RESEARCH AND DEVELOPMENT OF TASK SPECIFIC FUNCTIONAL ORGANIC MOLECULES

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Abstract

Over the years, research in the area of organic chemistry has contributed immensely towards the development of functional organic molecules for various departmental projects and societal benefits. Expertise of organic synthesis is being utilized to design and syntheses of numerous small molecules as well as supramolecules to carry out various task specific functions. Syntheses of ligands useful for actinides and lanthanides extraction in back end fuel cycles always remain as one of the major activities. Fluorescent organic molecules also are being used for many applications such as liquid dye lasers, fluorescent gamma dosimeters, sensors for chemo/bio analytes, bio-imaging agents and photosensitizers for photodynamic therapy of cancers. Similarly, research in the areas of supramolecular host-guest interactions and molecular electronics are also carried out towards the advanced technological developments. In this chapter, research activities carried out in these areas are summarized.

1. Introduction

The activities in the area of organic chemistry are wide spread from developing organic reaction methodologies to their applications for final products required in departmental projects as well as for societal benefits. In this chapter, specific examples of development of these task specific organic molecules are presented. Custom made organic molecules are always in high demand especially in nuclear science and technology. Thus organic chemistry research is always focused towards the design and development of tailor made molecules for various projects of DAE. For example, in back end fuel cycle, organic ligands are indispensable for actinides and lanthanides separation from nuclear wastes. Thus, synthesis and development of small molecule based organic ligands useful in backend fuel cycles remain as one of the major activities. During the beginning of 21st Century, two new activities based on supramolecules and fluorescent molecules were started which were also driven by the departmental requirements. Slowly these novel molecules were also used for developing hi-tech molecular systems as well as for societal applications, as summarized in this chapter. The intricate R&D work involved during the innovations are not discussed in detail, rather this chapter is focused mainly on the applications of the synthesized molecules.

2. Synthesis of organic ligands for back end fuel cycle

2.1. Small molecule based ligands

In the back end nuclear fuel cycle, one of the most challenging tasks is trivalent actinides (An) and lanthanides (Ln) separation. Thus, numerous ligands containing S and N donor atoms are checked for the separation studies of Ln/An. Four separation techniques are mostly used in different partitioning strategies of back end nuclear fuel cycle: (1) U and Pu partitioning from spent nuclear fuel, (2) heat-generating fission products separation, (3) trivalent An and Ln co-extraction and (4) trivalent An separation form the trivalent Ln. Amongst these, the separation of An from Ln is an urgent and important problem for waste management and processing of fuels from the nuclear plants. Over the years, organic chemistry research has been significantly contributing toward design and synthesis of various extractants to support back end fuel cycle.

In 1985-1988, Horwitz group (Argonne National Laboratory, USA) developed the Trans Uranium Extraction (TRUEX) process for the removal of long-lived alpha emitters from transuranic (TRU) waste solutions using various phosphine oxide ligands. In the early 1990s, similar work was carried in collaboration with the Fuel Reprocessing Division (FRD) and Radiochemistry Division (RCD). Major contribution i.e. partitioning of actinides from high level radioactive wastes, were initiated by synthesising organophosphorus ligands like carbamoyl methylene phosphine oxide (CMPO), TBP etc (**Fig 1**). CMPO was quite efficient for An extraction, but its selectivity was poor. In 1992, a slightly modified three-step procedure [from the reported method by Horwitz group] for CMPO synthesis in substantial quantities was developed. CMPO and TBP mixture was used as the extractant to avoid the formation of third phase hurdle, which could reduce the alpha activity of HAW and HLW solution substantially (~4 nCi/ml). The R&D activities on synthesising new extractants/ligands are continuously pursued over the years. In early 2000, extensive works were carried out on the development of several amides/diamides (e.g. N,N′-dimethyl,N,N′-dibutylteradecylmalonamide (DMDBTDMA)) (**Fig. 1**) based organic ligands as alternate extractants in the back end of nuclear fuel cycle. The major challenge was faced for purification of the long chain amides by distillation under very high vacuum as well as maintaining optimum temperature to avoid degradation of amide. To meet the growing demands of extractant, these ligands were synthesized and delivered in multi-kilogram scale.

