and Ti-Si-N nanocomposite coating by reactive dc magnetron sputtering in Ar-N₂ gas mixture. The coatings were uniform with columnar surface morphology. A maximum hardness value of 39GPa was observed for Ti-Si-N. Multilayer coatings had better

hemocompatibility than single layer and bare AISI 316LSS substrates. The attachment of bacteria on multilayer coatings was found to be very minimum and without colonization. The multilayer coated 316L surfaces showed a significant reduction of the presence of bacteria, and this fact could probably be important in the decrease of the inflammation of the peri-implant soft tissues. The increase in charge transfer resistance (R_{ct}) and decrease in double layer capacitance (C_{dl}) value shows the better corrosion resistance for the coated sample. Potentiodynamic polarization curves showed that the positive shift in E_{corr} and decrease in I_{corr} values for multilayer coating signifies that it exhibits higher corrosion resistance than single layer and bare substrate in simulated body fluid. It is concluded that by using the transition metal nitride based multilayer coated 316L SS as a human body implant, improvement of corrosion resistance as an indication of biocompatibility could be obtained.

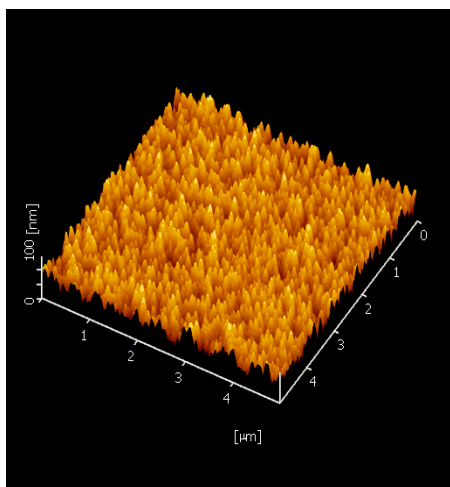


Fig.1.61a. AFM 3D image of TiN/NbN multilayers

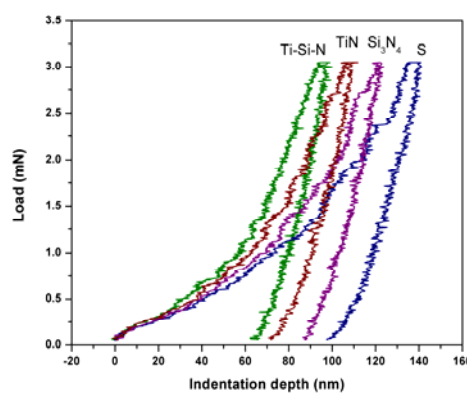


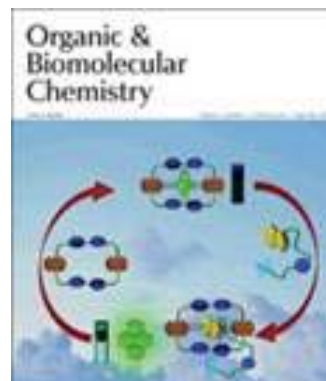
Fig. 1.61b Typical load vs. displacement curves for the Ti-Si-N nanocomposite coatings at 3 mN load

Attogram sensing of trinitrotoluene with a self-assembled molecular gelator

Trinitrotoluene (TNT) is a widely used explosive in landmines and military operations that contaminates the environment and groundwater, posing a threat to human health. Further, detection of this explosive is of utmost importance due to illegal transport and terrorist activities. Achieving the detection of explosives at a sub-femtogram level using a molecular sensor is a challenge. CSIR-NIIST has demonstrated that a fluorescent organogelator exhibits superior detection capability for TNT in the gel form when compared to that in the solution state. The gel when coated on disposable paper strips detects TNT at a record attogram (10^{-18} gm) level (~ 12 ag/cm²) with a detection limit of 0.23 ppq. This is a simple and low-cost method for the detection of TNT on surfaces or in aqueous solutions in a contact mode, taking advantage of the unique molecular packing of an organogelator and the associated photophysical properties.

