

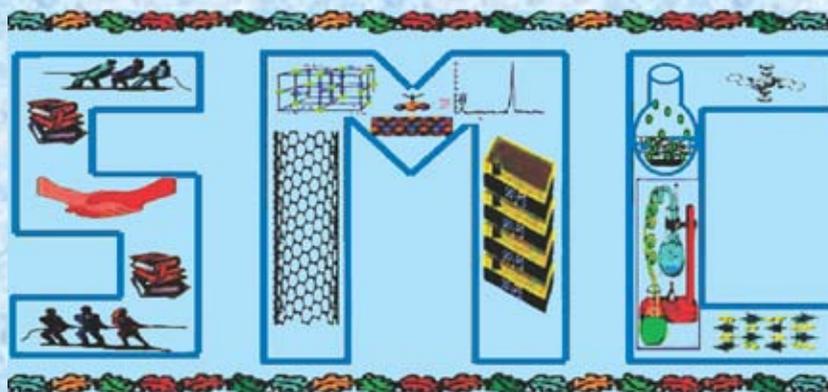
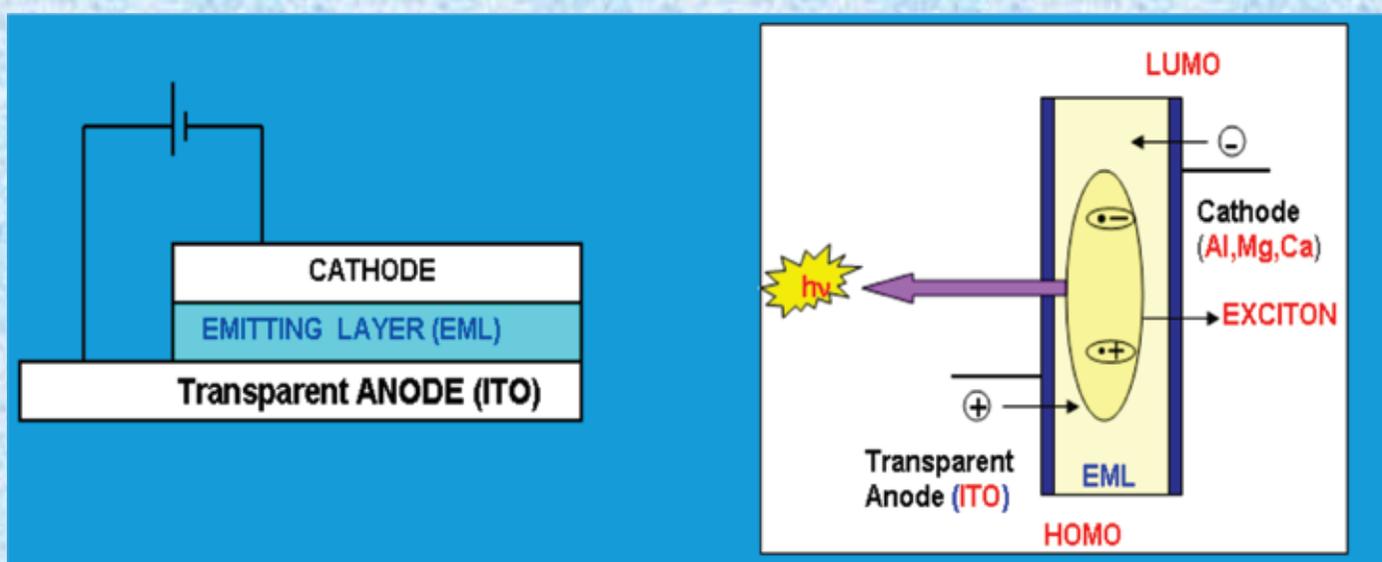
SMC Bulletin

A Publication of the Society for Materials Chemistry

Volume 3

No. 1

April 2012



SOCIETY FOR MATERIALS CHEMISTRY

Society for Materials Chemistry

Society for Materials Chemistry was mooted in 2007 with following aims and objectives:

- to help the advancement, dissemination and application of the knowledge in the field of materials chemistry,
- to promote active interaction among all material scientists, bodies, institutions and industries interested in achieving the advancement, dissemination and application of the knowledge of materials chemistry,
- to disseminate information in the field of materials chemistry by publication of bulletins, reports, newsletters, journals.
- to provide a common platform to young researchers and active scientists by arranging seminars, lectures, workshops, conferences on current research topics in the area of materials chemistry,
- to provide financial and other assistance to needy deserving researchers for participation to present their work in symposia, conference, etc.
- to provide an incentive by way of cash awards to researchers for best thesis, best paper published in journal/national/international conferences for the advancement of materials chemistry,
- to undertake and execute all other acts as mentioned in the constitution of SMC.

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Bhabha Atomic Research Centre
Trombay, Mumbai, 400 085
mukherji@barc.gov.in

Vice-Presidents

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Trombay, Mumbai, 400 085
dasd@barc.gov.in

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Indira Gandhi Centre for Atomic
Research
Kalpakkam, 603102 (TN)
knag@igcar.gov.in

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Trombay, Mumbai, 400 085
aktyagi@barc.gov.in

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rkvatsa@barc.gov.in

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Indira Gandhi Centre for Atomic
Research
Kalpakkam, 603102 (TN)
vasu@igcar.gov.in

Dr. S.K. Kulshrestha
Atomic Energy Education Society
Western Sector, AEES-6
Anushaktinagar, Mumbai, 400 094
kulshres@gmail.com

Dr. V.K. Jain
Bhabha Atomic Research Centre
Trombay, Mumbai, 400 085
jainvk@barc.gov.in

Dr. C.G.S. Pillai
Bhabha Atomic Research Centre
Trombay, Mumbai, 400 085
cgspil@barc.gov.in

Dr. S.R. Bharadwaj
Bhabha Atomic Research Centre
Trombay, Mumbai, 400 085
shyamala@barc.gov.in

Dr. Manidipa Basu
Bhabha Atomic Research Centre
Trombay, Mumbai, 400 085
deepa@barc.gov.in

Dr. Sandeep Nigam
Bhabha Atomic Research Centre
Trombay, Mumbai, 400 085
snigam@barc.gov.in

Co-opted Members

Dr. Aparna Banerjee
Bhabha Atomic Research Centre
Trombay, Mumbai, 400 085
aparnab@barc.gov.in

Dr. A.K. Tripathi
Bhabha Atomic Research Centre
Trombay, Mumbai, 400 085
catal@barc.gov.in

Prof. S.D. Samant
Institute of Chemical Technology
Matunga, Mumbai-400 019
samantsd@udct.org

Prof. G.P. Das
Indian Association for the
Cultivation of Science (IACS)
Jadavpur, Kolkata-700 032,
msgpd@iacs.res.in

Prof. Ashok K. Ganguli
Indian Institute of Technology
Hauz Khas, New Delhi 110 016
ashok@chemistry.iitd.ernet.in

Contact address

Society for Materials Chemistry

C/o Chemistry Division

Bhabha Atomic Research Centre, Trombay, Mumbai, 400 085, India

Tel: +91-22-25592001, E-mail: socmatchem@gmail.com

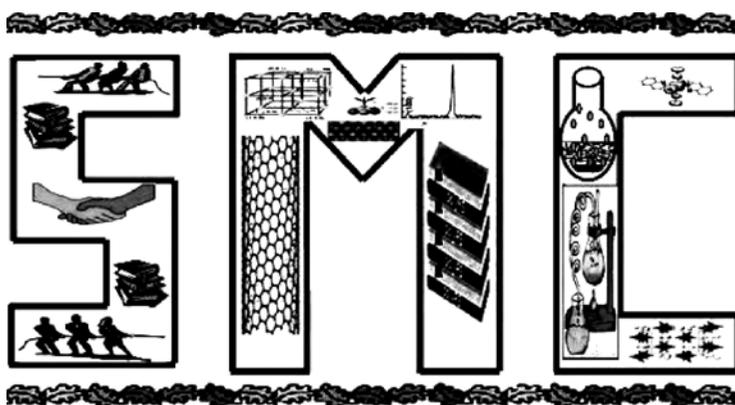
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Editorial Board

Dr. Arvind Kumar Tripathi
Chemistry Division
Bhabha Atomic Research Centre
Trombay, Mumbai, 400 085
e-mail: catal@barc.gov.in

Dr. Shyamala Bharadwaj
Chemistry Division
Bhabha Atomic Research Centre
Trombay, Mumbai, 400 085
e-mail: shyamala@barc.gov.in

Dr. Manidipa Basu
Chemistry Division
Bhabha Atomic Research Centre
Trombay, Mumbai, 400 085
e-mail: deepa@barc.gov.in

Dr. Aparna Banerjee
Product Development Division
Bhabha Atomic Research Centre
Trombay, Mumbai, 400 085
e-mail: aparnab@barc.gov.in

Dr. Sandeep Nigam
Chemistry Division
Bhabha Atomic Research Centre
Trombay, Mumbai, 400 085
e-mail: snigam@barc.gov.in

Published by
Society for Materials Chemistry
C/o. Chemistry Division
Bhabha Atomic Research Centre, Trombay, Mumbai, 400 085
E-mail: socmatchem@gmail.com,
Tel: +91-22-25592001

*Please note that the authors of the paper are alone responsible for the technical contents of papers and references cited therein.
Front cover shows a typical single layer device structure and the operating principle of OLED*

Editorial Note

We are happy to present the third issue of the SMC bulletin, a thematic one, on “Chemistry of Functional Materials”. The area of functional materials is quite vast as all materials have some or the other functionality associated with them. This issue presents four research articles including a feature article on ‘Organic Light Emitting Devices (OLEDs): Working Principle’. These articles deal with different functional materials like carbon nano tubes for hydrogen storage applications, optimization of lithium ferrites to improve its electrical and magnetic properties, functionalized-organosilicon compounds with region/stereo-selectivities for synthesis of natural product precursors and drug molecules.

The next issues of the bulletin are proposed to be on the following themes: Thermophysical Properties of Nuclear Materials and Fuel Cell Materials. Readers are encouraged to send their feedbacks which will enable us to improve the SMC bulletin.

Editors

From the President's Desk

Dear Fellow members,

It is really gratifying to note that in a short span of time the Society for Materials Chemistry (SMC) has become a vibrant national body with around 550 life members hailing from different academic and research institutes of our country. In the past, our Society has organized biennial international symposia on Materials Chemistry (ISMC-2006, ISMC-2008 and ISMC-2010) while a National Workshop on Materials Chemistry (NWMC-2011) on 'Functional Materials' (FUN-MAT) was successfully conducted in December 2011 in Mumbai. ISMC-2012, 4th biennial symposium in the series, will be organized by the society this year during 11-15 December. Members may kindly note that due to logistic reasons the name of this symposium has been marginally modified from "International Symposium on Materials Chemistry" to "Interdisciplinary Symposium on Materials Chemistry" and the same will be used hereafter. The abbreviation ISMC, however, remains unchanged.

I am happy to note that the SMC bulletin brought out by the society is well received by our members. We are making efforts to increase the frequency of the bulletin. I hope that the theme based issues are quite useful to our members, especially to the young researchers working in the area of materials chemistry. I am quite confident that the bulletin will continue to provide a platform to highlight the advances made in the field of materials chemistry and anticipate that the members will contribute articles to enrich the goals of the bulletin. Members are also encouraged to send a brief note on major instrumental facilities available in their institutes and also major awards/achievements received.

T. Mukherjee

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Organic Light Emitting Devices (OLEDs): Working Principle

M. Ananth Reddy,^{a,b} G. Malleshm,^{a,b} K. Bhanuprakash,^{*b} V. Jayathirtha Rao^{*a}

^aOrganic Chemistry Division-II, Indian Institute of Chemical Technology,
Uppal Road, Tarnaka, Hyderabad-500 607, India; E-mail: jrao@iict.res.in

^bInorganic & Physical Chemistry Division, Indian Institute of Chemical Technology, Uppal Road,
Tarnaka, Hyderabad-500 607, India; E-mail: bhanu2505@yahoo.co.in

Electroluminescence in Organic Materials

Conversion of electrical energy into light energy is termed as "electroluminescence". Enhancing the electroluminescence of organic molecules has profound role to play in "Organic Light Emitting Light Devices". Flat-panel displays have attracted researchers, where OLEDs have become prominent to understand their functioning and possible applicability. This requirement greatly accelerated research globally to develop new, novel and small organic molecules having role to play in OLEDs. Therefore OLEDs have become "globally emerging technology" for the development of different display technologies. OLEDs constitute a new and exciting emissive display technology. π -Conjugated organic semiconducting materials, small molecules have attracted much scientific and commercial interest. The main objective is to improve the electroluminescent property of many π -conjugated compounds [1]. Electroluminescence (EL) was first reported by Pope *et al.* in 1963 by passing very large voltages through anthracene crystals [2]. They reported EL from a thick anthracene crystal (10 μ m-5mm), when a bias of several hundred volts was applied across it. This phenomenon did not trigger much interest among researchers to initiate work, because of the applied bias was very high. Two years later Helfrich carried out further studies on anthracene systems, attributing the EL to the recombination of electrons (radical anion) and holes (radical cation) inside the crystals [3]. The high (*ca.* 400 V) voltages were applied to observe EL phenomenon which is due to the thickness of the crystals. Later Vincett *et al.* reported EL from thin anthracene films sublimed onto oxidised aluminium electrodes [4] at an operating voltage of *ca.* 30 V.

A significant breakthrough was achieved by Tang and VanSlyke [5] in 1987, who made a bilayer structure by thermally evaporating the small molecular weight organic materials, N, N'-diphenyl-N, N'-bis(3-methylphenyl) 1, 1'-biphenyl-4, 4' diamine (TPD) and tris(8-hydroxyquinoline) aluminum (Alq₃) to achieve a total thickness of ~100 nm. They achieved a very bright green emitting OLED with brightness higher than 1000 cd/m² and an external

quantum efficiency of ~1% when a low bias of 10 V was applied across the structure [5]. This discovery spurred tremendous research activity both in academia and industry. Shortly afterwards, Friend and coworkers at the University of Cambridge constructed a similar device. Electroluminescence from conjugated polymers was first reported in 1990, using poly (p-phenylene vinylene), PPV, as the single semiconductor layer sandwiched between metallic electrodes with poly(p-phenylenevinylene) acting as organic emitter [6]. Friend's innovation was built on the discovery of conducting polymers by Heeger, MacDiarmid, and Shirakawa in the 1970s, which earned them the 2000 Nobel Prize in chemistry [7]. These discoveries have provided a new impetus to the development of OLED for display and other purposes.

Organic EL displays represent an alternative to the well-established display technologies based on cathode-ray tubes (CRTs) and liquid crystal displays (LCDs), particularly with respect to large-area displays for which existing methods are not well suited. Moreover, the rapid growing market of portable electronic devices such as laptops, hand-held computers, media players, pagers, and cellular phones has driven the search for a new generation of display technology. Portable display technology is constrained by the need for (1) high efficiency, (2) full color, (3) low cost, (4) battery-compatible driving voltage, (5) reasonable lifetime, (6) resistance to the temperature extremes for outdoor and (7) automobile use. Most approaches, such as plasma displays, vacuum fluorescence, and inorganic thin-film EL, face some of these obstacles [8] or the combination. Conventional light-emitting devices (LEDs) commercially available today are mostly made from inorganic crystals such as GaAs or GaN. Although these devices work remarkably well for many applications, their use in large area displays or on flexible substrates is limited or even impossible because of the brittle crystals grown by expensive epitaxial methods [9a]. As a result, the demand has been largely left to LCDs, which require backlighting and have small viewing angle. OLEDs have several advantages like: (1) brighter, (2) thinner, (3) lighter, (4) wide viewing angle (>165°), (5) less power to operate,

(6) faster than LCDs, (7) higher contrast, and (8) have great potential to be cheaper to manufacture. OLEDs are threatening to challenge LCDs as dominant flat panel display in a broad range of portable electronics [8].