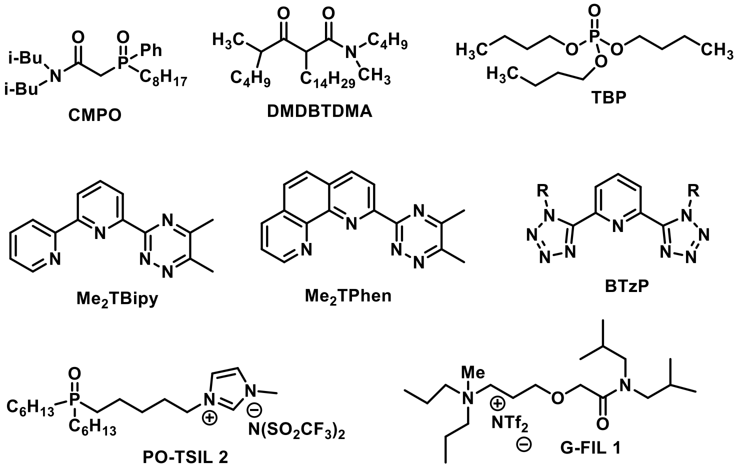


Fig. 1: Chemical structures of different small molecule based ligands

In early 2010, development of new classes of extractants such as heterocyclic based, ionic liquid based, solid supported resin based etc. was started for Ln/An separation. Towards this, heterocyclic based terdentate 'N' donor ligands with different structural rigidity, *viz*. 5,6-dimethyl-(1,2,4)-triazinylbipyridine (Me_2TBipy) and 5,6-dimethyl-(1,2,4)-triazinylphenanthroline (Me_2TPhen) (**Fig. 1**) were designed and synthesized and their Ln^{3+} complexation studies were done in collaboration with Radiochemistry Division (RCD). In continuation, another class of pyridine-triazole based terdentate multiple 'N' donor ligand, 2,6-bis(1H-tetrazol-5-yl)pyridine (H_2BTzP), was developed and its complexation behaviour with trivalent americium, neodymium, and europium were also evaluated.

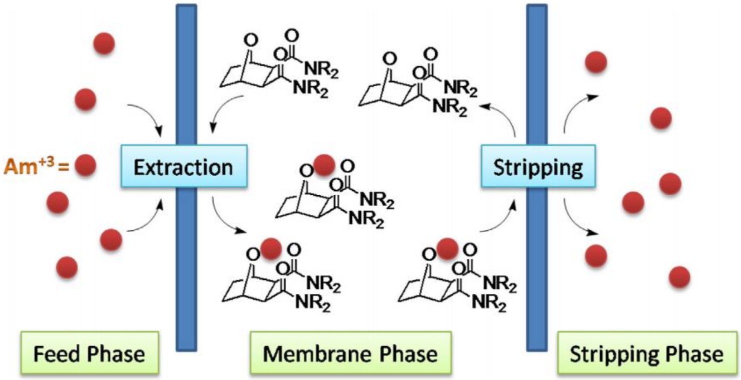


Fig. 2: Transport Am(III) from HNO_3 medium across a supported liquid membrane.

During this investigation, (N,N,N',N'-tetra-2-ethylhexyl)7-oxabicyclo[2.2.1]heptane-2,3-dicarboxamide (OBDA), a new class of conformationally constrained diamide, was developed. It showed selective transportation of Am(III) from HNO_3 medium across a Supported Liquid Membrane (SLM) with good transport rate, diffusion coefficient over other fission products (**Fig 2**). Utilizing this same concept, oxa-bridged tricyclo-dicarboxamide (OTDA) was synthesized which showed selective extraction of tetravalent actinides relevant to the Plutonium Uranium Redox EXtraction (PUREX) process. In continuation, liquid membrane based on OTDA was also prepared which showed promising separation of Pu^{4+} from nuclear waste with high selectivity. Ruthenium (Ru) is one of the most hazardous fission products of nuclear waste, although ^{106}Ru has application in radiotherapy. Besides, Ru compounds are also highly useful in catalysis and analytical applications in various fields. In this context, dipropylmethyl-2-(N,N-diiso butyl) acetamidoammonium iodide impregnated Amberlite XAD-4 resin was investigated for Ru sorption from nitric acid medium (**Fig. 3**). This method could be useful for Ru separation from waste solutions. Studies towards utilizing ionic liquid (IL) as an extractant in the back-end fuel cycle were also carried out. A glycolamide-functionalized ionic liquid was designed and synthesized which was used for trivalent Ln(III) and Ac(III) extractions from low acid feed solutions (in collaboration with RCD). Task specific ionic liquid (POTSIL) based on trialkyl-phosphine oxide and NTf_2^- counter anion was developed for the extraction of UO_2^{2+} and Pu^{4+} from acidic feed solutions. The trialkyl-phosphine oxide based ionic liquid was materialized into an inert polymeric material XAD-7 to obtain a Solvent Impregnated Resin (SIR). This SIR was used for sorptions of both U(VI) and Pu(IV). Another new class of triaryl-pyridine/diaryl pyridine (TAP/DAP) amide based extractans were designed and materialized for extraction in back end fuel cycle. The 3,3′-bis (2-oxydialkyl acetamide) triaryl pyridine based room temperature ionic liquids (RTIL) diluents are also developed for selective Pu(IV) extraction from nitric acid solutions.