Synthesis of a novel cyclophanes

CSIR-NIIST has synthesized a few novel cyclophanes CP-1 to CP-4 containing anthracene units linked together through different bridging and spacer groups and have



investigated their interactions with various nucleosides and nucleotides. Of these systems, CP-1 and CP-3 showed selectivity for 5'-GTP and 5'-ATP as compared to other nucleotides and nucleosides, whereas negligible selectivity was observed with CP-2 and CP-4. Interestingly, CP-1, CP-2 and CP-3 exhibited significant binding interactions with the fluorescent indicator, 8-hydroxy-1,3,6-pyrene trisulfonate (HPTS), resulting in the formation of non-fluorescent complexes. Titration of these complexes with nucleosides and nucleotides resulted in the displacement of HPTS, leading to the revival of its fluorescence intensity. It was observed that 5'-GTP induced the maximum displacement of HPTS from the complex [CP-1·HPTS] with an overall fluorescence enhancement of ca. 150-fold, while 5'-ATP induced ca. 45-fold. Although the displacement of HPTS from the complexes [CP-2·HPTS] and [CP-3·HPTS] was found to be similar to that of [CP-1·HPTS], these complexes showed lesser selectivity and sensitivity. In contrast, negligible displacement of HPTS was observed from the complex [CP-4·HPTS] under similar conditions. These results indicate that CP-1, having a well-defined cavity and good electron acceptor (viologen), is capable of forming selective and stable complexes. Though **CP-2** and **CP-3** retain the good electron acceptor (viologen), their reduced aromatic surface and larger cavity, respectively, resulted in lesser sensitivity. In contrast, **CP-4** having a large cavity and a poor acceptor (1,2-bis(pyridin-4-yl)ethene) showed negligible selectivity, thereby indicating the importance of cavity size, bridging unit and aromatic surface on biomolecular recognition properties of cyclophanes.

Technology Developed

Pharma Grade Synthetic Anionic Clay

CSIR-CSMCRI has developed a knowhow for pharma grade synthetic anionic clay commonly known as synthetic hydrotalcite which is basically a magnesium aluminium hydroxyl carbonate. Magnesium aluminium hydroxide octahedral forms positively charged layers and balancing anionic carbonate ions are located between the layers as interlayer anions. The institute has standardised a process to convert hazardous effluents to value added product and the knowhow for the preparation of synthetic hydrotalcite from effluent streams generated in the dye (copper phthalocyanine green) manufacturing plant of M/s Heubach Colour Pvt. Ltd., Ankleshwar was successfully transferred. The effluent mainly contained aluminium chloride and ammonium carbonate. The source of magnesium was bittern- the mother liquor left out after recovery of salt from brines. M/s Heubach installed a commercial plant of 1000 TPA based on CSIR-CSMCRI's knowhow.



Fig. 1.63 Inauguration of 1000 TPA SHT plant set up by M/s Heubach Colour Pvt. Ltd., Ankleshwar

Microsurfacing using chrome shavings as filler

Large quantities of solid and liquid wastes of toxic nature generated in tanning industry may percolate into the soil and contaminate the ground water. The biological solid waste such as chrome shavings- the chrome tanned collagenous scrap, a refuse, cause pollution upon the degradation of the organic matter with subsequent release of inorganic chromium. Degradation of chrome shavings could be arrested by encapsulating using hydrophobic (water repelling) bituminous binder. A bituminous mixture containing chrome shavings as one of the ingredients could be an alternative road construction material to provide a sustainable pavement layer.



Fig. 1.64 Experts examine microsurfacing of the experimental stretch

An experimental road stretch with Chrome Shaving as alternate filler was used by CSIR-CLRI in micro-surfacing as protective layer in the busiest road namely Sardar Patel road, Chennai having traffic volume of more than 1500 CVPD (commercial vehicles per day). Another test track was laid in Anna University, Chennai where the traffic volume is less than 1500 CVPD, using conventional concrete mixer. By utilizing the highly voluminous chrome shavings in road construction, the problem of waste disposal can be solved. The bituminous mixture containing chrome shavings of spongy nature would provide a rattle free road with possible skid resistance and would not release any chromium into the soil.