From both, basic as well as academic research perspectives, the OLEDs pose challenging problems. The OLEDs fall in the category of (a) luminescence observation from constrained media [10] or (b) origin of luminescence from packed organic layers or (c) manufacturing excited state (exciton) for luminescence with interlayer interactions. The challenge may be, particularly understanding the diffusion of organic molecules across the multilayer device system. Understanding the mechanism of formation of excited state (exciton) and the species responsible for luminescence are the interesting aspects behind OLEDs.

OLEDs include both small-molecular- and polymer-based devices and are recognized as a promising display technology. As the dramatic improvements in the devices unfolded over the past two decades, the investment of research and development resources in this field grew exponentially. The fascination with these devices is due to several potential advantages [9b]:

- Self-luminous- The efficiency of OLEDs is better than that of other display technologies without the use of backlight, diffusers, and polarizers.
- Low cost and easy fabrication- Roll-to-roll manufacturing process, such as, inkjet printing and screen printing, are possible for polymer OLEDs.
- Slimmer- Lightweight, compact and thin devices - OLEDs are generally very thin, measuring only ~100 nm
- Flexibility- OLEDs can be easily fabricated on plastic substrates paving the way for flexible electronics. Displays that can bend!
- High brightness and high resolution - OLEDs are very bright at low operating voltage (White OLEDs can be as bright as 150,000 cd/m²)
- Wide viewing angle- OLED viewing angle is as high as 160 degrees, because of its self luminous nature.
- Fast response- much better response time than other displays. OLEDs EL decay time is < 1μs.
- Efficient in Energy- OLED displays consume less energy as compared to LCD displays and other display screens. This is especially useful for devices that are supplied by battery power. No backlight is required in these screens which is the biggest OLED advantage for use in portable gadgets.

- Low operating voltages are generally between 2 and 10 Volts.
- Displays powered by OLED are allowing a broader operating temperature range than traditional displays.

A general comparison between common bulb versus OLED is given below to highlight the characteristic differences.

	OLED at 1000 cd/m²	Common Light Bulb
Operating Voltage	2 to 15 Volts	200 to 240 Volts (100-140 Volts)
Power Efficiency	14 lm/watt (expected to improve a lot)	10 lm/watt
CIE Color Coordinates	(0.45; 0.42)	(0.45; 0.40)
Color Rendering Index	91	100

OLED device structure and working Principle

A single layer device architecture is the simplest OLED structure. Single layer OLEDs typically consist of a metal cathode with a low work function (e.g. Ca, Al, Mg, Ba), an organic emissive layer and a transparent anode e.g. indium tin oxide (ITO), which is a nonstoichiometric composite of SnO₂ and In₂O₃ immobilized on a transparent carrier material such as glass or a flexible polymer [11]. A suitable cathode material has a low work function in order to ensure efficient electron injection into the organic semiconductor. In a single layer setup the organic semiconductor acts as emitter and charge transport material (holes and electrons) at the same time. The basic device structure and the working principle are shown in Fig. 1. Under action of a driving voltage, electrons are injected from the cathode into the lowest unoccupied molecular orbital (LUMO) of the adjacent organic layer, while the anode injects holes into the highest occupied molecular orbital (HOMO) of the organic material. The electrons and holes move through the organic layer and recombine to form an electron-hole pair called "exciton" or "excited state" capable of relaxing to the ground state by emission of light (Fig. 1.) [12]. This process which is referred to as "electroluminescence" and also as "electrochemiluminescence" is the basic principle of OLEDs. Thus, the fundamental physical processes involved in EL are (i) charge injection, (ii) charge transport, (iii) charge recombination, (iv) formation of excited state (exciton), and (iv) radiative decay - the luminescence [13].

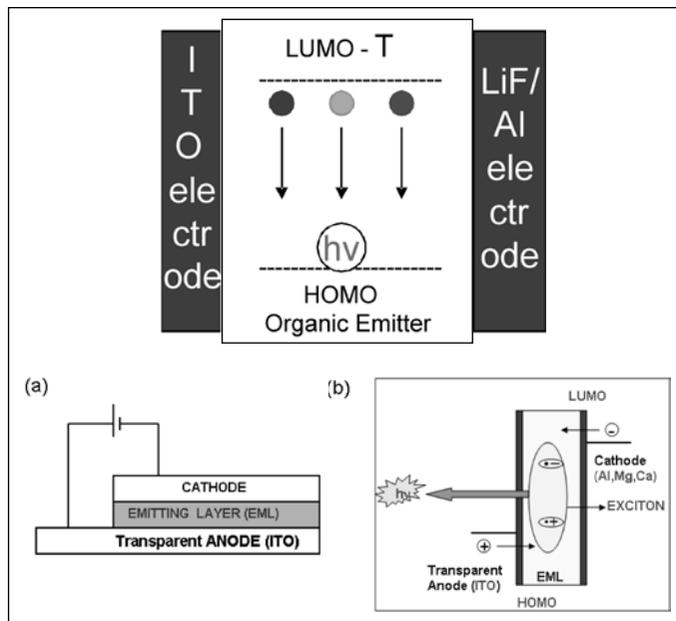


Fig. 1: A typical single layer (a) device structure and (b) operating principle.

The efficiency of an OLED is determined by the number of charge carriers that are injected, the number of holes and electrons that successfully recombine, the number of excited states (excitons) generated and the number of photons leading to emission of light. The materials used in single layer devices are usually better hole conductors than electron conductors [14]. As the holes are moving faster through the emitting layer than the electrons, the recombination (hole and electron) zone is shifted towards the cathode which usually leads to a non-radiative loss of energy [15]. Consequently, the efficiency of the device decreases [16a]. In order to attain high quantum efficiency for electroluminescence (EL), it is necessary to achieve - efficient charge injection from the electrodes at low drive voltage, good charge balance,

and confinement of the injected charge carriers within the emitting layer to increase the probability of the desired emissive recombination [16b].

In order to improve device efficiency, the multi layer OLED architecture was introduced which is shown in Fig.2. A multi-layer device consists of (i) cathode interface material (CIM) - CIM facilitate injection of electron from cathode, (ii) electron transport material (ETM) - ETM facilitate the transport of electrons, (iii) hole blocking material (HBM) - HBM holds the +ve charge, (iv) LIGHT EMITTING MATERIAL (LEM), (v) electron blocking material (EBM) - EBM holds the electron, (vi) hole transport material (HTM) - HTM facilitate movement of holes (+ve charge), (vii) hole injection material (HIM) - HIM facilitate movement of hole from anode, along with two electrodes and transparent material. The various functions of these materials are self explanatory. The presence of these layers of materials is to reduce the barriers across the layers and for the smooth functioning of the device with better performance and life time. This general structure serves three main purposes: (1) it facilitates charge carrier injection by reducing the respective injection barriers; (2) the recombination of electrons or charge carriers is blocked by the opposite transport layer (the HTL is a barrier for electrons and the ETL for holes); (3) the recombination area is shifted towards the middle of the device and thus quenching of the excitons at the electrodes is avoided [16c].

Emission mechanism in OLEDs

There are various types of luminescence (i) Bioluminescence; (ii) Chemiluminescence; (iii) Crystalluminescence; (iv) Electroluminescence; (v) Mechanoluminescence (Tribo/Fracto/Piezo luminescence); (vi) Photoluminescence (Fluorescence and Phosphorescence); (vii) Radioluminescence; (viii) Thermoluminescence; (ix) Sonoluminescence, which are classified based on the energy supplied to excite the luminescent materials [17]. The different kinds of luminescence can be distinguished by different ways of excitation. If a material is excited optically, an electron from the highest occupied molecular orbital (HOMO, S_0) is excited to the lowest unoccupied molecular orbital (LUMO, S_1). The excited electron rapidly relaxes to the ground state S_0 with the emission of light - Fluorescence. The wavelength of the emitted light, many a times is longer than the absorption wavelength. Jablonski diagram (Fig. 3) explains about optical excitation and relaxation (deexcitation) processes for a given organic molecule.

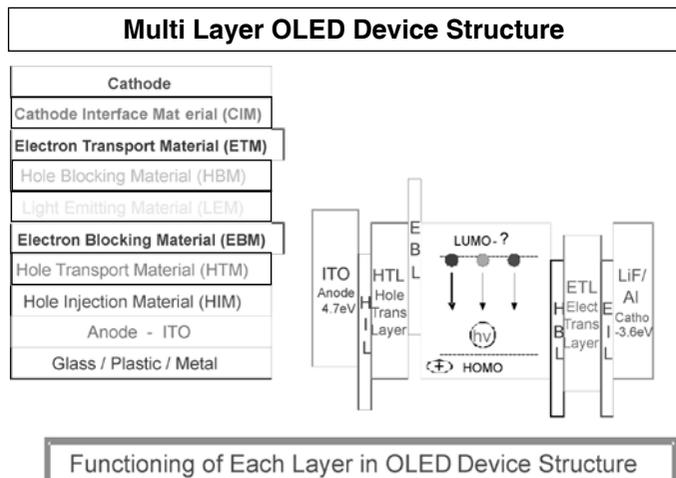


Fig. 2: A multilayer (a) device structure and (b) operating principle.

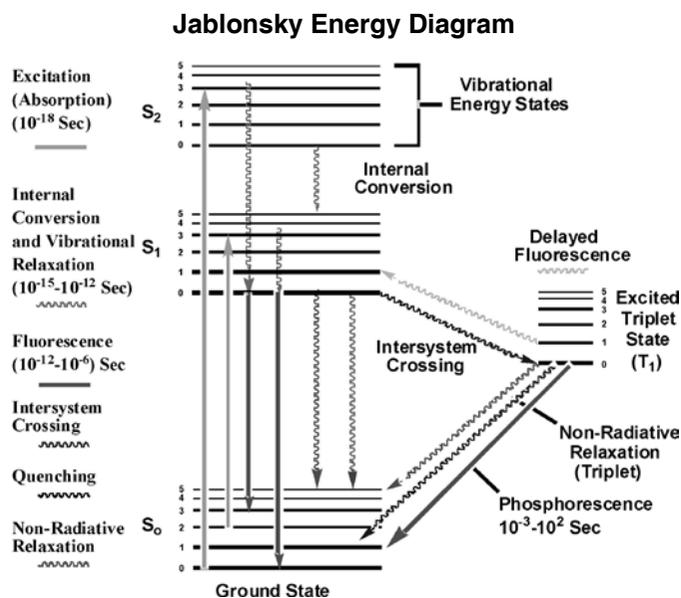


Fig. 3: Jablonski Energy Diagram (Ref. 19)

Applying voltage to an organic semiconducting material is another possibility to obtain luminescence. This kind of light generation is called electroluminescence (EL) and many a times it is called electrochemiluminescence (ECL) which was discovered by Pope [2] and Helfrich *et al.* [3]. Electrochemiluminescence can be defined in a general way as the emission of light due to the injection of charges of opposite sign [18] and followed by recombination of opposite charges. When voltage is applied to the device electrons are injected into the LUMO and holes into the HOMO of the molecule. The resulting radical anion and radical cation migrate under the influence of the electric field, recombine to form an electron-hole pair leading to excited state (exciton). The formation singlet (exciton) excited state is illustrated in Fig. 4. These excited states are populated either singlet or triplet [20]. This also sets an upper limit for the electroluminescence quantum efficiency for small molecule based OLEDs to 25%, as about 75% of the excited states formed by the recombination of injected electrons and holes are in the triplet state. Recent reports show that the ratio of singlet excitons may be higher [21]. More studies are required to understand the multiplicity of the excited state (singlet or triplet) generated by applying voltage across the organic layers sandwiched by electrodes.

Usually the ground state of an organic molecule is a singlet state (S_0) and absorption of a photon (time scale $<10^{-15}$ sec) leads to the first excited singlet state (S_1). Typical lifetimes of the S_1 state are in the range 10^{-6} to 10^{-12} sec, thus leading to a rapid transition back to the S_0 ground state via fluorescence or nonradiative transitions (IC = internal conversion). In the excited singlet state there is a

probability for intersystem crossing (ISC) to the triplet state (T_1), from which the excitation energy can be released either by phosphorescence or non-radiatively (ISC). However, since intersystem crossing is a forbidden weak process, triplet lifetimes are usually in the range of 1 sec to 10^{-6} sec for aromatic hydrocarbons, and radiative decay via phosphorescence is usually not observed at room temperature. Triplet lifetimes can be considerably shorter in molecules incorporating heavy atoms, such as Pt or Ir. Therefore metal organic complexes incorporating these elements are becoming more and more important in OLEDs [1].

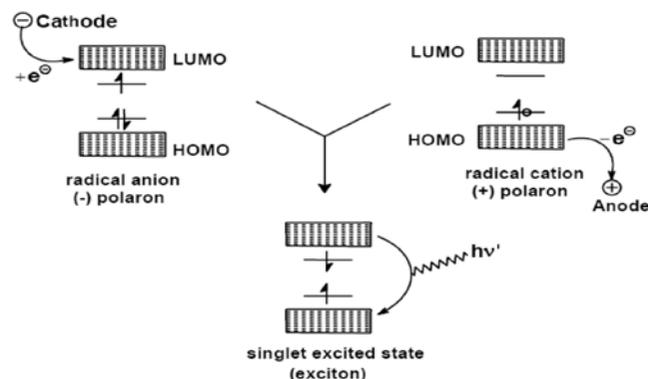


Fig. 4: Recombination of radical cation and radical anion to form a singlet excited state (exciton) under applied voltage.

Mechanism of Luminescence in OLEDs

- 1) $OM + \text{electron} \rightarrow OM^-$ (radical anion)
 - 2) $OM \rightarrow OM^+ + \text{electron}$ (radical cation)
 - 3) $OM^- + OM^+ \rightarrow OM + OM^{*1}$ (singlet excited state)
 - 4) $OM^{*1} \rightarrow OM + h\nu$ (fluorescence)
 - 5) $OM^- + OM^+ \rightarrow OM + OM^{*3}$ (triplet excited state)
 - 6) $OM^{*3} \rightarrow OM + h\nu$ (phosphorescence)
 - 7) $OM^{*3} + OM^{*3} \rightarrow OM^{*1} + OM$ (fluorescence: triplet-triplet annihilation)
 - 8) $OM^{*1} + OM \rightarrow [OM \dots OM]^*$ (singlet excimer)
 - 9) $OM^{*1} + OM \rightarrow [OM \dots OM]^*$ (singlet exciplex)
 - 10) $OM^{*3} + OM \rightarrow [OM \dots OM]^*$ (triplet excimer)
 - 11) $OM^{*3} + OM \rightarrow [OM \dots OM]^*$ (triplet exciplex)
 - 12) $OM^{*1} + OM_2 \rightarrow OM + OM_2^*$ [Singlet - Singlet Energy Transfer]
 - 13) $OM^{*1} + OM_3 \rightarrow OM + OM_3^{*3}$ [Singlet - Triplet Energy Transfer]
 - 14) $OM^{*3} + OM_4 \rightarrow OM + OM_4^{*3}$ [Triplet - Triplet Energy Transfer]
 - 15) $OM^* + OM \rightarrow OM + OM$ [Self Quenching]
 - 16) $OM^* + M \rightarrow OM + M$ [Quenching]
- (OM = Organic Molecule; *1 = Excited Singlet; *3 = Excited Triplet)

Mechanism of luminescence in OLEDs is given above by considering many possibilities. There are various light emitting species involved in OLEDs: (i) fluorescence from singlet excited state (eq. 4; eq. 7; eq. 11), (ii) phosphorescence from triplet excited state (eq. 5; eq. 12; eq. 13), (iii) excimer or exciplex emission (eq. 8-11). Probing the mechanism in-terms of excited state formation will be interesting and also explaining the emission maxima upon comparing with the solution and solid state fluorescence will be much more interesting.