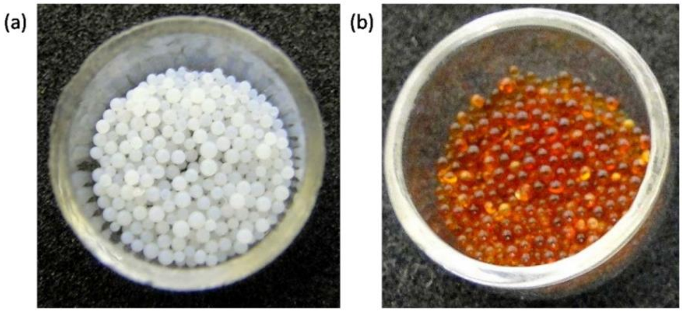


Fig. 3: Amberlite XAD-4 resin beads; (a) before and (b) after Ru impregnation

In another effort in collaboration with Fuel Chemistry Division, a novel deep eutectic solvent (DES) based on alkyl triphenyl phosphonium salt and decanoic acid was developed, which showed promising results in selective sequestration of Pu(IV). This novel hydrophobic DES was synthesized using a facile and green mechanochemical route, employing alkyl triphenyl phosphonium bromide and decanoic acid (DA) as the hydrogen bond acceptor and donor respectively. The formation of strong hydrogen bonds led to exceptionally high binding energy of DES, which imparted its stability and made it useful for radioactive waste management. Additionally, a technique for decontaminating radioactive surfaces by employing a strippable gel (RADGEL), composed of a deep eutectic solvent and polyvinyl alcohol, was used for radioactive surface decontamination, with the goal of enabling reuse of the surface post-decontamination. The fabricated gel was able to decontaminate various contaminated surfaces upto 99%. In another effort, pyridinium and methyl ammonium based macroporous bifunctional anion exchange resin was prepared by chemical modification of Reillex^{TM} 402 poly(4-vinyl pyridine) which showed efficient separation of plutonium(IV) and neptunium(IV) from acidic solution.

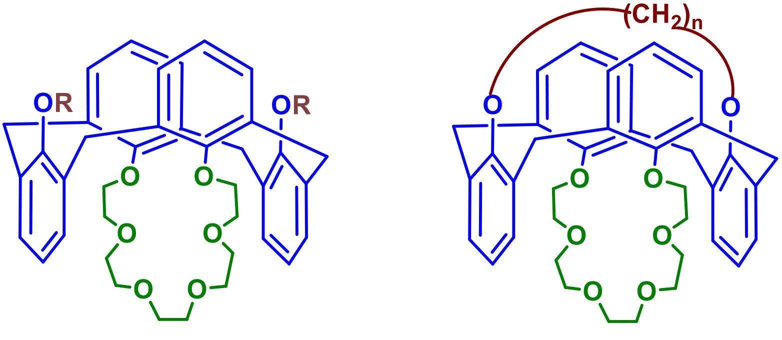
2.2. Supramolecular ligands.

Calix[n]arenes (n = 4, 6, 8), a class of cyclic oligomers, are highly important in supramolecular chemistry because of their hydrophobic cage-like structure with choisable/tunable polar functional groups at the rims. Hence these are potentially useful supramolecular ligands for selective metal extraction. Since early 2000, extensive research work was carried out towards design and synthesis of various calix[4]arene and calix[6]arene derivatives as host molecules. Selective alkylation of the phenolic OH groups of calixarenes is essential for their subsequent functionalization to tailored molecules having pre-organized structures with specific recognition abilities for metal ions or molecules. Hence, a new methodology was developed using ultrasound irradiation for quick access to a series of 4-*tert*-butylcalix[6]arene mono-alkylethers in higher yields as compared to the conventional refluxing procedure (*Tetrahedron*, 2002, *58*, 5287–5290.). Some of these calix[6]arene derivatives were used for the syntheses of molecular hosts for departmental requirements.

Bis-calixarenes attracted considerable attention because of their multi-cavity structure for guest complexation and the probability of higher molecular recognition property due to possible co-operative and/or allosteric effects. Synthesis of such compounds suffers from challenges of protection/deprotection of chemically similar phenolic groups prior to intermolecular coupling. Therefore, efforts were made to realize a practical and efficient synthesis for this important class of molecules. A singly bridged *bis*-calix[6]arene was synthesized by coupling two 4-*tert*-butylcalix[6]arene units and one diethyleneglycol ditosylate molecule. Complexation studies revealed that the synthesized singly bridged *bis*-calix[6]arene is more selective for K^+ ion and has the ability to discriminate between different alkali metal ions.

The safe handling and disposal of high level radioactive waste (HLW) is one of the major challenges faced in nuclear industry. ^{137}Cs producing high energy γ radiation (661.9 keV) with a long half-life ($t_{1/2}$ = 30.1 years) constitutes the major heat source in these wastes. Therefore, separation of radioactive cesium from the nuclear waste is essential to minimize the health hazards associated in management of nuclear waste along with its safe storage and ultimate disposal. Also, the isolated ^{137}Cs is an alternative radiation source for sterilization of blood, medical accessories, food etc. Among different calix[4]-crown ethers, 1,3-dioctyloxycalix[4]arene-crown-6 (**A**, **Fig. 4**) in its 1,3-alternate conformation is well known for its high efficiency in selective extraction of cesium ions ($K_{Cs+}/K_{Na+} > 33000$) from highly acidic nuclear waste in the presence of even large concentrations of sodium ions. Conventional route for synthesis of compound **A** involves 1,3-distal dialkylation of phenolic-OH groups in calix[4]arene followed by attaching the polyether linkages to the remaining phenolic OH group using cesium carbonate (Cs_2CO_3) as a template. But, one of the major challenges involved in the synthesis of such a molecule is in the first di-alkylation step, which usually is very sluggish for longer chain (> C5) alkyl halides, requires long time (5–6 days) even under refluxing conditions, provide the products in moderate yields along with unwanted side products. For the first time, it was shown that use of microwave irradiation (MWI) could furnish the desired 1,3-dialkylated calix[4]arenes (in cone-conformation as the predominant/sole product) in substantially increased yields (71-85%) within a very short reaction time (0.5–2.5 h), eliminating the undesired side reactions.