Salt Free Tanning

Given the total volume of hide or skin processed in India to a level of 2300 tonnes/day, the amount of salt used and discharged in the effluent is about 200 tonnes/day. The tanneries employ membrane separation like Reverse Osmosis in effluent treatment systems for removal of chlorides to meet discharge standards. The cost associated with the treatment and the disposal of huge quantities of reject arising from the RO plants after treatment also cause of concern for the tanners.

To overcome these problems CSIR-CLRI has developed a novel tanning composition for effecting salt free tanning technology. This new technology not only eliminates salt usage,

but also enables avoiding pickling of hides and skins and an operation called basification in mineral tanning where in neutralization of the tanning medium is carried out which also contributes to the generation of large amounts of neutral salts and total dissolved solids in tannery effluents.

Hollow fibre ultrafiltration membranes

CSIR-CSMCRI has developed and licensed a process for preparation of hollow fiber ultrafiltration membrane using polysulphone / polyacrylonitrile. The technology has been licensed to M/s Uniflux Membranes LLP, Pune. A commercial unit for production of hollow fibre membrane modules has been commissioned.



Fig. 1.65 HF membrane modules based on CSIR-CSMCRI knowhow prepared by M/s Uniflux Membranes LLP, Pune

Electrochemical Defluoridator

CSIR-CECRI has developed a fluoride removal unit for providing fluoride-free drinking water. The removal of fluoride in drinking water is effected by flowing the water through an electrochemical cell. The electrolyser consists of soluble aluminum alloy anodes which on the supply of electricity generator aluminum hydroxide precipitate. The aluminum hydroxide adsorbs the fluoride and easily settles within 30 minutes. The fluoride content in the settled water is at the safe level. Further, aluminum hydroxide also removes other colloidal impurities providing a safe and pure drinking water. The unit is: easy to install; on-line connectable and wall mountable; with indigenous materials; and energy consumption only about 0.3 to 0.4 unit per kilolitre. The technology has been transferred to: M/s Sandur Fluid Controls (P) Ltd, Bengaluru; and M/s Nagpur Aquatech (P) Ltd., Nagpur.

Institute has also developed electro-chemical De-arsenator.



Fig. 1.66 Large capacity community unit of Electrochemical Defluoridator and De-Arsenator

Catalyst Thoxcat ES for sweetening of LPG

The presence of mercaptans in petroleum products like LPG, naphtha, gasoline, ATF and kerosene is undesirable due to their foul odour and highly corrosive nature. In commercial practice, the low molecular weight mercaptans present in LPG and light straight run naphtha (LSRN) are first extracted with alkali and subsequently catalytically oxidized to disulfides with air.

The technology for the production of catalyst Thoxcat ES useful in extractive sweetening of LPG and liquid-liquid sweetening of lighter petroleum fractions viz, light straight run naphtha (LSRN), light thermally/catalytically cracked gasoline has been developed by CSIR-IIP in collaboration with BPCL. Thoxcat ES catalyst is in liquid form containing catalyst active matter in dilute aqueous alkaline solution. This catalyzes the oxidation of mercaptans present in lighter petroleum fractions to less deleterious disulfides. This is superior to commercial catalyst being used globally in terms of activity, lesser cost and catalyst consumption rate.

Cobalt phthalocyanine disulphonates are being used as commercial catalyst for extractive sweetening of LPG. CSIR-IIP has developed cobalt phthalocyanine sulphonamide as a new superior catalyst for using in same process.

The technology for the production of Thoxcat has been licensed to M/s Lona Industries Ltd, Mumbai. By using this catalyst refineries have been benefited by savings in foreign exchange as the product is indigenous and cost-effective. BPCL R&D Centre is collaborator / partner for the development and commercialization of this catalyst.



Fig. 1.67 Main reactor in catalyst production unit at M/s Lona Industries Ltd., Mumbai

Process for Dodecane Fraction from Straight-run Kerosene.

Reprocessing of spent nuclear fuel is an indispensable process for the economical use of actinides in the nuclear energy production. Such process involves the separation of reusable actinides from unwanted fission products by solvent extraction. The commercially used process employs tri-butyl phosphate (TBP) diluted with normal dodecane fraction as solvent for the extraction.