Organic compounds (materials) are used in OLEDs with the following bench mark of device properties: (i) a minimum of 1000 cd/m² brightness must be exhibited, (ii) 10,000 h Life Time is preferred; (iii) Bilayer is Fine, but Single Layer is Preferred; (iv) Multilayer is OK for specialized purposes; (v) Energy Balance must be satisfied; (v) Color Contrast must be maintained.

Quality of LIGHT EMITTING MATERIAL becomes important and some of them are mentioned below as possible criteria to be attended in making suitable organic materials for OLED applications:

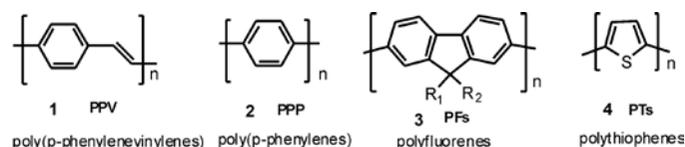
1. UV-Vis Absorption
2. Fluorescence - High Luminescence Quantum Yield
3. HOMO-LUMO Energy Gap
4. Melting Point
5. Glass Transition Temperature
6. Amorphous Nature of the Compound
7. Thermal Decomposition Temperature
8. Oxidation and Reduction Potentials
9. Ability to form thin Layers
10. Ability to Conduct Charge
11. Photochemical Stability
12. Radical cation or radical anion chemistry
13. Color Purity
14. Generation of Triplet → Phosphorescence (Second Generation)

The above mentioned properties become important for designing new organic materials suitable for OLEDs. The mentioned each property has a role to play in its functioning. It is obvious that satisfying multi property parameters is a real challenge to design and develop new organic materials for OLEDs.

Classification of OLED materials

OLED materials can be divided by their molar mass into low molecular weight (small molecule) and high molecular weight compounds (polymer compounds).

These two major classes of organic semiconductors are low-molecular weight materials and as well as polymers [22]. Both have one thing in common *i.e.* a conjugated π -electron system. Therefore, the lowest electronic excitations of conjugated molecules are the π - π^* transitions with an energy gap typically between 1.5 and 3 eV leading to light absorption or emission in the visible spectral range. In detail, the electronic properties of a molecule depend on factors like the conjugation length or the presence of electron donating or withdrawing groups. Thus organic chemistry offers wide range of possibilities to tune the optoelectronic properties of organic semiconducting materials. Substantial worldwide efforts in both industry and academia have focused on the synthesis and design of electroluminescent polymeric and low-molecular-weight organic materials. In the last decade, several types of conjugated polymer structures have been developed, including poly(p-phenylenevinylenes) **1**, polyphenylenes **2**, polyfluorenes **3**, polythiophenes **4**, among others (scheme 1). Many high-efficiency, high-brightness, and long-lived devices have been demonstrated using these materials [23].



Scheme 1: Core structures of widely used emissive conjugated polymers.

An important difference between the two classes of materials lies in the way they are processed to form thin films. Many small molecule based semiconductors are rather rigid and planar molecules which are generally insoluble in many organic solvents. Therefore, they need to be incorporated into electroluminescent devices by sublimation techniques [24]. However, vacuum-deposition techniques require costly processes that are limited to practical substrate size and relatively low yields in the manufacture of high volume products using masking technologies [25]. Whereas small molecules are usually deposited from the gas phase by sublimation or evaporation, conjugated polymers can only be processed from solution, *e.g.*, by spin-coating or printing techniques. Small molecules are advantageous because they can be (i) purified by common techniques such as recrystallization, chromatography, and sublimation and (ii) vacuum deposited in multilayer stacks, both important for device lifetime and efficiency [26]. On the other hand, polymers are generally of lower purity than small molecules but can be used to achieve larger display sizes at much lower costs using technologies such as ink jet and screen printing [27].

But for multilayer device structures, low molecular weight materials are in principle more suitable than polymers.

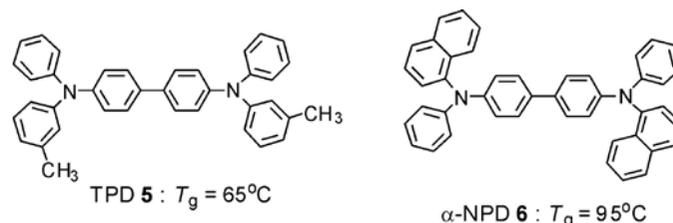
Low molecular weight materials in OLEDs (SMOLEDs)

Since the basic principles of electroluminescence are essentially the same, no matter which type of organic material is used, the choice of materials is usually determined by the method of preferred fabrication. As previously mentioned, conjugated polymers are processed from solution by coating techniques. Due to their low molecular weight, small organic semiconductors can also be vacuum deposited as thin films [24]. This preparation technique to build up electroluminescent devices was first utilized by Tang and VanSlyke at Kodak in their basic work on OLEDs in 1987 [5]. Due to inefficient recombination in a single layer device, multilayer devices were designed to raise the efficiencies of the OLEDs. In a multilayer device each layer has a specific function *i.e.* emission, hole transport, electron transport, hole blocking, electron blocking etc. depending on the complexity of the fabricated device. In contrast to the development of polymer-based OLEDs, the concept of designing materials with only one or two specific functions was realized at an early stage in OLED history. On account of their function in electroluminescent devices, low molecular weight materials can be broadly classified as - hole transport materials/ hole transporting emitters, electron transport materials / electron transporting emitters, Red-Green-Blue emitters and host materials for triplet emitters. Generally, for the materials to find application in OLED, the following criterion needs to be met. Materials should possess suitable ionization potentials and electron affinities, *i.e.*, well-matched energy levels for the injection of charge carriers from the electrodes and adjacent organic layers, be capable of forming smooth, uniform films without pinholes, be both morphologically and thermally stable *i.e.* they possess high glass transition temperatures (T_g). In addition to these general requirements, materials should meet further specialized needs depending upon the roles that they play in devices [16b]. The below mentioned categories of organic materials having specified function will be discussed.

Hole transporting materials (HTM)

Hole transport materials (HTMs) are common in small molecule based OLEDs. Materials which have low ionization potentials together with low electron affinities usually function as hole-transporting materials. In other words, materials with electron donating properties serve as HTMs. The main function of these materials is to transfer the positive charge carriers (holes) to the emitting layer. The hole transport layer in a multilayer device facilitates hole

injection from the anode and transport the injected holes to the emitting layer. Therefore, an ideal hole-transporting material should undergo reversible anodic oxidation to form stable cation radicals and should possess high hole mobilities. It is commonly believed that a good HTM should have both a low energy barrier from the anode and a relatively high T_g .

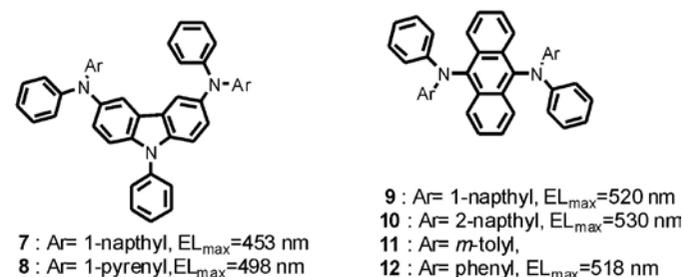


Scheme 2: Triaryl amine based HTMs

Triaryl amines are extensively used as hole transport materials in OLEDs. Two of the most widely used HTMs of the triarylamine family in OLEDs are *N,N'*-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD, **5**) and *c* (α -NPD, **6**) (Scheme 2). However, TPD and α -NPD, which have low glass transition temperature (T_g) of 65°C and 95°C , respectively, tend to crystallize or expand during device operation [28]. As the low thermal stability is highly detrimental to the lifetimes of devices, organic amorphous HTMs that exhibit high T_g s are much sought after.

Hole transport emitting materials

The OLED devices can be simplified to a double-layer structure if materials with dual functions, *i.e.*, emitting and electron transporting or emitting and hole transporting, were used. There are only a few instances of amines that function both as emitting as well as hole-transporting materials. J. T. Lin *et al.* reported a series of light-emitting peripheral diarylamine derivatives containing carbazole units, which possess dual functions, as both active emitting materials and HTMs. Two representative structures (**7**, **8**) from these set of compounds is shown in Scheme 3 [29]. These luminescent materials are amorphous, with high T_g (120 – 194°C), high thermal stability ($T_d > 450^\circ\text{C}$), and with HOMO energy levels of 4.86 – 5.04 eV are also suitable for HTMs. Stable OLED devices were fabricated using these materials.



Scheme 3: Chemical structures of emitting HTMs

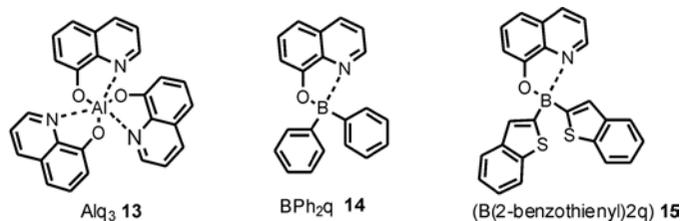
Diaminoanthracene derivatives 9,10-Bis(1-naphthylphenylamino)anthracene (α -NPA, **9**), 9,10-Bis(2-naphthylphenylamino)anthracene (β -NPA, **10**) 9,10-Bis(*m*-tolylphenylamino)anthracene (TPA, **11**) and 9,10-Bis(diphenylamino)anthracene (PPA, **12**) as green emitting hole transport layer were investigated (Scheme 3). Devices consisting of diaminoanthracene (**9**, **10**, or **12**)/Alq₃ were shown to emit intensive green light from the diaminoanthracene layer which show high brightness and current efficiency, very narrow emission bandwidth, and excellent CIE coordinates [30].

Electron transporting materials (ETMs)

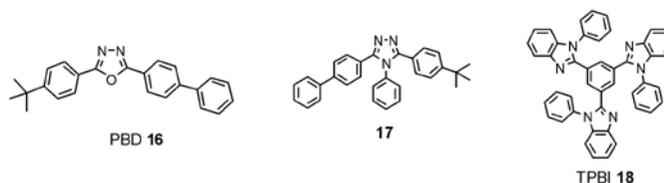
The electron transport layer plays the role of facilitating electron injection from the cathode into the organic layer. Materials which have high electron affinities together with high ionization potentials usually function as electron-transporting materials *i.e.* materials with electron accepting properties and high electron mobilities serve as ETMs. The cathodic reduction processes of electron-transporting materials should be reversible to form stable anion radicals. In addition, they should form homogeneous thin films with morphological and thermal stability. The electron-transport layer in OLEDs plays a role in hole blocking as well as injection and transport of electrons [31].

A well-known green emitter tris(8-quinolinolato)aluminum (Alq₃) **13**, (Scheme 4) has been used as a good electron transport material. Alq₃ remains the most widely studied metal chelate owing to its superior properties such as high EA (~3.0 eV) and IP (~5.95 eV), and good thermal stability ($T_g \sim 172$ °C) [32]. Boron-containing complexes such as 8-hydroxyquinoline biphenylboron BPh₂q (**14**) and B(2-benzothienyl)₂q (**15**) (Scheme 4) have also been reported as candidates for electron transporters [31,33,34].

1,3,4-Oxadiazole containing molecules are among the most widely investigated electron transport materials for OLEDs [32]. Oxadiazole derivatives, such as 2-(biphenyl-4-yl)-5-(4-tertbutylphenyl)-1,3,4-oxadiazole (PBD)**16**, have been widely used as ETL in OLEDs [33], with an EA of 2.16 eV and an IP of 6.06 eV [34]. The significance of the electron transport layer is demonstrated by the bilayer OLED device which shows 10⁴ times more efficiency than without PBD in an OLED [35].



Scheme 4: Chemical structures of metal chelates

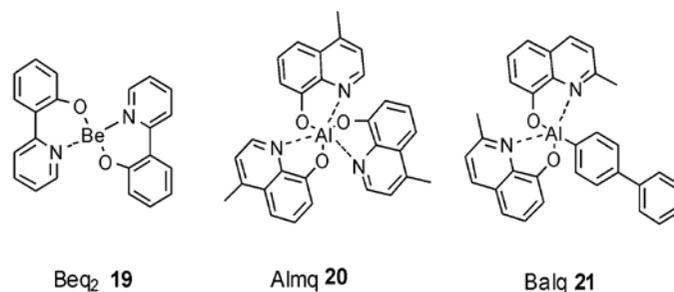


Scheme 5: Examples of heterocyclic cored ETMs

Triazoles are another interesting class of electron deficient thermostable materials similar to oxadiazoles. The use of 1,2,4-triazoles as electron transporting and hole blocking material was first demonstrated by Kido *et al.* [36]. The most representative derivative is 3-(1,1'-biphenyl-4-yl)-5-(4-tert-butylphenyl)-4-phenyl-4H-1,2,4-triazole **17**, which is not only a good electron transporter but also a better hole blocker than PBD [24,36]. 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBI, **18**) has emerged as key ETM in OLED. TPBI's structure is shown in Scheme 5. The electron mobility of TPBI is of the order of 10⁻⁶-10⁻⁵ cm²/(V s), which is slightly higher than Alq₃ [37, 38]. [54,55].

Electron transport emitting materials

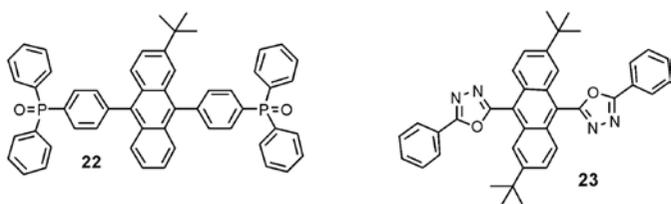
Molecules which possess good emission (fluorescence or phosphorescence) efficiency along with electron transporting characteristic can be a potential electron transporting emitters (ET-EM). This dual functionality of the molecule reduces the number of layers to be fabricated in the OLED device. Metal chelates (Scheme 4) and in particular Alq₃ **13** is the most prevalent electron transport emitters in organic EL devices [24]. Thin films of Alq₃ exhibit green photoluminescence with a quantum efficiency around 32% [39]. Since the first report of electroluminescence from Alq₃ in 1987 [5] it has been extensively used as an active material in OLEDs. Beq₂ (beryllium quinoline) **19** [40] and Alm_q (4-methyl-8-hydroxyquinoline) **20**, [41] in particular, were found to have much better performance than Alq₃. Also, a blue emitter, aluminum (III) bis(2-methyl-8-quinolinato)-4-phenylphenolate (Balq) **21**, was synthesized and investigated as electron transporting emitting material [42].



Scheme 6: Chemical structures of metal chelates (emitting electron transporters)

A highly efficient blue-light emitter, 2-tert-butyl-9,10-bis[40-(diphenylphosphoryl) phenyl]anthracene **22** [43] comprising electron-deficient triphenylphosphine oxide side groups appended to the 9- and 10-positions of a 2-tert-butylanthracene core were synthesized. In addition to serving as an electron-transporting blue light-emitting material, **22** also facilitates electron injection from the Al cathode to itself.

Recently a series of anthracene-oxadiazole derivatives were synthesized and their emitting and electron transporting properties evaluated. Appending oxadiazole units improved the electron affinity (~ 3.0 eV) of the anthracene derivatives (structure **23**) and also retains its emissive property [44].



