



Prof James Clark

President of the Green Chemistry



Network

The Green Chemistry Network (GCN) (www.greenchemistrynetwork.org) was established by the Royal Society of Chemistry in 1998 to promote green and sustainable chemistry in all sectors of education and industry. In its current role as an international charity, it also represents the green chemistry community on the national and international stages. In 2013, the GCN started a new initiative to encourage better communication between the very many green chemistry centres emerging in countries across the world and to help new emerging centres. This new "G2C2" network will be hosted by the GCN and plans to hold annual meetings of Centres to promote collaboration and encourage networking. We are delighted that the 2nd G2C2 meeting will be held in South Africa, whose vital resources and growing markets are so important for a future sustainable society.

Prof Danie Visser

Deputy Vice Chancellor, Research, UCT



The University of Cape Town is proud to host the second symposium of the Global Green Chemistry Network (GCN) to be held at the Two Oceans Aquarium from 24 – 26 August 2014. As a University, we are committed to sustainability – as evidenced by, for example, the fact that the Vice-Chancellor, Dr Max Price, signed the ISCN/GULF Sustainable Campus Charter. In terms of this charter, we have pledged to align the University's core mission with sustainable development and to ensure that our facilities, research and teaching are linked to create a living laboratory for sustainability. The GCN philosophy for sustainable chemistry is very much in line with these commitments and we are very happy to partner with the Network in presenting this important symposium. It is our hope that it will create an important opportunity to advance the cause of green chemistry and serve as a meeting point between academia and industry, and between academics and students from around the world. We look forward to welcoming you in Cape Town.



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Sunday 24 August

Venue: I&J Predator Exhibit

Strategies for Green Chemistry Innovation at the University of Cape Town

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Keywords: university technology transfer, innovation, green chemistry, fuel cell, algal technology, hydroxytyrosol.

The presentation will consider various strategies that have been developed to overcome various challenges relating to the commercialisation of specific green chemistry intellectual property (IP) developed at the University of Cape Town.

A Department of Science and Technology funded Centre of Competence (HySA) has been established at the university to foster the development of hydrogen fuel cells. This builds synergistically on the world-class catalysis research that is already conducted in the Department of Chemical Engineering. Strategic international partnering with commercial entities and in-licensing of IP has enabled the programme to fast-track to a point where cutting edge South African inventions can be integrated into existing technology, rather than requiring South Africa to develop the 'basics' in order to participate in this space. Hydrogen Fuel cells require platinum-based catalysts and as such, represent an important opportunity for South Africa to perform value-addition to its mineral resources, rather than exporting the platinum metal.

The olive industry is burgeoning in the Western Cape and there is increased olive production, with concomitant waste emanating from brining processes. Technology developed by UCT, in a project funded by the Water Research Commission, has enabled the antioxidant hydroxytyrosol to be recovered from the brine waste. The actual waste that needs to be treated has been reduced considerably and the bulk of the water is able to be recycled.

The Centre for Bioengineering Research (CeBER) has developed a number of algal bioprocesses. Recent project-work on the cultivation of spirulina has highlighted the significance of having a pilot facility in close proximity to the university to improve the chance of successful technology scale-up and commercialisation. This has required a compromise in terms of optimal weather conditions, which impacts the figures of merit that can be achieved. Robust techno-economic modelling also focusses research on the key bottlenecks, or major input costs and underpins the analysis of viability of specific products, as well as operating locations.

Monday 25 August

Venue: Think Tank

Innovating Towards a More Sustainable World – The Design Imperative

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Without a doubt, chemists have created an amazing variety of molecules to support our modern way of life. For a majority of compounds synthesized or extracted from natural products, we have a surprisingly limited amount of information upon which to make reasonable decisions about their toxicity to humans or the environment, their degradability (biological or otherwise), our ability to recycle or reuse them, or their renewability. In order to innovate towards a more sustainable world, chemists need to take more of a systems-based and life cycle approach to the design of new molecules, materials and processes that considers these sorts of issues as part of the design process. This talk will provide a rationale for the problem, lay out some grand sustainability challenges and offer a few examples of products that are perhaps moving in the right direction.



Renewable Raw Materials at the Brazilian Green Chemistry School

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The Brazilian Green Chemistry School was established at the Graduate Program on Chemical and Biochemical Processes of the Federal University of Rio de Janeiro four years ago and, in 2012, began introducing new courses that were designed to provide basic knowledge of Green Chemistry as well as of the tools that are used to compare different alternatives and evaluate their chances of success. From the outset, its activities were organized according to well-defined objectives. Of particular importance was the need to raise the competitiveness of local industry through innovation in processes and products based on renewable starting materials since Brazil largely exports commodities and imports manufactured goods. It has industries that face problems common to developing countries, such as lack of international competitiveness while there are also large and highly productive sectors of the economy, such as those related to the agribusiness. It occupies a unique position as a tropical country with significant access to land, water and sunlight and, in a relatively short period of time, has developed a large and efficient program on biofuels. Thus, in terms of local priorities, Green Chemistry principle seven (the use of renewable raw materials), is by far the most important. In this respect sugar cane has already proven its potential and other sources of sugars, starches, fats and oils as well as agricultural residues (orange bagasse and cashew nut shell liquids, for example) are also under investigation. Common economic considerations applied to local characteristics such as logistics and taxes may not render renewable raw materials competitive. However, in certain cases, corporate strategies may include higher prices for niche markets, as is the case with green polyethylene. Furthermore, as factors such as energy balances and carbon dioxide capture are compared to land and water consumption under local conditions, metrics become considerably more favorable for renewable raw materials. Our experience in developing Green Chemistry programs that address local needs may be of interest to colleagues who work on similar initiatives or plan to do so in the near future.