The synthetic utility of this microwave-assisted protocol was also elaborated for base catalysed partial etherification of the phenolic-OH groups in calix[4]arene/4-tert-butylcalix[4]arene with different electrophiles. The 1,3-di-*n*-octyloxycalix[4]arene synthesized by this protocol was further utilized towards the synthesis of 1,3-di-*n*-octyloxycalix[4]arene-crown-6 (**A**, **Fig. 4**) in 1,3-alternate conformation using Cs_2CO_3/pentaethyleneglycol ditosylate in acetonitrile solvent. The solvent extraction studies done in collaboration with Radiochemistry Division (RCD), suggested that calix-crown ligand **A** can be effectively used for selective recovery of cesium ion from the acidic feed solutions including high level nuclear wastes (HLW).



A; R = C_8H_{17}

B; n = 14, 10, 8

Fig. 4: (A) Chemical structures of cesium ion selective 1,3-di-octyloxycalix[4]crown-6 (B) 1,3-cyclodialkyloxycalix[4]arene-crown-6

In a related, but significantly more challenging effort, design and synthesis of some 1,3-cyclodialkyloxycalix[4]arene-crown-6 (**B**, **Fig. 4**), with similar functionality like compound **A**, but having more rigid structure was also accomplished. Using these 1,3-cycloalkyloxy bridged calix[4]arenecrown-6-ethers (**B**) as ionophores, liquid membrane based Ion Selective Electrodes (ISE) for determination of cesium ion content in HLW were developed in collaboration with Radioanalytical Chemistry Division (RACD). The best response was obtained for the 1,3-cyclotetradecyloxycalix[4]arenecrown-6 (**B**, n = 14) where the ISE showed low detection limit (3.7×10^{-8} M Cs^+) with quick response time (< 20 seconds). In addition, other calixcrown compounds such as, di-hydroxycalix[4]arene-crown-6, tetra-*tert*-butyl-dimethoxycalix[4]arene-crown-6 and 1,3-dioctyloxycalix[4]crown-6 were also synthesized and investigated for their use as ionophore in polyvinylchloride (PVC) based liquid membranes ISE for detection of cesium ion. It was found that ISE developed with 1,3-dioctyloxycalix[4]crown-6 which was highly selective for cesium ion as compaed to other alkali, alkaline earth and transition metal ions in the pH range 4 to 11. The lifetime (10 months) of the electrode was the highest amongst the membrane based Cs-ISE reported till then.

The studies were extended to synthesize homocalixarenes also which are metacyclophanes having structures similar to that of calixarenes but having at least one bridging group between the phenyl rings larger than a methylene group. Hence, they possess bigger cavity sizes and therefore have the ability to accommodate larger guests. In parallel to the host-guest interaction studies with different metal ions, supramolecular interactions of different calix[4]arene, calix[6]arene, *bis*-calixarene, homocalixarene and calix[4]pyrrole derivatives with C_{60} and C_{70} fullerenes were also investigated by UV-Visible, fluorescence, NMR and theoretical studies that provided newer insights in the host-guest (supramolecular chemistry) interactions. The resultant publications in a host of high impact journals are often referred even today.

3. Design and development of organic fluorescent dyes for diverse applications

During the early 2000, research and development of organic dyes was started. The primary focus was to design and synthesis of fluorescent laser dyes for departmental requirements. As per the requirement of Laser & Plasma Technology Division (L&PTD), boron dipyrromethene (BODIPY) based laser dyes were synthesized in multi-gram scales, which were used by the user groups for further applications in various departmental projects. Two technologies ("Laser Dye Pyrromethane 567" and "Laser Dye Pyrromethane PM597") related to the synthesis of BODIPY based laser dyes were transferred to a private company. In continuation, extensive research work was done to develop new highly photostable laser dyes.

Due to better solubility in water and reasonably large portal cavity, cucurbit[7]uril (CB[7]) (**Fig. 5**) appears as a promising host for organic laser dyes to enhance their service life used by L&PTD. The high cost of CB[7] prompted us to develop an indigenous template mediated protocol for its high yielding synthesis of CB[7] during 2013-2014. Thus, a high yielding (up to 20%) and gram scale synthesis of CB[7] was developed wherein organic dyes and small molecules were used as the templates. Extensive host-guest interactions studies with several organic laser dyes using sophisticated spectroscopic techniques, established that a BODIPY dye in association with CB[7] could be used on continuous runs for isotope separation.

Rhodamine B is another important dye used as active medium in dye laser research. However, aggregation and poor photochemical stability in water restrict its use in aqueous dye laser studies. It was demonstrated that encapsulation of rhodamine B inside CB[7] cavity is able to suppress its aggregation to improve its fluorescence efficiency and photochemical stability dramatically. The synthesized CB[7] was successfully utilised in improving laser performances of Rhodamine B based aqueous dye laser system in collaboration with Laser and Plasma Technology Division (L&PTD). Together, these findings established CB[7] as an efficient modifier in aqueous dye laser systems as it improved the photochemical parameters of active medium immensely.