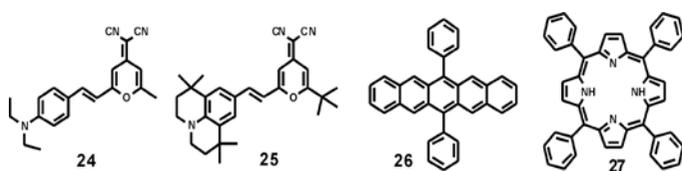
Scheme 7: Chemical structures of electron transporting emitters

Fluorescent Emitting materials

Red emitters

Red OLEDs are an indispensable component in full colour displays. Short wavelength light-emitting blue or green fluorescent materials are commonly used as either host emitter or dopants. But red fluorescent materials acting as emitters are less and mostly limited to the dopant usage in the fabrication of red OLEDs. This is due to the nature of red fluorescent materials. Fluorophores emitting longer wavelength region ($\lambda_{\max} > 610$ nm) are usually polar, such as electron-donor- substituted pyran-containing compounds 4-(Dicyanomethylene)-2-methyl-6-[p-(dimethylamino)styryl]-4H-pyran **24** [45] and **25** [46], or nonpolar but extensively π -conjugated, such as 6,13-diphenylpentacene **26** [47] or porphyrin-type macrocyclic compounds tetraphenyl-21H, 23H porphine **27** [48].

However, all these red fluorophores are prone to aggregation in solid state, due to either attractive dipole-dipole interactions or effective intermolecular π -stacking. Therefore, they are highly susceptible to concentration

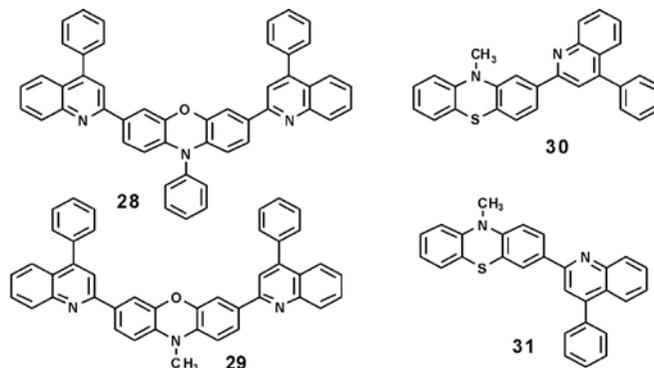


Scheme 8: Chemical structures of dopant red emitters as polycyclic aromatic hydrocarbon

quenching and become either weakly emissive or even not emissive at all in solid state.

Green emitters

Highly fluorescent donor acceptor (D-A) molecules incorporating phenoxazine as the donor and phenylquinoline as the acceptor were synthesized (**28** and **29**). These molecules exhibited fluorescence with 80-83% quantum yield in solution, and possess high glass transition temperatures (~ 140 - 150 °C). Uniform green EL with satisfactory brightness (up to 900 cd/m²) was observed from evaporated thin films of each D-A molecule with maximum emission at 510 nm in a single-layer diodes of configuration, Indium tin oxide (ITO)/ D-A(45 nm)/ LiF/ Al [49]. Jenekhe *et al.* investigated the effects of structural isomerism on the photophysical, electrochemical, and electroluminescent properties of two D-A molecules, 2-(4-phenyl-2-quinoly)-10-methylphenothiazine **30** and 3-(4-phenyl-2-quinoly)-10-methylphenothiazine **31**. The EL spectra of **30** and **31** showed peaks at 526 nm and 512 nm respectively [50].

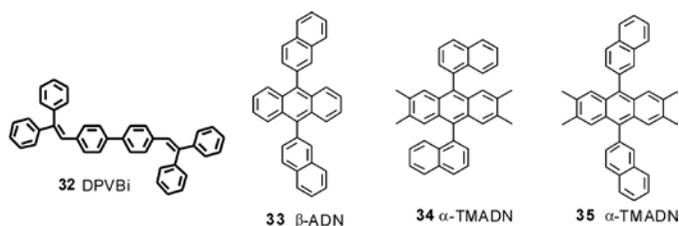


Scheme 9: Chemical structures of green emitters

Blue emitters

If there is one clear need in the field of OLED materials it continues to be in the area of blue emitters. A blue emissive material with good color coordinates CIE (0.10, <0.10) coupled with long device lifetime (>10,000 h) and high electrical efficiency (>5 cd/A) is the holy grail of materials chemists in this field [28]. A major effort to find such materials continues in many laboratories. However, the current best candidates for blue emitters in the SMOLED area compromise many desirable properties - the most troublesome being long lifetime. High-performance, blue-light emitting ones are rare, because of the intrinsic wide band-gap required for such materials. Many large band-gap organic materials have been explored for blue emission. They include the distyrylarylene series, anthracenes, perylenes, fluorenes, heterocyclic compounds, and metal complexes.

Blue-emitting materials were studied extensively by Hosokawa and coworkers [51]. Among them, 4, 4'-bis (2,2'-diphenylvinyl)-1,1'-biphenyl **32** has proven to be a particularly promising material for blue OLEDs. Anthracene derivatives form an important class of highly efficient, stable, blue-light emitting materials (Scheme 10). 9, 10-di (naphthalene-2-yl)anthracene β -ADN **33**, as the emitter, was suggested by Shi and Tang, and they found that the device structure NPB/ADN/Alq₃ produced a good efficiency of 1.9 cd/A [52]. As ADN proved to be morphologically unstable due to crystallization, Qiu's group modified the ADN structure and synthesized α -TMADN **34** and β -TMADN **35** that contain tetra methyl substitutions on the anthracene ring [53]. This sterically congested nonplanar structure hinders the close spacing of the molecules and improves the film-forming properties. Among the blue emitting materials anthracene is the most investigated material for OLEDs in the recent literature [54].



Scheme 10: Chemical structures of blue emitters

White light emitters

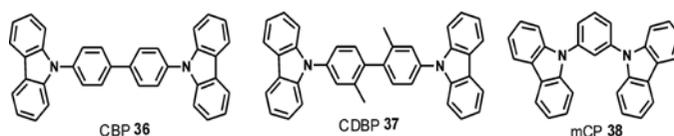
Recently, white OLEDs are of growing interests due to their potential utilization in low-cost, large-area backlights for flat panel displays and in solid lighting sources [55,56]. A "pure" white OLED is characterized by an emission that covers the full spectral range of the visible region (400-700 nm) and a Commission International d'Éclairage (CIE) chromaticity coordinate of (0.33, 0.33) [56]. To realize white emission, various strategies have been developed. The most common approach in WOLEDs is to use three separate emitters, that is, blue, green and red. It has been demonstrated that three emitters can be mixed together in a single layer to achieve the desired white emission [57]. Another approach to obtain white light is through the excimer/exciplex emission [58].

Host materials for Phosphorescent OLEDs

Phosphorescent organic light-emitting diodes (PHOLEDs) continue to attract intense interest because they can, in theory, approach 100% internal quantum efficiency by utilizing both singlet and triplet excitons [59]. Phosphorescent emitters typically possess longer lifetimes leading to undesired concentration quenching or

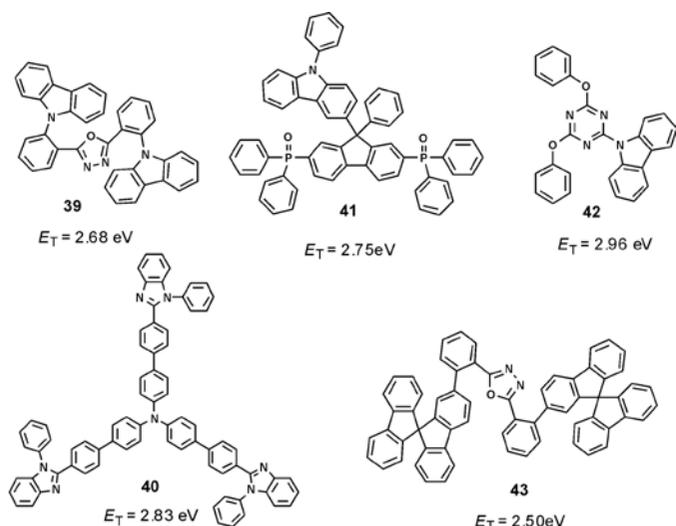
T_1 - T_1 annihilation and thereby declining performance [60]. To overcome this drawback, the triplet phosphorescent emitters are usually doped into an appropriate host. Thus the synthesis of host materials and dopants are equally important for the formation of efficient PHOLEDs. It is desirable that the host materials have a triplet energy gap, larger than that of the triplet emitter, thereby preventing reverse energy transfer from the guest to the host [61], good carrier transport properties, and energy-level matching with neighboring layers for effective charge injection.

A widely used hole transporting host material for triplet emitters is 4, 4'-bis(9-carbazolyl)-biphenyl (CBP) **36**. The HOMO and LUMO energy levels of CBP are \sim 6.30 and \sim 3.0 eV, respectively. The triplet energy level (E_T) of CBP is 2.67 eV ($E_T = T_1 - S_0$) [62]. CBP acts as a good host material for green, yellow, and red triplet emitters. The triplet energy level is too low to yield highly efficient devices with blue triplet emitters. To improve this, Tokito *et al.* reported a CBP derivative, 4,4'-bis(9-carbazolyl)-2,2'-dimethylbiphenyl (CDBP, **37**), in which two methyl groups are grafted onto the biphenyl unit, which enforces a nonplanar structure and generates a significant blue-shift of the triplet state (from 2.67 to 3.0 eV) [61d]. One example of a large band-gap host material reported by the Forrest group is N,N'-dicarbazolyl-3,5-benzene (mCP, **38**) [61c]. mCP and CBP have similar charge injection and transport properties, but mCP has a very high triplet energy of 3.0 eV. This large triplet energy allows efficient energy transfer to the triplet emitter guest.



Scheme 11: Chemical structures of commonly used host materials in PHOLED

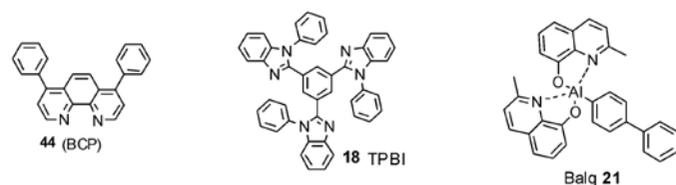
Most of the existing triplet host materials are capable of preferentially transporting holes or electrons. Charge balance is a key element in achieving both the efficiencies and lifetimes necessary to make a viable OLED device. Since most of the commercially available host materials are not ambipolar, recent efforts have been made to synthesize ambipolar host materials in order to optimize charge balance in phosphorescent organic light emitting devices [63,64]. There are recent reports of efficient bipolar host materials such as - carbazole/oxadiazole hybrids **39** [59], triphenylamine/ benzimidazoles **40** [65], carbazole/ phosphine oxide **41** [64], carbazole/1, 3, 5-triazine **42** [66], spirobifluorene/ oxadiazole **43** [67] etc. Examples for these hybrid host materials are shown in Scheme 12.



Scheme 12: Chemical structures of bipolar host materials

Hole Blocking Materials

Recently, electron-transporting materials have also been employed to perform the holeblocking function in EL devices using phosphorescent materials, such as iridium and platinum complexes, to afford high external quantum efficiency [68]. Various materials with high electron affinities have been synthesized and investigated. Among them, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, known as bathocuproine (BCP) [69], and bis(2-methyl-8-quinolinolato)-mono(4-phenylphenolato)-aluminium (BALq) are known as typical hole blocking materials [70]. TPBI as a hole blocking material replacing BCP was investigated by Hung *et al* [71].



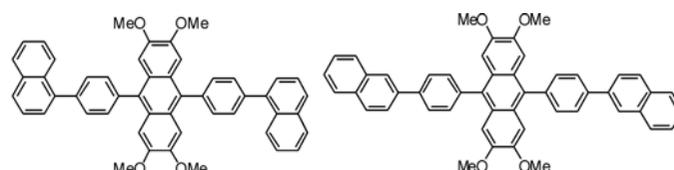
Scheme 13: Chemical structures of hole blocking materials

Electron Blocking Materials

Electron-blocking materials serve similar function as the hole blocking materials. These materials block the electrons from reaching the hole transport layer or the anode and improve the device efficiency. Electron blocking materials should have wide band gap, shallow LUMO level, HOMO level matching the adjacent hole transport layer. The concept of using Electron blocking materials was first presented by the Forrest group in the study of white phosphorescent OLEDs [59].

A series of 2,3;6,7-tetra(methoxy)-9,10-di(aryl)anthracene derivatives have been readily synthesized and the HOMO: -5.23– -5.28 eV/LUMO: -2.11– -2.28 eV,

energy levels were found to be energetically favorable for use as hole-transporting/electron-blocking layers in organic light-emitting devices (OLEDs). These bifunctional derivatives with hole-transporting/electron-blocking properties hold great promise in the fabrication of highly efficient OLEDs with simple architecture.



Scheme 14: Structures of the electron blocking materials.

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<p>Manda Ananth Reddy born in Adilabad-Andhra Pradesh, India (1981) received his bachelors degree (2002) and Master's degree (2004) from Osmania University, Hyderabad, Andhra Pradesh. He has completed is Ph.D (2011) from Indian Institute of Chemical Technology (IICT), Hyderabad under the supervision of Dr. V. Jayathirtha Rao and Dr. K. Bhanuprakash. His research interest lies in the synthesis of novel organic molecules for Light Emitting Devices and photovoltaic applications. Presently working as a scientist in Laurus Labs Limited, Turkapally, Hyderabad. He has seven international publications, three conference presentations.</p>	
<p>Godumala Malleshm born in Akkenapally-Andhra Pradesh, India (1984) received his bachelors degree (2006) from Osmania University, Hyderabad and Master's degree (2006) from Kakatiya University, Warangal, Andhra Pradesh. He is CSIR-JRF and Senior Research Fellowship holder. Currently he is pursuing Ph.D at CSIR-Indian Institute of Chemical Technology (IICT), Hyderabad under the supervision of Dr. V. Jayathirtha Rao, Chief Scientist and Dr. K. Bhanuprakash, Senior Principal Scientist. His research interest is synthesis of novel organic molecules for Light Emitting Devices. He has two international publications, four conference presentations and seven book chapters.</p>	
<p>Bhanuprakash Kotamarthi obtained his Master's degree in Chemistry (1979-1981) from University of Hyderabad, Hyderabad and his PhD degree from IISc, Bangalore in 1986 under the guidance of Prof. A. K. Chandra. He then worked as a postdoctoral fellow at Wuppertal University, Wuppertal, Germany in Prof. R. J. Buecker's group from 1986 to 1990. Immediately after his postdoctoral work he joined IICT under quick recruitment scheme as a scientist and since then he has been associated with this institute. He is basically a theoretical /computational chemist and his interests are in the area of organic materials like OLED, DSSC, NLO and OPV. He was a visiting scientist in 1998-1999 at ICS-UNIDO, Trieste, Italy and 2003-2004 at Georgia Tech, Atlanta, USA. He has guided about 11 students and at present 5 more students are working under his guidance. He has to his credit about 100 publications.</p>	
<p>Vaidya Jayathirtha Rao obtained his Master's degree (1978) from Gadwal Osmania University, Hyderabad and Ph.D degree (1983) from Indian Institute of Science Bengaluru under guidance of Prof. V. Ramamurthy. He was post doctoral Fellow at Univ. of Hawaii (1983-84), USA, with Prof. RSH Liu and PDF at Columbia University, New York City (1985-86), USA, with Prof. Koji Nakanishi. He was three time Alexander von Humboldt Fellow, Germany (1987, 1998 & 2003) and visited Germany as a Univ. of Wuerzburg Alumni (2011). He was visiting scientist at Tulane Univ., New Orleans, USA (1996-97) and also at Univ. of Miami, Miami, USA (2006-2007). He has been associated with Indian Institute of Chemical Technology (IICT) since 1988. Presently he is Chief Scientist and Professor at Organic Chemistry Division - II, IICT. His research interests are: (i) synthesis of heterocycles for bioevaluation; (ii) synthesis of organic materials for devices; (iii) organic photochemistry; (iv) HPLC method development for Active Pharma Ingredients; and (v) Process Development and Technology.</p> <p>He is Alexander von Humboldt Fellow (AvH Fellow) - Germany; Fellow of the Royal Society of Chemistry (FRSC) - London; Fellow of The Andhra Pradesh Academy of Sciences (FAPAS) - Hyderabad; Fellow of the Indian Chemical Society (FICS) - Kolkatta and Fellow of Indian Council of Chemists (FICC) Agra.</p> <p>He has guided 29 PhDs and 36 Master students. Presently there are 14 PhDs and 10 Master students working. He has ~180 Publications (papers + patents + processes....), three book chapters and ONE e-Book for his credit. He was involved in transferring two technologies and developed several processes.</p>	

Functionalized Organosilicon Compounds: Synthesis and Applications

Pintu K. Kundu and Sunil K. Ghosh*

Bio-Organic Division, Bhabha Atomic Research Centre

Trombay, Mumbai 400085, India

E-mail: ghsunil@barc.gov.in / pintukkundu@gmail.com

Abstract

Functionalized organosilicon compounds are very important because they can cater small organic molecules useful for biological and materials research. Utilizing different properties of silicon, we have developed diverse organic reactions and methods to provide functionalized organic molecules with desired levels of regio- and/ or stereo-selectivities. In this regards, silicon functionalized cyclopropane, cyclobutane, allylsilanes, 3,4-bis-silylated adipates/adipamides, β -C-silylated as well as β,β -disilylated carbonyl compounds have been synthesized. Some of these intermediate organosilicon compounds have been utilized for the syntheses of natural product precursors such as enantiopure 2,6-dioxabicyclo[3.3.0]octane-3,7-diones and potential therapeutic drugs such as fagomine isomers.