Biobased synthesis of cyclic and aromatic building blocks from sugar

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Keywords: biobased building blocks, cyclic and aromatic monomers, C5~C6 molecules, drop-in aromatics

The development of biobased materials has been extended from the synthesis of aliphatic molecules to aromatic molecules to balance the supply of renewable building blocks both in linear and ring structures to replace petroleum based drop-in compounds. While the biobased platform chemicals are drawing more interest as potential monomer precursors for commodity bioplastics, a variety of synthesizing and processing pathways of sugar derived arene compounds has been investigated. As a corresponding research KITECH is aiming at sustainable production of C5~C6 cyclic and aromatic building blocks. The recent successful synthesis of isosorbide, furanics and muconic acid from industrial sugar and crude polysaccharides may allow us to replace oil based harmful drop-in aromatics such as terephthalate and bis-phenol A preferentially. The noble catalysis and biocatalysis along with some trials of derivatization and copolymerization are in progress.

Cradle-to-Cradle: disruptive innovation in Green Analytical Chemistry in the context of the circular economy

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Keywords: Analytical Chemistry, circular processes, green materials, valorisation.



Green Analytical Chemistry is a relatively new area of activity emerging in the early 2000s and, since then, has attracted great interest all over the world [1]. Besides the need for development in instrumentation and methodologies towards improvements in the quality of chemical analyses, efforts have been made to reduce the negative impact of chemical analyses in the human health and environment and to enable the insertion of green chemistry principles into analytical laboratories [2]. However, a new perspective beyond these principles should be taken into account, including the circular economy concept. Based on a comprehensive design, a number of so-called wastes derived from agro-industrial biomass can be employed to prepare solvents and other materials especially useful in making alternative tools, equipment as well as proposing new techniques and methods for the determination of a given compound or compounds in different samples, normally of high complexity (e.g., environmental, food, pharmaceutical, industrial and biomedical nature). In this paper an innovative approach in Green Analytical Chemistry will be discussed, using some examples to introduce the cradle-to-cradle philosophy for the development and application of analytical methods. As an example, pectin extracted from fruit peels can be used as starting material for the preparation of mesoporous carbon chromatographic columns for Solid Phase Extraction (SPE) which [3, 4], in turn, allows the determination of high-value natural products present in the same fruits or their wastes, as is the case of flavonoids present in Brazilian samples, very well-known for its antioxidant properties. This new circular approach constitutes a real opportunity to bring together the Green Analytical Chemistry [5] and an integrated web of systems that use biological resources, maximize value creation and, as far as possible, work in close conjunction in terms of raw materials, water, by-products and energy.

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Sustainable Carbon Materials and Chemicals from Biomass Hydrothermal Processes

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Keywords: hydrothermal carbonization, porous carbon, levulinic acid, energy storage, heterogeneous catalysis

The creation of new and very importantly greener industries and new sustainable pathways are crucial to create a world in which energy use needs not be limited and where usable energy can be produced and stored wherever it is needed.

New materials based on carbon, ideally produced via inexpensive, low energy consumption methods, using renewable resources as precursors, with flexible morphologies, pore structures and functionalities, are increasingly viewed as ideal candidates to fulfil these goals. The resulting materials should be a feasible solution for the efficient storage of energy and gases.

Hydrothermal carbonization [1] is an ideal technology for the production of such low-cost but highly performing materials out of the most abundant renewable resource on the planet, i.e. lignocellulosic biomass. The practical approach is very simple and consists in placing a biomass precursor inside an autoclave, in water, followed by hydrothermal treatment overnight at 160-200°C. Since the production of carbon materials in general implies harsher and multi-step methodologies, this process has clear advantages, being greener, economical, mild and fast.

Here, I wish to present some of our latest results on the production and characterization of nanostructured hydrothermal carbons and their use in renewable energy related applications, [2], [3] as well as heterogeneous catalysts to convert levulinic acid to levulinate esters [4].

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Valorization of agro-industrial waste through its utilization as adsorbents for pollutants removal.

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Keywords: Adsorbent, agro-industrial waste, adsorption.

The environmental Mexican legislations become stricter and it is necessary to develop methods more efficient, and economic. In Mexico, high quantities of agro-wastes are generated annually that are not used by local industrial. Due to their high availability and physical-chemical properties, these wastes can be considered as a feasible alternative to generate new environmentally friendly, and low cost adsorbents to remove pollutants from wastewater.