Normal dodecane (n-C12) constitutes in an approximate weight percentage of 25-30 in straight run kerosene fraction boiling in the range 212-225°C with the rest being non-normal C12 components and minimum of lighters and heavies. Presently the whole demand of normal dodecane fraction is being met by import only due to non-availability of indigenous technology. CSIR-IIP is the only institute in India extended its research expertise for the development of process for the production of normal dodecane fraction from straight run kerosene. The developed process involves finely tuned dry urea adduction methodology to separate straight chain paraffins from straight run kerosene. The fraction obtained meets the required specifications to use as solvent necessary for spent nuclear fuel processing.

Feasibility study for development & production of Ramrocket Fuel as per GOST 12308-89

T-6 fuel is an endothermic, high density, very low freezing point and low aromatics missile fuel. Such missile fuel has not been developed in India so far. CSIR-IIP in collaboration with DRDO has developed high density thermo-stable missile fuel 'CEL-16'. An initial batch of 10 liters and second batch of 50 liters of CEL-16 have been tested by DRDO on laboratory scale and has passed all stringent quality and performance requirements. The successful formulation of the T-6 fuel is a testimony for the scientific excellence of CSIR-IIP at large.

Eco friendly process for converting waste plastics to transportation fuel and petrochemicals

The production and consumption of plastics is increasing rapidly all over the world, the rate of increase being much higher in India. It is estimated that polyolefins like polyethylene and polypropylene account for 60-70 % of the total plastics consumed and these usually end up as a waste in very small span of time. The plastic wastes being non biodegradable pose serious disposal problem and are environmental hazards. The usual methods of disposal like land filling and incineration have inherent disadvantages like turning land into waste and emitting toxic substances. Reutilization by mechanical recycling produces poor quality products apart from emitting harmful chemicals during processing. Hence a suitable process is required that can obviate these drawbacks. CSIR-IIP has developed a unique process by which waste polyolefinic can be converted exclusively to any one of the value added products like gasoline or diesel or aromatics. The process has the potential to solve the problem of waste disposal in an environment friendly manner as well as augment the supply of fuel, thereby conserving petroleum.

The novelty of the process lies in exclusive production of any one of the products viz. gasoline or diesel or aromatics along with simultaneous production of LPG in each case. The liquid fuels meet most of the specifications of automotive grade fuel and aromatics are rich in benzene, toluene and Xylenes (BTX), which are important petrochemicals. 1 Kg of clean waste plastics, free from fillers and contaminants, can produce either ~700 ml gasoline or

Diagram illustrating the self-assembly of a fluorinated dendritic molecule on gel-coated filter paper. The molecule structure is shown with fluorinated phenyl rings and alkoxy (OR) groups. The process involves self-assembly onto the gel-coated filter paper, resulting in a dark spot. The concentration of the molecule is varied, showing the effect on the assembly: 10^{-15} M ($\sim 12 \mu\text{g}/\text{cm}^2$), 10^{-7} M , and 10^{-3} M . The assembly is reversible, as indicated by the TNT label and the arrow pointing back to the molecule.

Fluorinated Ethylene Propylene (FEP-Resin) has strategic space research applications, as coating material for cryogenic polyamide pipelines, rockets and missiles. Besides coating FEP-Resin also finds applications in melt extrusion and impregnation. FEP-Resins are known for their excellent chemical resistance, superior electrical properties and high service temperatures of upto 200°C. FEP-Resins also provide outstanding low temperature toughness and unique flame resistance. Presently, there is no techno economically feasible process for hexafluoropropene available in India or elsewhere. CSIR-IICT has developed a process for FEP-Resin by copolymerization of HFP and TFE under specific conditions in collaboration with M/s Hindustan Fluorocarbons Limited (HFCL), Hyderabad. The process was successfully demonstrated to Vikram Sarabhai Space Centre (VSSC), ISRO Thiruvananthapuram.