Key Words: organosilicon compounds, cyclobutane, reductive coupling, allyl silane, dilactone, fagomine.

Introduction

The unique properties of silicon [1] have led to its wide utilization in organic chemistry ranging from protecting functional groups [2] to temporary tether [3] in general and as masking hydroxyl group [4], to highly controlled and selective organic reactions [1,5] in particular. A silicon group is known to stabilize either an electron deficient centre such as a carbocation at the β -position (β -effect) [6] or a carbanion at the α -position (α -effect) [7] with respect to it. These stabilizing effects play important roles in directing the regioselectivity in various organic reactions, especially in β -silyl carbonyl compounds.

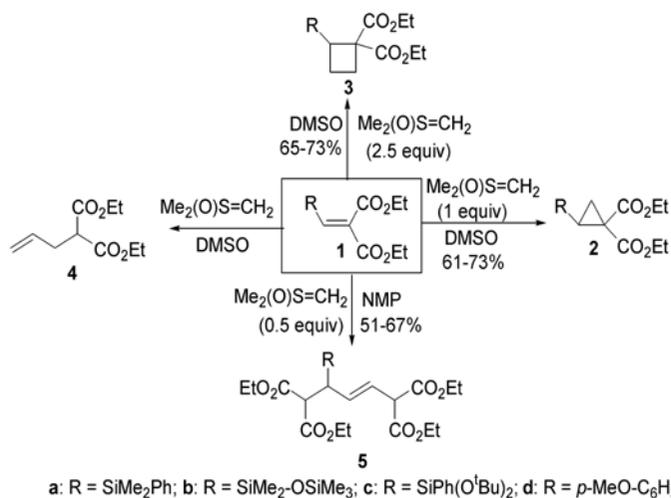
Some novel class of highly functionalized small organosilicon compounds such as silylated-cyclopropanes and cyclobutanes, allylsilanes, disilylated-adipic acid derivatives and β -silyl-propionates (Figure 1) are important intermediates in organic synthesis as well as can be tailored for materials development. Our objective therefore was to develop methodologies for these types of functionalized organosilicon compounds in a diversified manner so that various types of molecules could be obtained from the same set of substrates and just by changing the reaction conditions or reagent stoichiometry. We report here (i) the development of a diversified approach for the synthesis of silylated and functionalized cyclopropanes or cyclobutanes or allylsilanes from silylmethylene malonates and varying amount of dimethylsulfoxonium methylide (DIMSOY); (ii) a successful approach for the stereoselective syntheses of the chiral C_2 -symmetric 3,4-bis-silyl substituted adipic acid derivatives by a Mg/trimethylsilyl chloride mediated intramolecular reductive coupling of symmetrical disiloxanes of β -silylacrylic acid

oxazolidinone derivatives; (iii) the reductive C-silylation of β -dimethyl(aryl)silylacrylates/cinnamates at β -position and reductive C-silylation of δ -phenyldienoate at δ -position by a regiospecific reductive C-silylation using Mg/silyl chloride/DMF leading to functionalized allylsilanes; and (iv) utility of some of these intermediates for short and efficient syntheses of optically pure enantiomers of 2,6-dioxabicyclo[3.3.0]octane-3,7-dione and hydroxylated piperidine based natural products viz. D-fagomine and D-3,4-di-epifagomine.

Preparation of cyclobutane, cyclopropane and allylsilane derivatives [8]

Cyclobutane systems are commonly prepared by cycloaddition, cyclopropane ring expansion and ring contraction reactions. However, syntheses of suitably functionalized derivatives of cyclobutane as well as cyclopropane are very challenging. The reactivity of cyclobutane/cyclopropane derivatives is due to their inherent ring strain. Sulfonium and sulfoxonium ylides [9] are extensively used in organic chemistry to achieve the insertion of a methylene or a substituted methylene across the double bond of a carbonyl, an imine, or an electrophilic olefin to yield an oxirane, an aziridine, or a cyclopropane, respectively. A successful approach towards skeletal diversity oriented synthesis (Scheme 1) was achieved when silylmethylene malonate **1a** was allowed to react with DIMSOY. We have developed the conditions for the synthesis of individual products with very high selectivity merely by adjusting the stoichiometry of the ylide and reaction conditions. When excess DIMSOY, generated from the reaction of trimethylsulfoxonium iodide and sodium hydride in DMSO was reacted with the β -silylmethylene

malonate **1a** at room temperature, cyclopropane **2a** was formed albeit in moderate yield, associated with two unusual products *viz.* cyclobutane **3a** and the allylated malonate **4** (Scheme 1). However, when stoichiometric quantity of the ylide was used, besides cyclopropane **2a**, a new product, an allylsilane **5** was formed (Scheme 1). The optimized condition for the synthesis of cyclobutane derivatives **3** was to use 2.5 equivalents each of LiOBu-*t* and trimethylsulfoxonium iodide with respect to malonate **1a** in DMSO at 20 °C, which gave cyclobutane **3a** as the major product. To see the generality of this synthetic strategy, two more silylmethylene malonates **1b,c** were reacted under our optimized conditions and a mixture of cyclopropane **2b,c** and cyclobutane **3b,c** were formed in moderate yield and selectivity (**2b:3b** = 1:2 and **2c:3c** = 7:3) (Scheme 1). Next, we turned our attention towards the preparation of the functionalized allylsilane **5**. The best result was obtained by carrying out the reaction with 0.5 equiv of DIMSOY in DMF or NMP at 5 °C. To find the role played by the silicon group in these reactions, the aryldiene malonate **1d**, was reacted with varying amounts of the ylide, generated from the corresponding iodide and base. In all the cases, no trace of cyclobutane or the dimerization products was observed. The cyclopropane **2d** was the sole product associated with the unreacted starting material in cases where substoichiometric quantity of ylide was used.

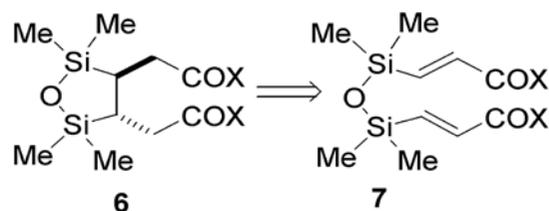


Scheme 1: Diversified reaction of β -silylmethylene malonate with DIMSOY

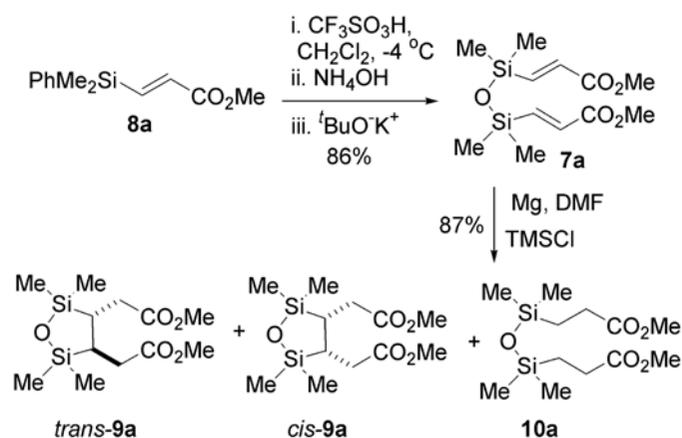
Synthesis of C₂-symmetric 3,4-bis-silyl-substituted adipic acid derivatives [10]

Molecules containing stereochemically defined two (or more) silicon-bearing centres and terminal functionalities are useful intermediates in organic synthesis. A silicon group can effect stereochemical control [11] in a 1,2-related and a 1,3-related fashion. Therefore, molecules with two adjacent silicon-bearing centres can effectively control

stereocentres which are 1, 4-related and beyond [12]. Highly stereoselective syntheses of the *meso* diastereoisomer of 3,4-bis-silylated adipates have been achieved with great stereo control [13]. These intermediates have been applied for the synthesis of many natural products [14] such as ribonolactone, deoxyribonolactone, both the enantiomers of nonactic acid as well as nonactin. The C₂-symmetric racemic diastereoisomers of 3, 4-bis-silylated adipates are also expected to be a starting point for the syntheses of complex molecules. Therefore, a stereoselective synthesis of chiral C₂-symmetric 3, 4-bis-silyl-substituted adipic acid derivatives was undertaken to show their reactivity and utility. Making a five membered ring with *trans* geometry of the substituents is energetically more favored. We, therefore, decided to resolve our problem of making C₂-symmetric racemic diastereoisomers of 3, 4-bis-silyl-substituted adipic acid derivative **6** by a five-membered ring formation (Scheme 2) which can be expected to be achieved by intramolecular reductive cyclization of symmetrical disiloxane tethered bis-acrylates **7**. Using the reported [15] procedure, silylacrylate **8a** was reacted with trifluoromethanesulfonic acid (TfOH) which gave the desired disiloxane **7a** in excellent yield (Scheme 3). Intramolecular reductive cyclization of the disiloxane **7a** was then attempted with different reducing conditions. The optimized conditions for the cyclization were found to use 12 equiv each of Mg and trimethylsilyl chloride (TMSCl) in DMF with a 30 mmolar concentration of the unsaturated



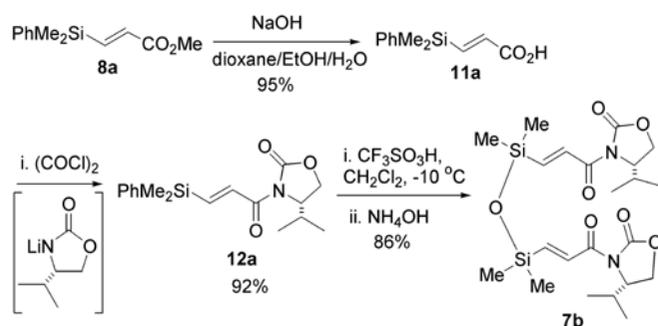
Scheme 2: Retrosynthetic approach for C₂-symmetric adipic acid derivative



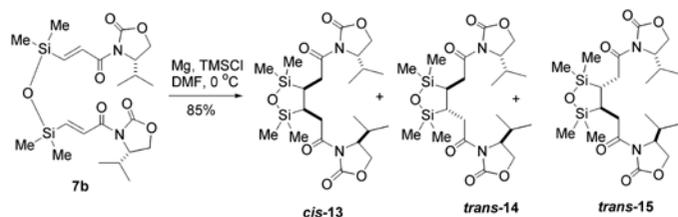
Scheme 3: Synthesis of disiloxane **7a** and its reductive coupling

ester **7a** at 0 °C which gave a mixture of *cis*-**9a**, *trans*-**9a** and reduced diester **10a** (*cis*-**9a**:*trans*-**9a**:**10a** = 42:42:16) in 87% isolated combined yield (Scheme 3).

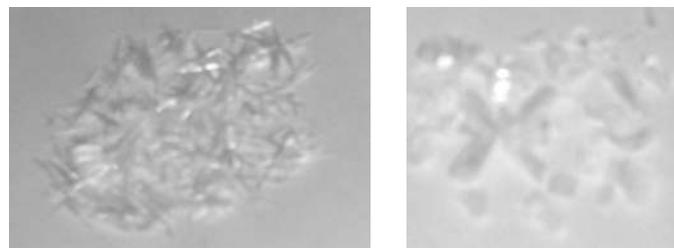
Our next aim was to improve the diastereoselectivity (*trans/cis*) as well as control the absolute configuration during the cyclization to obtain the *trans* isomer(s) in pure and enantiomeric form. It was envisaged that instead of an ester, the Mg/TMSCl-mediated coupling of the corresponding amide of a suitable chiral amine might be useful for this purpose. Amongst the amides, chiral oxazolidin-2-ones [16], initially introduced by Evans [17] are widely used as chiral auxiliaries. The *trans*- β -silylacrylic ester **8a** was hydrolyzed to the acid **11a**, which was then converted to the intermediate acid chloride by reacting with oxalyl chloride and subsequently reacted with the lithium salt of Evans' oxazolidin-2-one to give the oxazolidin-2-one derivative **12a** in 92% yield (Scheme 4). Reaction of amide **12a** with TfOH (3.6 equiv) in dichloromethane at -10 °C, followed by quenching with ammonium hydroxide, produced the disiloxane **7b** in very good yield. The disiloxane **7b** was subjected to the optimized reductive cyclization conditions described for disiloxane **7a**, using Mg/TMSCl in DMF at 0 °C which led to the formation of a mixture of diastereoisomeric cyclic products, *cis*-**13** and two *trans*-products (*trans*-**14**:*trans*-**15** = 60/40) with a strong preference for the desired *trans* isomers (*trans*:*cis* = 85/15) (Scheme 5). The isolated yield of the cyclic products was also very high (85%). The individual isomers were separated by fractional crystallization. The *trans*-**14** was obtained as needles whereas *trans*-**15** was sugar like crystals (Figure 1).