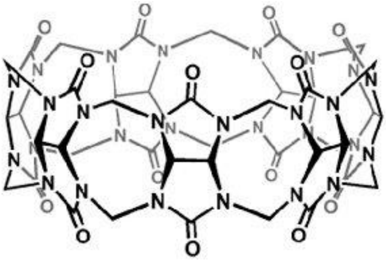


Fig. 5: Three dimensional structure of cucurbit[7]uril (CB[7])

Fluorescence based molecular probes are quite versatile considering their rapid response, easy setup and high sensitivity. These rely on changes in fluorescence colour or intensity during interactions with analytes. The first fluorescent chemosensor was reported in 1867 by Goppelsröder F. *et. al.* where they demonstrated detection of aluminium ions (Al^{3+}) using fluorescent morinchelate. During the late 1970s and early 1980s, Sousa, Bousa-Laurent, de Silva, Tsien, Czarnikand and others carried out pioneering investigations focusing on the development of fluorescent chemosensors. Since then, this field witnessed an exponential growth, thanks to its wide range of practical applications.

Contributions in this area were started since 2009-2010 with a number of synthesized dual chromophoric systems (**1**, **Fig. 6**) made of fluorescent BODIPY and pyrene dyes. One of those synthesized dyes was employed in FRET (Förster resonance energy transfer) based sensing of Fe^{2+} ions. Soon after this report, research interest was germinated within the group to develop BODIPY based fluorescent materials for sensor applications. Initially, research interest was focussed on developing new organic fluorescent materials as pH sensors, given that pH plays a crucial role in biological and chemical systems. In 2013, the imino-BODIPY (**2**, **Fig. 6**) based fluorescent materials for pH sensing was developed.

Copper and iron ions have play crucial roles in variety of physiological processes due to their catalytic and oxidative properties in living organisms. On the other side, their excessive accumulation can cause oxidative stress and may lead to neuro-degenerative diseases. They are involved in the formation of reactive oxygen species (ROS) that eventually damage the structures and functions of lipids, nucleic acids, and proteins. In view of these physiological importance, a number of fluorescence sensors such as the BODIPY-acetylacetone derivative (**5**, **Fig. 6**) and 1,10-phenanthroline tethered BODIPY (**6**, **Fig. 6**) were developed as Cu^{2+} ions sensors. In another effort, a BODIPY-TEMPO conjugate (**7**, **Fig. 6**) was synthesized for the detection of Fe^{2+} ions present in intracellular labile iron pool. A kit was also developed utilizing the similar concept which is available for technology transfer ("A Kit for Detection of Intracellular Iron (Fe^{2+}) in live cells"). In continuation, the solvent driven aggregation-deaggregation properties of the BODIPY nanoparticles were tactfully exploited in the accurate estimation of alcohols in different solvent mixtures. A technology based on this concept was developed which is available for technology transfer ("Accurate estimation of alcohol content in alcoholic products through easy synthesis of BODIPY dye").

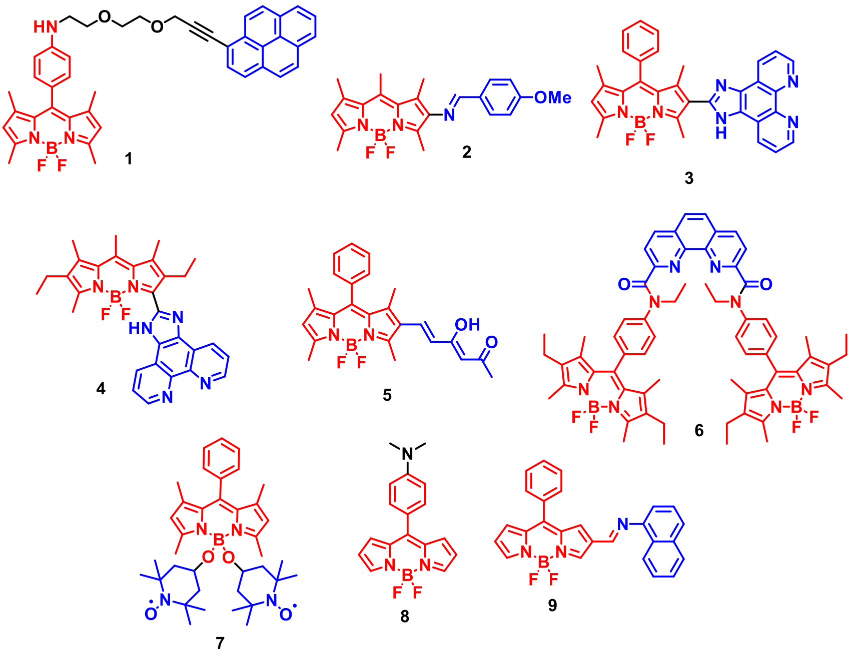


Fig. 6: BODIPY based fluorescence chemo-sensors

As a part of the chemical sensing work, a new project on development of gamma dosimeters was taken up during 2020. Scarcity of the highly sensitive, low cost and easy to use gamma dosimeters were the major motivation to develop fluorescent dye based gamma dosimeters for practical applications. Several fluorescence based gamma dosimeters were developed using the amino- and imino-BODIPY based dyes (**8** and **9**, **Fig. 7**). These dosimeters are highly sensitive, low cost, easy to use and can be used as colorimetric as well as fluorometric dosimeters. Most importantly, dynamic range of these dosimeters can be tuned by changing the dyes concentrations which are useful for measurement of absorbed gamma doses in food and blood irradiation processes.