Isolation of Tocopherols and Phytosterols

Tocopherols are natural antioxidants. Alpha and gamma tocopherols exhibit strong vitamin E and antioxidant activities respectively. Phytosterols exhibit several pharmaceutical and nutraceuticals applications. Deodorizer distillate (DOD) is a by-product obtained during the refining of vegetable oils and is a good source for the isolation of phytosterols and tocopherols. Deodorizer distillate generally contains about 35-40% triglycerides, 40-50% fatty acids, 4-10% sterols and 3-8% tocopherols. Isolation of tocopherols and phytosterols from DOD results in value addition to by-products of vegetable oil processing industry. CSIR-IICT has developed a process for the isolation and enrichment of tocopherols and phytosterols from soybean oil DOD for the first time in India. The process involves esterification and transesterification of DOD to fatty acid methyl esters (DOD-FAME). The phytosterols were separated from DOD-FAME by crystallization and tocopherols were enriched to required purity by separating the FAME using distillation techniques. The technology has been transferred to M/s. Biopharma Pvt. Ltd., Hyderabad and M/s Perfect Vitamins Pvt. Ltd., Mumbai.

Catalyst system for the preparation of Nitrotriazolone

Among the various energy materials, 3-nitro-1,2,4-triazol-5-one (NTO), a secondary high explosive of insensitive nature is mainly used in insensitive Munitions (IM). Conventionally, NTO is synthesized by nitration of TO using excess quantity of concentrated nitric acid. This process is associated with the disposal of hazardous waste (including residual nitro aromatic compounds) during the downstream processing. CSIR-IICT has developed green nitration process using solid acid catalysts for NTO. By using solid acid catalysts, most of these problems related to nitration are eliminated and the catalyst can be simply separated and recycled for subsequent use. The process was developed in collaboration with High Energy Materials Research Laboratory (HEMRL), Pune.

Bio-jet Fuels at CSIR-IIP

CSIR-IIP is the first institute in India to produce 15 litres of high quality biojet fuel from *Jatropha curcus* oil. This fuel has been tested by both Indian Oil Corporation and Hindustan Petrochemicals Ltd. and has been found to meet all specifications as per ASTM D 1655. A pilot plant has been built with a capacity of 20 litres per day and is in operation, which is expected to produce enough fuel for testing in engine of Pratt & Whitney, Canada.

The technology involves pre-treatment of oil followed by hydro deoxygenation, hydro-cracking followed by hydro isomerization. The innovativeness of this technology is that all these steps can be carried out by single catalyst.



Fig. 1.70 Bio-jet pilot plant at CSIR-IIP

Unique Major Facilities

Centre for Chemical Biology

To facilitate primary screening of new chemical entities and target based screening, CSIR-IICT has established a dedicated Chemical Biology facility. The facility provides necessary infrastructure and expertise for identification of chemical tools to study biological pathways and to discover lead compounds for the development of novel therapeutics, especially in the areas of diabetes, cancer, cardiovascular diseases and CNS disorder.

Centre for Semiochemicals

Considering the severe environmental pollution and serious health hazard problems caused by indiscriminate use of pesticides, it has been the endeavour of CSIR to look into various methodologies for pest control as alternative to pesticides. CSIR-IICT is the first Institute in India to utilise pheromones as an eco friendly alternative to pesticides. Insect pheromones, an important category of semiochemicals, are compounds released by insects for specific communication within their species. Having understood the versatility and the potential of insect pheromones to manage pest population in a given crop, CSIR-IICT launched an ambitious program to popularise Pheromone Application Technology (PAT) for the benefit of the society. With support from governmental agencies, it is envisaged that this program would establish PAT as a popular and affordable agro-practice in India.

High Resolutions GCMS

A New facility of HRGCMS has been setup at CSIR-IIP. The instrument is a double focusing magnetic analyzer with resolving power of 80000. The instrument is equipped with all glass heated inlet sample introduction system (AGHS) for characterizing hydrocarbon types in petroleum components. It is also coupled with HRGC, direct insertion probe (DIP) and high temperature probe for organic compound analysis. The instrument utilizes various ionization techniques such as electron ionization (EI), chemical ionization (CI) and field ionization/field desorption (FI/FD). The functioning and all performance specifications of the instrument were demonstrated during the commissioning activity.

New HPLC facility

For the study of petroleum heavy end products, petrochemicals, different reaction products has been installed at CSIR-IIP. (HPLC Agilent Technologies, 1260 infinity, USA with ELSD, DAD & Florescence Detector)