Scheme 4: Synthesis of modified disiloxane attached to chiral auxiliary



Scheme 5: Reductive coupling of disiloxane **7b**



trans-**14**

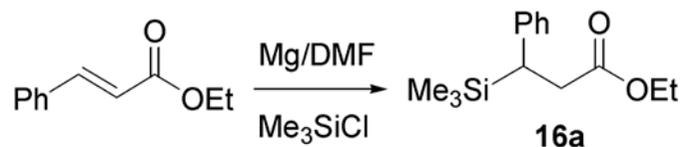
trans-**15**

Figure 1: View of crystals of pure *trans* isomers

Reductive C-silylation of β -silylacrylates, cinnamates and δ -phenyldienoate [18]

Carbonyl compounds having a silyl group at β -position are popular targets because of their versatile nature [19] and also excellent surrogate for the acetate aldol [20] reaction. Amongst the available methods of preparation of β -silyl carbonyl compounds, silylmetalation of unsaturated carbonyl compounds using dimethyl (phenyl) silyl lithium (Me_2PhSiLi) [21] as a source reagent is widely used. Although Me_2PhSi group is an equivalent to a hydroxyl group, its transformation to the later is not easy. The proposed mechanism [22] shows that the phenyl group undergoes an ipso-substitution by first reacting with an electrophile such as bromine or mercuric acetate. It is therefore expected that electron rich aryl ring would make this ipso-substitution more facile. But the major hurdle was the preparation of dimethyl (aryl) silyl lithiums from the corresponding silyl chlorides which does not occur [23] for electron rich aryl groups. So the popularity of Me_2PhSi group remained because of the easy preparation of Me_2PhSiLi from the commercially available silyl chloride and facile conjugate additions of mono- and bis-silylcuprate reagents derived from it to unsaturated carbonyl compounds.

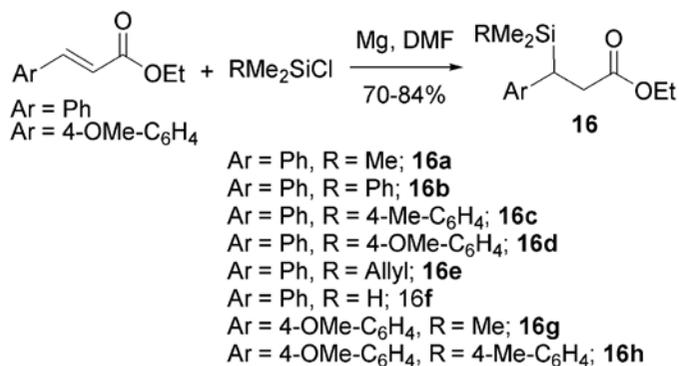
When we subjected ethyl cinnamate under our reported [10] reductive coupling reaction conditions using Mg/TMSCl/DMF, the formation of ethyl β -phenyl β -trimethylsilyl propionate **16a** was observed. The propionate was associated with a small amount of double bond reduced product, ethyl dihydrocinnamate (Scheme 6). No reductive dimerization product could be detected from the crude product. After several experimentations, we obtained the optimized conditions for the reductive silylation of ethyl cinnamate by addition of it to a mixture of 6 equiv. of TMSCl, 12 equiv. of Mg in DMF (0.2 M) at 30



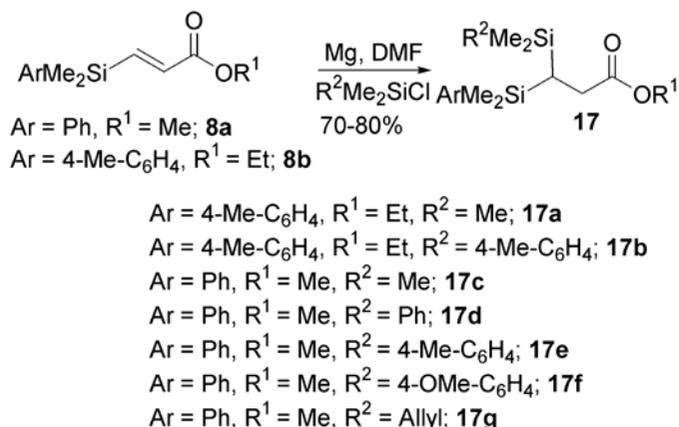
Scheme 6: Reductive silylation of ethyl cinnamate

°C for 0.5 h leading to β -silylated product **16a** in 84% yield. The yield of the double bond reduction product i.e ethyl 3-phenylpropionate was found to be negligible (~5%).

To generalize the Mg/TMSCl/DMF system for efficient reductive C-silylation at the β -position of ethyl cinnamate and substituted cinnamates, reductive silylation with PhMe_2SiCl and silyl chlorides which do not form the corresponding silyl lithium easily such as *p*-Tol Me_2SiCl , *p*-Ans Me_2SiCl and All Me_2SiCl were pursued. In all cases the β -silylated product **16b-h** was obtained in very good yield and purity (Scheme 7). A similar clean reductive C-silylation reaction took place for silyl acrylate ester **8a, b** when reacted with various silyl chlorides as presented in Scheme 8. The desired β,β -disilylated products **17a-g** were formed in moderate to good yield.

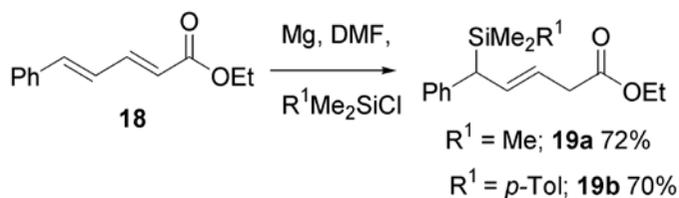


Scheme 7: Reductive silylation of cinnamates with various silyl chlorides



Scheme 8: Reductive silylation of β -silyl substituted acrylates with various silyl chlorides

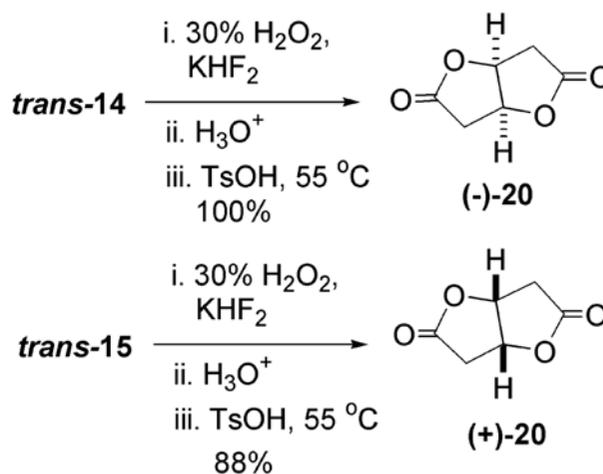
When the dienic ester **18** was treated under the optimized reductive silylation conditions as described for ethyl cinnamate using TMSCl the allyl silane **19a** was formed without a trace of the other regioisomer (Scheme 9). Moreover, the allylsilane was also formed with high stereoselectivity where (*E*)-isomer was found to be the major product. Silyl chloride such as *p*-Tol Me_2SiCl also gave the corresponding allyl silane **19b** in good yield.



Scheme 9: Reductive silylation of δ -phenyldienoate

Synthesis of dioxabicyclo [3.3.0] octane-3, 7-diones [10]

Dioxabicyclo [3.3.0] octane-3, 7-diones **20** has been shown to be a useful intermediate in the synthesis of some important biologically active compounds such as butenolides [24], eldanolide [25], the Geissman-Waiss lactone [26], prostaglandin analogues [27], *trans*-laurediols [28] and 8, 9-epoxyeicosatrienoic acid [29]. We have used the above synthesized *trans* diastereoisomers *viz.* *trans*-**14** and *trans*-**15** for the synthesis of enantiomerically pure bilactones **20**. Thus *trans*-**14** was subjected to Fleming-Tamao [4] oxidation using $\text{KHF}_2\text{-H}_2\text{O}_2$ in 1/1 THF-MeOH at 60 °C (Scheme 10). Besides conversion of the silyloxy group to a hydroxyl group, the oxazolidin-2-one group was also removed under these conditions to give the intermediate dipotassium salt. At this stage, a simple extraction of the reaction mixture with ethyl acetate gave back the oxazolidin-2-one (90%) and acidification of the residue gave the dilactone (-)-**20**. The (3*S*, 4*S*)-configuration of the silicon-bearing asymmetric centre in *trans*-**14** was confirmed from the specific rotation data of (-)-**20** ($[\alpha]_D^{23} = -145.3, c 0.64, \text{H}_2\text{O}$) ($[\alpha]_D^{19} = +143 \pm 2.5, c 0.785, \text{H}_2\text{O}$ for the antipode) [30]. Similarly, the *trans*-**15** under Fleming-Tamao oxidation using $\text{KHF}_2\text{-H}_2\text{O}_2$ in 1/1 THF-MeOH at 60 °C followed by acidification (Scheme 9) gave (+)-**20** as confirmed from the specific rotation data of (+)-**20** ($[\alpha]_D^{25} = +142.1, c 0.38, \text{H}_2\text{O}$) ($[\alpha]_D^{19} = +143 \pm 2.5, c 0.785, \text{H}_2\text{O}$) [30], thus confirming its (3*R*,4*R*)-configuration.

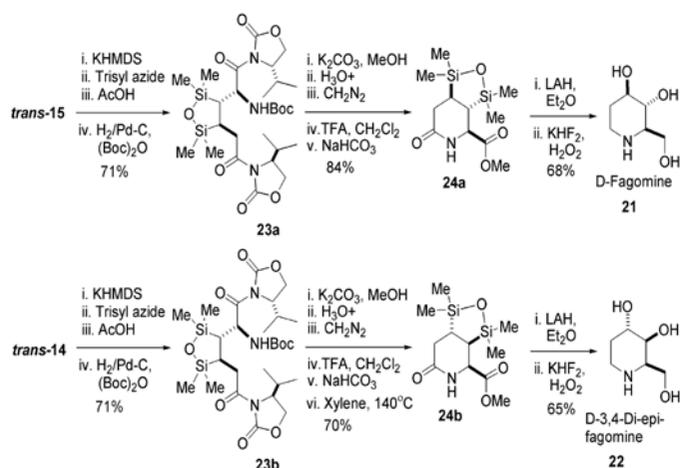


Scheme 10: Synthesis of (-) and (+)-dioxabicyclo[3.3.0]octane-3,7-diones

Asymmetric Syntheses of D-Fagomine Isomers [31]

Polyhydroxylated piperidines (azasugars) have got increasing synthetic interest due to their remarkable biological activity as glycosidase inhibitors [32]. Since glycosidases are involved in numerous biological processes, azasugars are potential therapeutic agents for the treatment of a wide range of diseases, including diabetes, cancer, AIDS, viral infections and many more [33]. 1, 2-Dideoxy-azasugars such as D-fagomine **21** and its stereoisomers **22** had been isolated from buckwheat seeds of Japanese buckwheat *Fagopyrum esculentum australe* Moench [34] and also from the seeds of *Castanospermum australe* (Leguminosae) [35]. Fagomine itself has strong inhibitory activity towards mammalian α -glucosidase, β -galactosidase [36], and also found to have a potent antihyperglycemic effect in streptozocin-induced diabetic mice and a potentiation of glucose-induced insulin secretion [37].

Synthesis of fagomine and its stereoisomers from 3, 4-bis-silyl substituted adipic acid derivatives **14**, **15** was achieved by stereoselective azidation and silicon to hydroxyl conversion as the key steps. For the synthesis of D-fagomine **21**, 3, 4-bis-silyl substituted adipic acid derivatives *trans*-**15** was chosen as the starting material whereas the synthesis of 3,4-di-*epi*-fagomine **22** was achieved from *trans*-**14**. The introduction of the azido group at the α -position of the carboxamide in *trans*-**15** and *trans*-**14** was carried out following the electrophilic azidation [38] using KHMDS and trisyl azide. Reduction of the azide **23a/23b** and in-situ protection of the intermediate amine was achieved by adding (Boc)₂O in H₂/Pd-C system. Removal of the oxazolidin-2-one groups and Boc-protection give the intermediate amine which underwent cyclization to lactam **24a/24b**. A LiAlH₄ reduction followed by Fleming-Tamao oxidation⁴ of the lactam yielded D-fagomine **21** and 3,4-di-*epi*-fagomine **22** (Scheme 11).



Scheme 11: Synthesis of D-Fagomine and D-3,4-Di-epi-fagomine

Conclusions

In conclusion, we have developed diverse organic reactions and methods to provide functionalized organic molecules with desired levels of regio- and/ or stereoselectivities using the directing properties of a silyl-group. Important synthetic intermediates viz. silicon functionalized cyclopropane, cyclobutane, allylsilanes, 3, 4-bis-silylated adipates/adipamides, β -C-silylated as well as β,β -disilylated carbonyl compounds have been synthesized and used in natural product and/or intermediate syntheses.

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Dr. Pintu Kumar Kundu has studied his B.Sc. in chemistry from University of Calcutta and subsequently M.Sc. from Indian Institute of Technology, Madras. He did his Ph.D. work at Bio-Organic Division, Bhabha Atomic Research Centre, Mumbai under the supervision of Dr. Sunil Kumar Ghosh and awarded the degree from Homi Bhabha National Institute, Mumbai in 2012. Currently, he is a post-doctoral fellow in Prof. Rafal Klajn's group at the Department of Organic Chemistry, Weizmann Institute of Science, Israel. His research interests are: organometallic chemistry, asymmetric synthesis and organic nano-materials.



Dr. Sunil Kumar Ghosh currently working as a Scientific Officer at Bio-Organic Division, Bhabha Atomic Research Centre (BARC), Mumbai. He did his M. Sc. (1984) and Ph. D. (1989, under the supervision of Prof. Tarun K. Sarkar) from Indian Institute of Technology, Kharagpur. He carried out his post-doctoral studies with Prof. Ian Fleming, FRS at the University of Cambridge, UK (1991-1993) and with Prof. Scott E. Denmark, FRS at the University of Illinois, Urbana-Champaign, USA (1999-2001). He is an Honorary Guide of Mumbai University and Honorary Professor of Homi Bhabha National Institute, Mumbai. He is the recipient of several awards including Homi Bhabha Award by BARC, Mumbai (1987) and Young Scientist Award by Indian National Science Academy (INSA), New Delhi (1992). His research interests are: organosilicon chemistry; sulfur ylide mediated reactions; asymmetric synthesis of natural products; structural and mechanistic studies; asymmetric organo-catalysis and labeled-compound synthesis.



Carbon Nanostructures synthesized from bitter Almond seeds and their Hydrogen Adsorption capacity

Sandesh Jaybhaye^{1*} Madhuri Sharon² and Maheshwar Sharon²

¹Nanotechnology Research Center, Birla College Kalyan – 421 307, M.S. India.

²NSN Research Center for Nanotechnology & Bionanotechnology, SICES College, Ambernath

jaysandesh@gmail.com; sharon@iitb.ac.in

Abstract

The goal of this research is to obtain a low cost carbon materials (CMs) which show hydrogen adsorption capacity. Such CNMs are prepared, using bitter almond (*Amgdalus communis amara*) oil, by chemical oil vapor deposition (COVD), and almond cake, by direct pyrolysis at 750°C in nitrogen atmosphere. The carbon nanotubes (CNTs) and micro porous carbon (MPC) obtained from almond oil and cake, respectively, have been purified with dilute nitric acid (HNO₃). These samples were characterized by scanning electron microscopy (SEM), Raman spectroscopy, thermo gravimetric analysis (TGA) and surface area measurement. The hydrogenation behavior of as-grown, purified samples of CNT and MPC has been studied at room temperature at 11Kg/cm². The hydrogen storage capacity of CMs (CNTs and MPC) are found to increase after purification up to 3h. The maximum hydrogen adsorption capacity of purified (10% HNO₃) CNTs and MPC is 1.4 wt. %, 0.36 wt. %, respectively.

Keywords: Micro porous carbon; Carbon nanotubes; Hydrogen storage; Bitter almond Oil; Almond cake.