Efforts were also made to develop fluorescent materials for the sensing of other classes of health-related important bio-molecules. In this area, water-soluble BODIPY (**10**, **Fig. 7**) nanoparticles were developed which were used for the detection of both bovine and human serum albumins. The BODIPY based nano material was further used to monitor formation of insulin oligomer useful for the early detection of diseases like type II diabetes. In a related effort, a BODIPY based salicylaldimine Schiff base (**11**, **Fig. 7**) and its corresponding boron complex were successfully shown to detect amyloid fibrils of lysozyme that may enable early detection of amyloid fibrils linked neurological disorders like Alzheimer's disease, Parkinson's disease etc. Recently, a distylrylamino BODIPY molecule (**12**, **Fig. 7**) was judiciously designed and synthesized for developing surfactant mediated detection of bio-medically important analytes like protamine (antidote of blood clotting agent heparine) and spermine (cancer marker). In another work, Kumujian-C, a β-carboline based fluorescent probe was synthesized starting from L-tryptophan which was successfully employed for detection of sulfite in real samples.

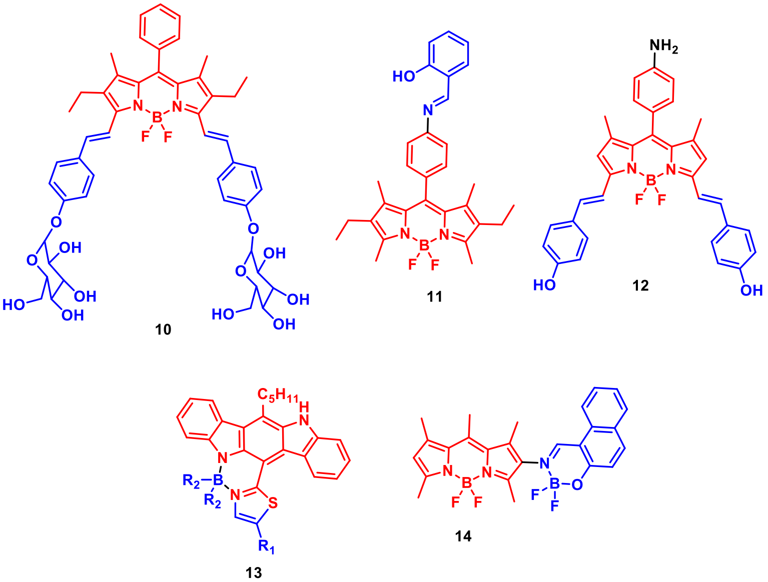


Fig. 7: BODIPY based fluorescent molecular sensors for biomolecules and photodynamic therapy of cancers

Fluorescence imaging is a highly sensitive and selective technique for biomolecules detection in organisms. Small molecular probe-based fluorescent imaging is indispensable because of its excellent selectivity and rapid response towards specific species in living systems. In this contribution, BODIPY and an indolo[3,2-b]carbazole-based boron complexes were synthesized that showed specific localization in different cellular organelles in different cell lines. The earlier mentioned probes like BODIPY-phenanthroline conjugate (**6**), BODIPY-TEMPO conjugate (**7**) and Kumujian-C are able to detect Cu^{2+}, Fe^{2+} and sulphite ions respectively by cellular imaging.

Besides cellular imaging, organic dyes are also utilized as photoinduced therapeutics in photodynamic therapy of cancer. In this type of therapy, on photoirradiation, BODIPY based triplet photosensitizer populates its triplet excited state through an efficient inter system crossing (ISC) from its singlet excited state which subsequently generate ROS *viz.*. singlet oxygen ($^1O_2$) inside cells, thereby killing cancer cells. In this area, BODIPY-O-glucoside conjugates were well studied as photodynamic agents. Recently, a series of BODIPY-helicenes dyes (**13**) with twisted structures were developed which act as efficient heavy-atom-free triplet photosensitizers showing promising potential as photodynamic agent. With the continuation of this work, a BODIPY-naphtholimine-BF_2 dyad (**14**) was developed which targets both endoplasmic reticulum and lipid droplets, and may be useful for dual imaging, while its photosensitizing ability may be highly useful for killing of cancer cells. This is an example of next generation photosensitizers (PS) which shows “organelle-targeted-PDT” and provides new paradigm in the field of precision medicines to address the current challenge for treating pancreatic ductal adenocarcinoma (PDAC) (*JACS Au*, 2024, *4*, 2838–2852). Many of these sensing and PDT works are published as cover page articles and cover profile in various reputed journals.