Introduction

Iijima 1991 [1] discovered the existence of multi-walled carbon nanotubes as an offshoot of fullerenes research. There has been considerable interest in finding appropriate CNMs which could be suitable for hydrogen storage. Reports on very high and reversible adsorption in nano structured carbon materials, such as carbon nanotubes (CNT) [2, 3], alkali-metal-doped nanotubes [4, 5] and graphitic nano fibers [6, 7], have stimulated many experimental works and theoretical calculations worldwide. Other structures, like graphite, have also been analyzed for hydrogen storage [8]. The bundles of SWNTs, obtained using co-evaporation of cobalt and graphite in an electric arc, showed the very high uptake hydrogen storage capacity [9]. Hou *et al.* have suggested that multi-walled carbon nanotubes (MWNTs) may exhibit higher hydrogen storage capacities than single-walled carbon nanotubes (SWNTs) [10]. Meeting volumetric target value (6.5 wt%) set by the U.S. Department of Energy's (DOE) requires major advances in storage density, energy efficiency, safety and cost effectiveness. Most of these issues could be resolved by a light-weight material capable of reversibly storing and releasing hydrogen in the range of near-ambient temperatures and pressures. In order to reduce the cost of making CNM and increase its hydrogen storage capability Sharon and his co-workers [11] have tried to use plant-based raw materials as a source for production of CNMs.

In this paper, detail synthesis, characterization and hydrogen adsorption capability of CNMs, obtained from bitter almond seeds (cake and oil), is discussed. The effect of 10%, 50% and 80% of HNO₃ treatment for 6h on surface area and hydrogen adsorption capacity of CNMs is also investigated. Hydrogen adsorption was studied by measuring change in pressure of hydrogen at room temperature.

Experimental

Pyrolysis of almond oil and cake

For production of CNT by COVD, it is necessary that the diameter of the Co catalyst particles should be in nano range (~ 40 to 60 nm). The catalyst particle of appropriate size was easily produced in large quantity by the urea decomposition method. In this method a mixture of cobalt hexa nitrate (CoNO₃·6 H₂O) and urea in ratio of 1:3 was taken in a crucible, and stirred by adding a little quantity of water to form a homogeneous solution. This solution was heated in air at 500°C to obtain Co oxides and then, reduced in hydrogen atmosphere at 700°C for 2h to get Co nano powder.

These Co particles were used to grow the CNTs from almond oil by COVD at 750°C in horizontal furnace. The pyrolysis apparatus and process is presented and described elsewhere [12]. The furnace consists of two electric heating coils and 1m long quartz tube. The catalyst Ni powder in a

quartz boat was kept in the pyrolysis furnace, and 25 cm³ oil containing boat was placed in the vaporizing furnace. At first, N₂ gas was passed through the quartz tube at the flow rate 0.6 cc / min to create inert atmosphere. After 5 min., the pyrolysis temperature was set at 750°C. When the pyrolysing furnace reached the desired temperature, vaporizing furnace, where the oil was kept, was switched on. This furnace was taken to a temperature near to the boiling point of the oil (approx. 179°C). The heating was continued till entire oil was completely vaporized. The heating of the paralyzing furnace was continued for 2h at constant set temperature (750°C). Paralyzing furnace was then allowed to cool to room temperature in N₂ atmosphere, and CNTs were collected from the boat.

For the pyrolysis of cake, only pyrolysing horizontal furnace was used, which is discussed elsewhere [11]. The dried and powdered 50g cake containing boat was placed in the center of the furnace. Initially, the N₂ gas was passed through the quartz tube at the flow rate 0.6 cc / min, for 5 min., to create inert atmosphere. The furnace was turned on to achieve set temperature (750°C) and heating was continued for 2h, for complete pyrolysis. Furnace was then allowed to cool to room temperature in N₂ atmosphere, and MPC was collected from the boat.

Purification

The CNMs obtained from the almond seeds by above method contained metals and amorphous carbon as impurities. To remove these impurities, powdered CM was reflux with dilute HNO₃ (10%, 50% and 80%) for 6h (typically 1 liter of acid per 10 g of raw material). It was then washed several times with water, acetone and finally dried in oven. The purified CM was annealed up to 700°C in H₂ atmosphere, for 2h.

Characterizations

The CNMs were characterized by SEM, Raman spectra, Surface area measurement and TGA. SEM studies were done, using a field emission scanning electron microscope FE-SEM; Hitachi S-4300. TGA was done, using a Mettler TA 3000 thermal analysis system and Raman spectroscopy on NRS-1500 W Laser Raman spectrometer. Surface area of CM was measured, before and after purification, using methylene blue absorption method. The detailed measurement is discussed elsewhere [11].

Hydrogen adsorption study

Hydrogen adsorption measurement was carried out, using low pressure Sharon's apparatus (LPSA); enables us to measure the hydrogen adsorption of CNMs by measuring decrease in hydrogen pressure. The detailed about apparatus, leak test and hydrogen adsorption measurement are discussed elsewhere [11].

Results and Discussion

Fig.1 (a) shows the SEM image of Co particles (40-60 nm) obtained by urea decomposition procedure. The oil pyrolysed on Co catalyst at 750°C gave 15% yield of CNTs, and cake, on pyrolysis, without catalyst, gave 68 % yield of MPC. Figs.1 (b) and 1 (c) show SEM images of 10 % HNO₃ treated CNTs and 10% HNO₃ treated MPC, respectively. Fig.1 (d) MPC purified with 50% HNO₃ shows surface area of 32.1 m²/g. The surface area measurement study shows that, MPC reflux with 10 % HNO₃ for 6h, gives a surface area of 36.3 m²/g and is better than that treated/purified with 50% HNO₃ (Table 1). SEM image of MPC purified with 80% HNO₃ shows a different morphology (Figure 1e) and also lowers the surface area to 21 m²/g.

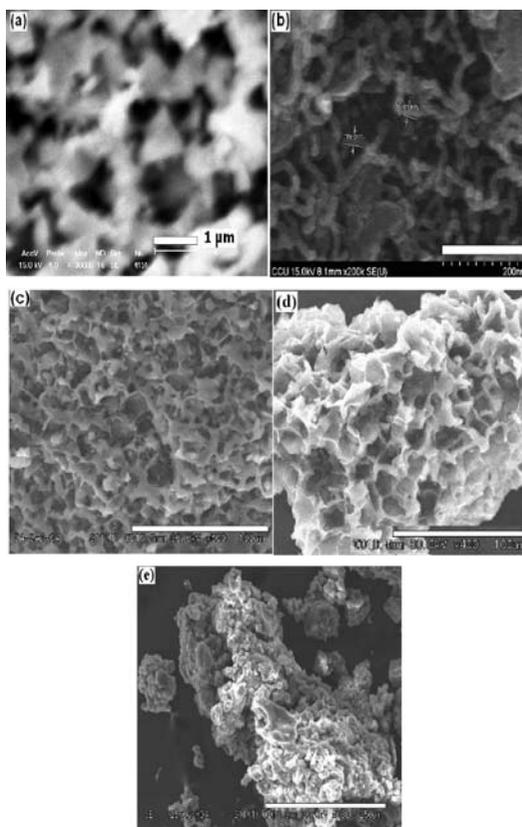


Fig.1: SEM Images of (a) Cobalt catalyst (b) 10% HNO₃ treated CNT, Purified MPC with (c) 10% HNO₃ (d) 50% HNO₃ and (e) 80% HNO₃ refluxed at 100 oC for 6h.

TGA analysis was used to calculate the purity of the CNMs and is shown in Fig.2. About 10 mg of 10% HNO₃ treated CNMs were used with ramp rate at 10°C/ min. in the air. TGA of CNTs shows the residual weight of 16 %, which implies that about 84 % of the product is pure. Whereas, the residual weight of MPC is approx 25 %, which shows that the purity of 10% HNO₃ treated MPC is 75 %.

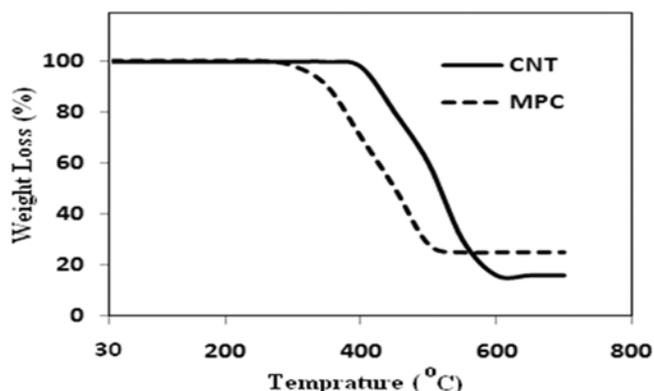


Fig.2: TGA of 10% HNO₃ treated CNTs and MPC obtained from almond seeds.

Fig.3 (a) shows typical Raman spectrum of 10% HNO₃ treated CNTs on quartz substrates, indicating two characteristic peaks. The sharp G-band peak at 1573 cm⁻¹ corresponds to in-plane oscillation of carbon atoms in the graphene wall of MWNT, and the lower D-band peak at 1318 cm⁻¹ represents the degree of defects or dangling bonds. Fig.3 (b) shows Raman spectrum of MPC with G-band at 1576 cm⁻¹ and D-band at 1309 cm⁻¹. The I_G/I_D ratio is less than 1, which shows the highly oriented crystallographic structure of CNTs and MPC.

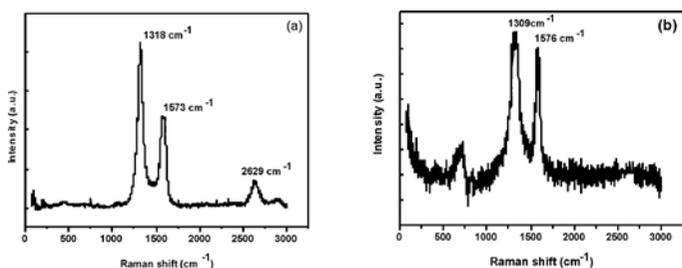


Fig.3: Raman spectrum of (a) CNTs (b) MPC purified with 10% HNO₃

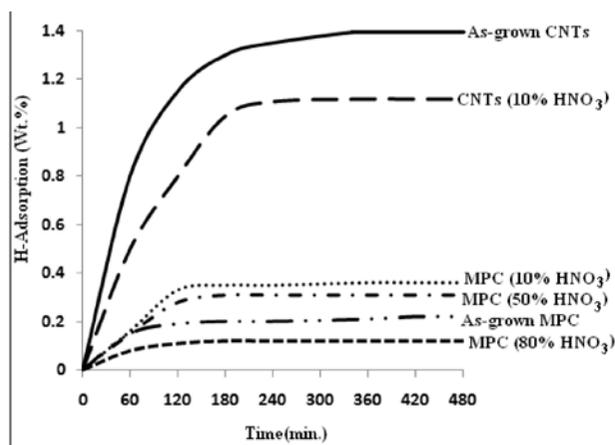


Fig.4: Plot of H-adsorption capacity of CNTs and MPC samples versus adsorption time.

These CNMs were used to measure the hydrogen adsorption capacity. The details of hydrogen adsorption measurements and surface area of CNMs are shown in Table 1. Hydrogen adsorption of 10% HNO₃ treated CNT at 11 kg/cm², at room temperature, is 1.4 wt% , and that of MPC is found to be 0.36 wt%. Treatment of HNO₃ showed some improvement in the surface area as well as the hydrogen adsorption capacity. It is found that reversible hydrogen adsorption on MPC is maximum up to 2h and then get saturated (Fig.4). However, CNTs shows gradual increase in hydrogen adsorption capacity up to 4h, and then, get saturated.

Table-1: Surface area and hydrogen adsorption capacity of CNTs and MPC obtained from almond seeds.

Sample history	Surface area (m ² /g)	H ₂ (wt.%) 11kg/cm ²
As-grown CNT	55.5	1.12
As-grown MPC	29.3	0.22
Purified CNTs (10% HNO ₃)	156	1.4
Purified MPC (10% HNO ₃)	36.3	0.36
Purified MPC (50% HNO ₃)	32.1	0.31
Purified MPC (80% HNO ₃)	21	0.12

Conclusions

It is observed that, plant-based oil seeds will be the alternative cheap source for growing cost effective CNMs. Bitter almond oil vapour pyrolysed on Co catalyst powder at 750°C produces CNTs, and its cake, on pyrolysis gives MPC. It is found that the CNMs obtained from Bitter almond seed refluxed with 10-50% HNO₃ for 6h, it removes amorphous carbon. However, it is important to note that increase in concentration of HNO₃ more than 50% not only damage the structure but also reduces the hydrogen storage capacity of MPC. This shows that 10% HNO₃ treatment for 6h to CNTs and MPC by refluxing method increases the active surface area and hydrogen adsorption capacity. MPC purified with 50% HNO₃ increase the surface area but the hydrogen storage capacity decreases. It is found that with increase in the active surface area, there is increase in hydrogen adsorption capacity.

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<p>Sandesh Jaybhaye received the M.Sc. in Chemistry and from Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, M.S. (India) in 1994. He pursued Ph.D from Dr. Babasaheb Ambedkar Technological University, Lonere, Dist Raigad, M.S. (India) in 2010 on topic Hydrogen adsorption/Desorption by Carbon nano materials. He has been working in the Birla College Kalyan as a Lecturer since 1999. He is a post doctoral fellow of Biophysical and Electronic Engineering Department, University of Genova, Italy. His research interest is synthesis of carbon nano materials and their applications. He is recognized Ph.D. Guide of JJT University Churu, Rajasthan. Currently he became a member of Ad-hoc Board of Studies in Nano-Science and Nanotechnology.</p>	
<p>Dr Madhuri Sharon completed her Ph.D. from Leicester University, UK in 1969 and was lecturer at in Bolton Institute of Technology UK. She returned to India in 1971 and joined Pune University as a lecturer. She served as Manger at CCC Shroff Reseach Institutute Mumbai, Vice President at Gufic life sciences and retied as Director of Life science from Relaince Life Science. Now she is Executive Director at NSNRC for Nanotechnology and Bionanotechnology, Ambernath. She continues her research and guide students for the Ph.D at this research center.</p>	
<p>Prof. Maheshawar Sharon completed his Ph.D. dfrom leiceser University and returned to India in 1971. He retired from IIT Bombay in 2003 as a professor in Chemistry. He is Director at NSNRC for nanotechnology and Bionanotechnology. He continues his research and guides research students for the degree of Ph.D.</p>	

A Study of Lithium Ferrites

Ibetombi Soibam, Sumitra Phanjoubam¹

Department of Physics, National Institute of Technology, Manipur, Takyel, Imphal-795 001

¹Department of Physics, Manipur University, Canchipur, Imphal-795 003

Email: ibetombi96@gmail.com

Abstract

Lithium ferrites are materials of great interest because of their scientific importance fundamentally and technologically. For many years they have been found to be used in electronic devices, telecommunication, magnetic components etc. due to their interesting electrical and magnetic properties. The properties can be optimized by varying a number of factors, viz. substitution, synthesis method, sintering temperature etc. This paper gives a brief review of the work carried out to optimize lithium ferrite material for specific device application.

Keywords: Lithium ferrites, Spinel structure, XRD, dielectric constant, Initial permeability

Introduction

Lithium and substituted lithium ferrites exhibit spinel structure. They have the general formula MFe_2O_4 , where M represents a divalent metal ion. The divalent metal ion can be one of the divalent ions of the transition elements like Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Mg^{2+} or a combination of these ions or a combination of ions having average valency of two, like $0.5Li^{1+} + 0.5Fe^{3+}$ as in $Li_{0.5}Fe_{2.5}O_4$. The trivalent ion such as Al^{3+} or Cr^{3+} and tetravalent ion such as Ti^{4+} or Ge^{4+} can completely or partly replace the Fe^{3+} ions in MFe_2O_4 [1]. Depending on the site preference of the cations a large variation in the properties of lithium ferrite is observed. Ferrites are versatile and the properties can be optimized for specific application by controlling several factors like type (di-, tri-, tetra-, or penta-valent) and amount of substitution, synthesis method, condition of preparation and sintering process. They have been found to be extensively used in electronic and communication devices such as radio receiver, television, telephones, computers, interference suppression. They are also used as temperature sensor, magnetic components such as magnetic recording head, ferrite cores etc and in certain microwave devices including gyrator, resonance isolator, phase shifter, circulator etc. [2-5]. The wide range of applications are due to their good electrical and magnetic properties such as high resistivity, wide range of operating frequency, low loss combined with high permeability, time and temperature stability and good hysteresis loop properties. A study of the conditions for optimization of properties may lead to the development of new materials with desired properties for specific applications.