4. Development small molecules for organo-electronics. Development of “Molecular Electronics” is an amalgam of physics, chemistry and engineering ideas. One of the ultimate goals of “Molecular Electronics” in nanotechnology is to build electronic devices using individual organic molecules. During the last two decades, BSG, in collaborative efforts with Physics Group contributed immensely towards the synthesis of various potential organic molecules for the development of “Molecular Electronics” as an alternative to silicon-based microelectronics. Porphyrin, pyrene, perylene and BODIPY molecules and their derivatives have been found to be good candidates for hybrid nanoelectronics such as molecular diodes, resonant tunnel diodes, molecular transistors etc.

For this, new class of molecules such as alkenyl (C-6 and C-11 chains) porphyrin, pyrene, perylene, BODIPY (σ–π systems) (**15-17**, **Fig. 8**) were designed and synthesized which were electro-grafted on H-terminated Si surfaces to form the respective monolayers. The I–V characteristics of the monolayers showed excellent rectification behaviour with very high rectification ratio (RR = 1000–5000) or negative differential resistance (NDR) with very high peak-to-valley ratio (PVR). Another interesting work was demonstrated based on donor–acceptor bilayers consisting of fullerene (C_{60}) and tetraphenyl porphyrin derivative that acted as molecular diode and showed very high (∼1500) current rectification ratio. In continuation, σ–π–σ systems based on di-O-alkylated porphyrins with phenyl and fluorophenyl groups were designed and synthesized. The monolayers of the porphyrin with fluorophenyl groups were more compact and showed a ten-fold PVR relative to those devoid of the fluorine atoms in the porphyrin moiety.

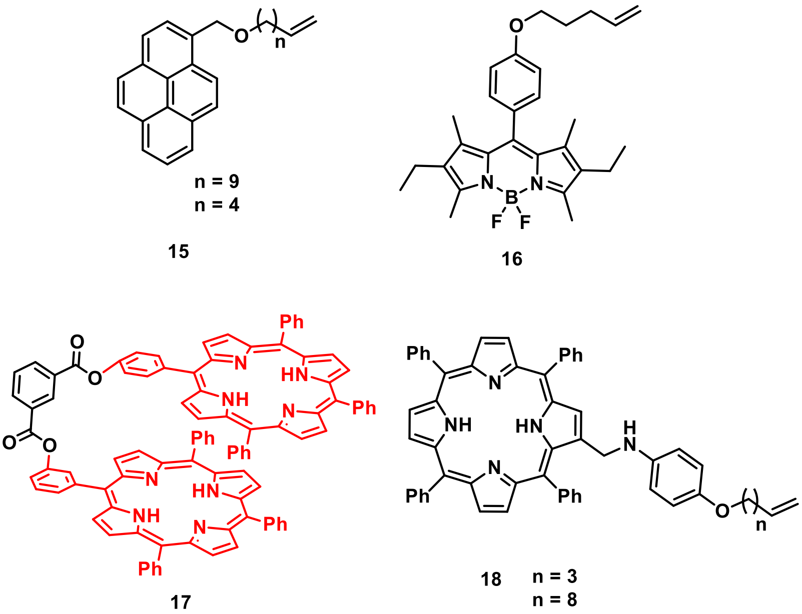


Fig. 8: Small molecules developed for molecular electronics applications

Further R&D on porphyrins resulted in the development of a new bis-porphyrin molecule (bis-TPP) (**17, Fig. 8**). The bis-porphyrin films were highly selective in sensing Cl_2 molecules with fast response (3 s) and recovery (~8 min) times, and sensitivity in the 10–500 ppb range. In another work, the bis-TPP and its Zn complex (Zn-bis-TPP) were used to develop two chemiresistive room temperature NH_3 gas (5–40 ppm in air) sensors with high selectivity, reproducibility and reversibility.

Another porphyrin (**18**, **Fig. 8**) based molecular rectifier was developed wherein a porphyrin (A) and an aniline (D) moiety were linked through a suitable spacer and electro-grafted onto Si-surfaces using the C-6/C-11 alkenyl chain at the aniline derivative as the linker to construct the respective MMS heterostructures. The C-11 containing molecular assemblies exhibited a 10^5 times higher rectification ratio (RR) than its C-6 congener, possibly because of the compact packing (*Chem. Sci.*, 2016, *7*, 1548-1557).

5. Sugar acrylamides: Tunable materials for manifold applications.

D-glucose, D-mannose, and D-galactose, three common naturally occurring hexoses, were chemically converted in to their monoacrylamide derivatives and a bisacrylamide (Glc-bis, crosslinker) from D-glucose (**Fig. 9A**). The applications of these acrylamide constituents, studied in collaboration with Chemistry Group, were demonstrated in various fields, which include controlled drug delivery, cell imaging, bio-sensing, nanoparticle preparations etc. Homogeneous carbohydrate gels (**Fig. 9A**) made from these sugar constituents were found to be bio-compatible and hence their application in stimuli-controlled drug delivery (**Fig. 9B**) was explored in conjugation with *N*-succinyl chitosan.