Optimizing lithium ferrite for specific application

Substitution plays a major role in modifying the properties of lithium ferrite. The substituents can be

divalent, trivalent, tetravalent, and pentavalent ions, each incorporated to play a different role in controlling the properties of the material for one or more specific purposes. The beneficial and detrimental effects of some of these substituents are discussed.

Zinc substitution appears to be a remarkable factor for increasing the saturation magnetization. It enters the tetrahedral site of the system and the cation distribution is $(Zn_xFe_{1-x})[Li_{0.5-0.5x}Fe_{1.5+0.5x}]$. However for $x \geq 0.4$ the exchange interaction weakens leading to a fall in saturation magnetization. It is effective in lowering the anisotropy but promotes densification and grain growth which contribute to the decrease in coercivity [6]. Some of the deleterious effect includes decrease in the Curie temperature, squareness, remanence ratio etc [7]. As such simultaneous substitution of Zn with other substituents is taken under consideration. Ni^{2+} substitution is found useful in enhancing the squareness, remanence ratio with low magnetostriction[12]. It also increases the resistivity [8]. On the other hand Mn^{3+} helps in diminishing porosity and a small amount of Mn^{3+} are added to lower dielectric loss and reduce conductivity [9]. As a consequence of the above discussion Zn and Mn are incorporated along with Ni by Joshi et al. High value of Curie temperature and saturation magnetization are observed. The studied compositional formula being $Li_{0.25-0.25x}Zn_{0.5-0.5x}Ni_xMn_{0.1}Fe_{2.15-0.25x}O_4$ which are essential in EMI application. The reported resistivity observed is also very high which is beneficial to avoid short circuit when applied in EMI as ferrite cores [10].

Effect of simultaneous substitution of Ti^{4+} and Zn^{2+} ions on the various electrical and magnetic properties have also been reported by many workers. It was found that saturation magnetization, Curie temperature and magnetocrystalline anisotropy decrease with increasing

Ti⁴⁺ concentration. The combined effect of the substitution on the device properties are to some extent same with Li-Zn ferrites however for large simultaneous substitution the behaviour is complex and at some instances even Curie temperature increases. The d.c. resistivity increased with increasing Ti⁴⁺ concentration [11-13] Such cases may exhibit promising properties for device application and can be investigated in depth.

The Co²⁺ substitution in presence of Zn is also effective in the various properties of the material. Besides increasing magnetization it has the benefit of increasing temperature stability which is much essential in electronic device application. The Co²⁺ substitution has the ability of enhancing power handling capacity of the material which in fact makes the material applicable in transformer and motor cores, a major application of ferrimagnetic materials [14, 15].

Another important additive mainly used in ceramic processing of ferrite is Bi₂O₃. The addition of Bi₂O₃ gives densification at low temperature by forming glassy phase at the grain boundary. The addition of Bi minimizes the decrease in saturation magnetization. Also it was reported that switching speed as in digital computers was enhanced due to action of Bi₂O₃ by shifting the location of pores from interior of grains to the grain boundary. However the addition of Bi gives detrimental effect on certain properties, like electromagnetic properties. Hence a need arise for low temperature sintered ferrites without additives [16-18]. This is achieved to some extent by using fine powders that is synthesized by wet chemical method.

Previously the most widely used method for the preparation of lithium ferrite is the direct solid state reaction. In this method a precursor is mixed followed by pre-firing process about 700°C. During the pre-firing process decomposition of the carbonates and oxides, evaporation of volatile impurities along with homogenisation of powder mixture takes place. Finally the powder is ground and dry pressed to give final sintering. However in this process the temperature in which the ferrite forms is high, nearly 1000°C or above. Hence sintering aids are added to lower down the temperature. In such cases Bi₂O₃ are added which gives negative effect on the properties. Nowadays wet chemical method which has the advantage of forming material at low temperature without additives is used. Besides, this method enables to achieve material with high purity, high degree of homogenisation and with a small particle size in the range of nanometer. The wet chemical method comprise of varieties of synthesis methods, some of which are chemical coprecipitation, citrate precursor, sol gel method etc [19-21]. However each synthesis method has

its own special condition and thus may not be possible to give a universal set of conditions applicable to all synthesis method. By controlling carefully the experimental conditions like pH, refluxing time, temperature etc, material with desired properties can be obtained. The citrate precursor method is discussed briefly.

In citrate precursor method the metal ions from the starting materials such as nitrates are complexed in an aqueous solution with α -carboxylic acids such as citric acid. The ratio of metal nitrates to citric acid is taken in the ratio of 1:1 in order to make uniformity in the chelation of the metal ions. The solution is stirred continuously by magnetic stirrer using a magnetic agitator until the formation of a transparent clear solution. Ammonia solution was added to control pH value. After controlling pH, it was refluxed at an ambient temperature with continuous stirring for about half an hour. The solution was then put in an oven at a temperature of about 100°C. A highly viscous mass is then formed by this slow evaporation process. The citric acid act as a fuel for the ignition step of the process and finally auto-combustion process takes place giving the ash-synthesized ferrite powder. The ash-synthesized product so obtained is the typical spinel structured nanocrystalline lithium ferrite powder.

The firing or sintering of the obtained ferrite powder tailors the properties of the material for specific application. Proper control in firing procedure gives final electrical, magnetic and mechanical characteristics to the product. There are two broad class of sintering namely pressure sintering and conventional sintering or pressureless sintering. The method used in pressure sintering are hot pressing where pressure is applied uniaxially to the powder and hot isostatic pressing where pressure is applied isotropically by means of a gas. It is generally used in high cost ceramics giving high density and fine grain microstructure. The conventional sintering processes are of two types, furnace heating and microwave heating. Microwave sintering shows a considerable enhancement in certain characteristic properties of the material. Again both types of sintering, furnace as well as microwave depend on the firing schedule and atmosphere surrounding the powder compact. The firing schedule includes the change in sintering temperature, sintering time, rate of heating, cooling rate etc. [5]. Even though pre-sintering can be avoided in wet chemical method, it has been observed that certain properties like dielectric constant, initial permeability etc. are different for samples prepared with and without pre-sintering. This can be seen by considering Li_{0.49}Fe_{1.49}Co_{0.02}O₄ ferrite prepared using the citrate precursor method [22], where one of the samples

was presintered before final sintering while the other was directly given final sintering.

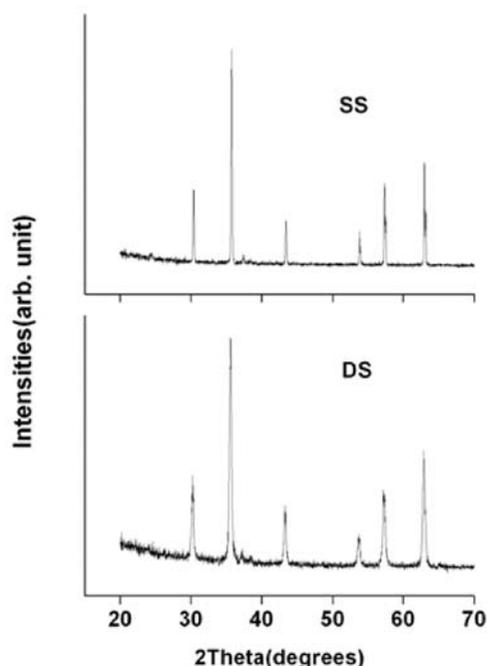


Fig. 1: XRD for $Li_{0.49}Fe_{1.49}Co_{0.02}O_4$ (a) without pre sintering, (b) with pre sintering

Formation of lithium ferrite at 100°C was confirmed from the powder XRD studies (Philips powder X-ray diffractometer) [Fig.1]. The first sample (DS) is pre-sintered at a temperature of 540°C followed by final sintering at 1080°C whereas the second sample (SS) was given final sintering at 1080°C without a pre-sintering process. The heating rate and the sintering time were kept same in both the case and furnace cooled. The room temperature dielectric constant, dielectric loss and initial permeability were measured using an LCR meter. The values of dielectric constant, dielectric loss and initial permeability were observed to be less for DS.

Table - 1: Dielectric constant, dielectric loss and initial permeability of $Li_{0.49}Fe_{1.49}Co_{0.02}O_4$

Sample	Dielectric constant	Dielectric loss	Initial permeability
SS	70.012	0.091	51.4
DS	67.342	0.04	8.42

However the variation of initial permeability with frequency exhibits the same nature. They show dispersion with increasing frequency and at much higher frequency it becomes frequency independent [Fig.2]

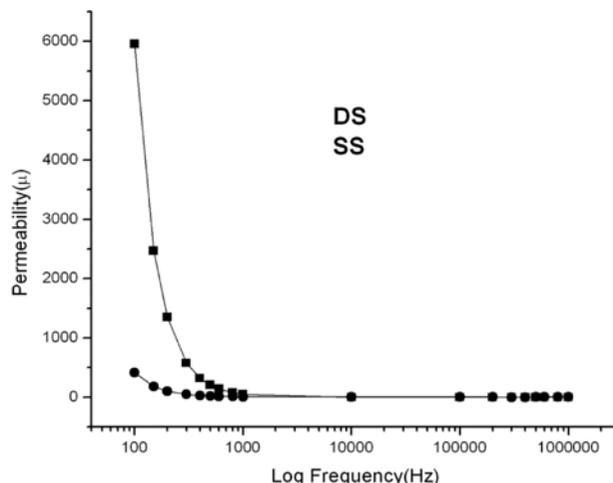


Fig. 2: Variation of initial permeability with frequency

Thus variation in the substitution, the synthesis method and sintering process can be used to influence the properties of lithium ferrite for specific desired application. Each step plays a different role in controlling the desired properties.

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Dr Ibetombi Soibam was awarded MSc (Physics) in 2003 from Manipur University and earned her PhD Degree (Material Science) in December 2009 from the same University. She joined NIT Manipur in the year 2010 as Assistant Professor in Physics. Her field of interest include Mössbauer, Electrical and Magnetic studies along with Nanoscience and Nanotechnology.



Dr Sumitra Phanjoubam got her MSc from Delhi University in the year 1983. She did her PhD on "Mössbauer, Electrical and Magnetic study of Substituted Li-Ferrites" from the same university in the year 1989. She joined Manipur University as Assistant Professor in the year 1988.



News and Forthcoming Events

Some of the National Conferences being organized in India, in the year 2012-13 are:

1. Seventeenth National Convention of Electrochemists, (NCE-17), Chennai, India, September 14-15, 2012, website: <http://www.saest.com>
2. 4th Interdisciplinary Symposium on Materials Chemistry (ISMC-2012), B.A.R.C. Mumbai, India, December 11-15, 2012, website: <http://www.barc.gov.in/symposium/ismc-2012>
3. 5th ISAEC Triennial International Conference on Advances and recent trends in Electrochemistry, Hyderabad, India, January 16-20, 2013, website: <http://www.iseac.org/elac2013>
4. Nuclear and Radiochemistry, NUCAR 2013, Jabalpur, India, February 19-23, 2013, website: <http://www.barc.gov.in/symposium/nucar2013>

Some of the International Conferences being organised in the year 2012-13 are:

1. 4th International Symposium on Structure-Property Relationships in Solid State Materials, June 24-29, 2012, Bordeaux, France, e-mail: contact@spssm4.com

2. 15th International Congress on Catalysis, Munich, Germany, July 1-6, 2012, email: tagungen@dechema.de
3. ICACCE 2012: International Conference on Applied Chemistry and Chemical Engineering Amsterdam, Netherlands, July 25-27, 2012. website: <http://www.waset.org>
4. XXI International Materials Research Congress (IMRC) 2012, Cancun (Mexico) August 13-17, 2012. website: <http://www.mrs.org/imrc2012/>
5. 4th EuCheMS Chemistry Congress Prague, Czech Republic, August 26-30, 2012, e-mail: info@euchems-prague2012
6. ISCRE 22, International Symposium on Chemical Reaction and Engineering, Maastricht, Netherlands, September 2-5, 2012, e-mail: info@iscre22.com
7. MS&T'12: Materials Science & Technology Conference and Exhibition, combined with ACerS 114th Annual Meeting Pittsburgh (USA) October 7-11, 2012, website: <http://ceramics.org/>
8. Electrochemistry 2013, Canary Islands (Spain) February 25-28, 2013, website: <http://www.zingconferences.com/>

Achievements, Honours and Awards received by the SMC members

Name of the member & affiliation	Name of the award/honour	Conferred by
Dr. Rajendra N. Basu CSIR-CGCRI, Kolkata	National Metallurgist Day Award - 2011	Ministry of Steel, Government of India
Prof. Bhalchandra M. Bhanage Institute of Chemical Technology, Mumbai	CRSI-Bronze Medal	Chemical Research Society of India
	ISCMA-Outstanding Professor of the Year	Indian Chemicals Manufacturers Association
Dr. (Mrs.) S. R. Bharadwaj and co-workers BARC, Mumbai	DAE Group Achievement Award-2010	Department of Atomic Energy
Dr.V. R. Chumbhale NCL, Pune	Member, Editorial Board	International Journal of Chemistry and Applications (IJCA)
Dr.S.J. Dhoble R.T.M.Nagpur University, Nagpur	Advanced Materials Scientist Letter Awards-2011	International Conference on Nanomaterials and Nanotechnology
Dr. Hirendra N. Ghosh BARC, Mumbai	CRSI Bronze Medal	Chemical Research Society of India
Dr. Neelam Goyal BARC, Mumbai	Award for 'Outstanding contribution in Nuclear Science & Technology' 2010	Department of Atomic Energy
Dheeraj Jain BARC, Mumbai	TA Instruments-ITAS Young Scientist Award	Indian Thermal Analysis Society, Mumbai and TA Instruments, USA
Dr. O.D. Jayakumar BARC, Mumbai	DAE Scientific & Technical Excellence Award	Department of Atomic Energy
Professor Prafulla K. Jha Bhavnagar University	UGC Research Award	University Grants Commission, New Delhi
Dr. Manoj Mohapatra BARC, Mumbai	DAE Group Achievement Award-2010	Department of Atomic Energy
Dr. Dhanraj T. Masram University of Delhi, Delhi	SERB-DST Young Scientist Award	Department of Science and Technology, Delhi
Dr. Tulsi Mukherjee BARC, Mumbai	CRSI Silver Medal (2012)	Chemical Research Society of India
	Lifetime Contribution Award in Free Radical Research	Society for Free Radical Research, India
	Lifetime contribution in the area of radiation and photochemistry	Indian Society of Radiation and Photochemistry
Dr. Soumyaditya Mula BARC, Mumbai	Young Associateship-2011	Maharashtra Academy of Sciences
Dr. K. N. Shinde N.S. Science and Arts College, Bhadrawati, Chandrapur, (MH)	IAAM Scientist Award-2011	1 st International congress of Advanced Materials - 2011 , Jinan, China
Dr. V. Sudarsan BARC, Mumbai	DAE Scientific & Technical Excellence Award	Department of Atomic Energy
Dr. A. K. Tyagi BARC, Mumbai	CRSI CNR Rao National Prize in Chemical Sciences	Chemical Research Society of India

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