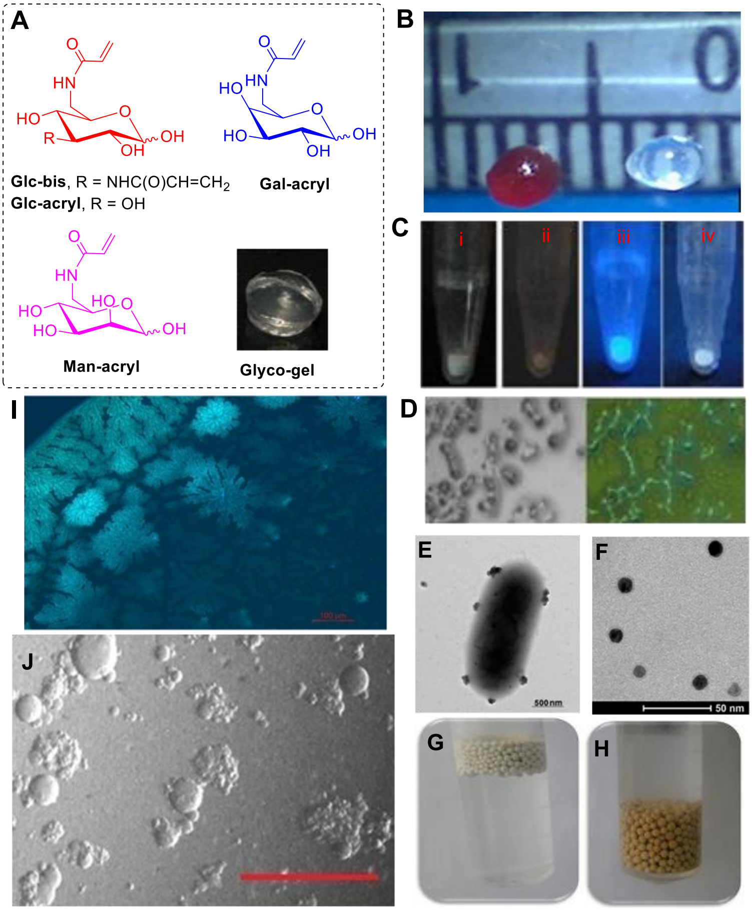


Fig. 9: (A) Structures of acrylamide derivatives of hexoses and swollen gel made from Glc-bis and Glc-acryl; (B) Optical microscope image of doxorubicin (DOX) loaded (red) and unloaded (transparent) swollen Glc-gel beads; (C) Photographic image of solid sample of Glc-acryl and Glc-bis under white light (i and ii); under UV (iii and iv); (D) Fluorescent image of Glc-acryl; (E) TEM image of the *E. coli* after treatment with Glc-bis@AuNPs; (F) TEM image of Glc-bis capped AuNPs; (G) Photographic image of commercial resin before glyco-conjugation and (H) after glyco conjugation; (I) Fractal formation observed with galacto-acrylamide; (J) Agglutination of microspheres (scale bar = 4 cm) upon interaction with *E. coli* bacterial cells

Detection of pathogenic bacteria and lectins are another important area that has been explored using the acrylamide templates. Depending on the carbohydrate units present in them, the sugar acrylamides displayed selectivity to different lectins. Another interesting property of sugar acrylamides is the inherent fluorescence exhibited by them due to Aggregated Induced Emission (AIE) (**Fig. 10C** & **10D**) phenomenon. To date, the afore mentioned acrylamides are the smallest sugar derivatives that display AIE phenomenon. This property was utilized to detect pathogenic *E. coli* bacteria (**Fig. 1E**) and lectins, *via* "*turn-on-turn-off*" mechanism in conjunction with sugar capped gold nanoparticles. The sugar acrylamides-based nanoparticles (**Fig. 9F**) displayed exceptional stability, even on storage at room temperature for months without any aggregation. The glycopolymers, made from these acrylamides, were functionalized on a commercial resin (**Fig. 9G & 9H**) and were used for the capture, detection and quantification of pathogenic bacteria and lectins. This system can sequestrate bacteria from a bulk solution without any volume reduction using external means. Formation of fractals (**Fig. 9I**) is another interesting structural characteristics observed with these small molecules. More recently, a system, based on silver loaded microspheres (**Fig 9J**) were constructed that could detect (visual observation), quantify and kill pathogenic bacteria. The outcomes clearly demonstrated the potential of the synthetic sugar acrylamides as tunable materials for multiple applications.

6. Conclusions

Over the years, organic chemistry research lead to the development of various classes of functional materials useful for different departmental projects as well as societal benefits. These includes (i) synthesis of ligands useful for Ln/An separation, (ii) development of new ligands for backend fuel cycles, (iii) synthesis of laser dyes in multi-gram scale, (iv) development of photostable laser dyes, (v) synthesis of organic supramolecules for metal extraction and laser applications, (vi) development of small organic molecules for opto-electronic applications like chemo/bio-sensing, molecular electronics, dosimetry etc, and, (vii) development of small molecules for diagnostics and therapies. Extensive research was pursued for these developments during the past years. All these resulted in new technologies for laser dyes syntheses and healthcare applications, along with high quality publications in various reputed journals. "High quality basic research towards the development of deliverables for departmental applications as well as societal applications" remains the goal of the research in organic chemistry since decades and the efforts and endeavour will continue with full vigour in the future years to come.

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