In this research, three different types of adsorbents were used to remove inorganic or organic pollutants from aqueous solution: a) raw agro-industrial wastes b) chemically modified agro-industrial wastes and c) Activated carbon obtained from agro-industrial wastes. Spent coffee ground and barley husk were used as raw materials to develop new adsorbents, and the removal of phenol and heavy metal from aqueous solution were studied. To understand the adsorption mechanism, the characterization of adsorbents, batch adsorption kinetic and, adsorption-desorption were carried out. The functional groups on modified and non-modified adsorbents were identified and quantified by attenuated total reflection Fourier transform infrared analyses and potentiometric titrations. Ion exchange between protons of carboxylic groups (bound to the modified spent coffee grounds) and heavy-metal cations are suggested as the most probable adsorption mechanism. By other hand, the adsorption of phenol onto barley husk activated carbon at pH<5 occurs by an electron donor-acceptor complex formation at the carbon surface. This complex was formed by the interactions between the oxygen of carbonyl group (electron donor) on the carbon surface and the aromatic ring of phenol (electron acceptor). The adsorption capacities obtained with these types of adsorbents were comparable and in some cases higher than adsorption capacities of commercially available adsorbents.

In this study, the technical feasibility to use agro-industrial waste as adsorbents for removing pollutants from aqueous solution was demonstrated with phenol for carbonyl oxygen sites, where the adsorption occurs by an electron donor-acceptor complex formation at the carbon surface

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Chemical Modification of Renewables for Sustainable Chemicals Development

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Keywords: renewables, biopolymer modification, valorisation, synthesis, sophorolipids.

The Faculty of Bioscience Engineering at Ghent University comprises 14 Departments covering many different aspects of the production, downstream processing and application of renewable resources. The faculty employs 100 professors and about 1000 academic staff to carry out fundamental and applied research related to renewable resources and environmental science. The SynBioC group within the Department of Sustainable Organic Chemistry and Technology is working on slight chemical modifications of renewable resources in order to alter the degree of functionalization for the development of new applications.

The European chemical industry pays a lot of attention to shift from fossil to renewable resources in pursuit of sustainability. Renewable molecules with a complex structure are of special interest because their use can drastically reduce the number of synthetic steps (when derived from petrochemical building blocks) required to obtain high value products. Chemical modification of such important building blocks thus directly contributes to the sustainability of the process and the end product.

Specific examples will be discussed in which the chemical modification of renewable resources has led to innovative applications some of which have been applied industrially.

A mobile process has been developed to transform crude palm oil into biodiesel which is now being used on several plantations in Africa to fuel the vehicle fleet on the plantations. The B100 fuel is now in use for five years and has not resulted in any motor problem related to the biodiesel use.

The Castor bean plant (*Euphorbiaceae*) grows in (sub)tropical areas and is now mainly produced in India, China and Brasil. Because it contains toxic components, the oil cannot be used for food purposes. The oil from the castor seeds contains up to 90% of ricinoleic acid, a unique unsaturated hydroxylated C18-fatty acid. This fatty acid can be converted into other derivatives such as sebacic acid



and 10-undecenoic acid. Undecenoic acid has been elaborated to a multifunctionalized C22-building block (acyloin) which is being developed as renewable crosslinker for the polymer industry. The acrylated monomer shows good radical polymerization properties, resulting in a hard glassy compound with thermoset-like properties.

Other examples will illustrate the use of modified chitosan and modified sphorolipids. Chitosan, the biopolymer prepared from crustaceae waste, has been chemically modified and its fungicidal and insecticidal properties have been studied. The modified polymers show promising activity against *Spodoptera littoralis* as a pest insect and show a 10 fold increased fungicidal activity compared to unmodified chitosan. The valorization of chitosan from food waste rest streams is interesting and can be developed in a limited number of chemical steps.

Synthesis of Unsaturated Benzolactone and Kairomone from Anarcadic Acid.

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In search for functional materials and chemicals from renewable resource, cashew nut shells wastes have proved to be among the most versatile bio-based renewables. Cashew nut shells which are agro-waste of cashew nut processing factories, produce cashew nut shell liquid (CNSL). For solvent extracted method CNSL is up to about 30-35 wt.% and the liquid is comprised of anarcadic acid, cardanol, cardol and methyl cardol. The liquid offers interesting opportunities for the production of speciality chemicals, nanomaterials, high value products and polymers. Our recent research has shown that constituents of CNSL can be transformed into speciality chemicals including kairomone and polymers. This will highlight on these product with particular interest on the synthesis of crystalline unsaturated lactone, 8-hydroxy-3-tridecyl-1H-isochromen-1-one by isomerization of heterogeneous anarcadic acid, a component of CNSL. The hydrogenation of 8-hydroxy-3-tridecyl-1H-isochromen-1-one produced a saturated lactone, 8-hydroxy-3-tridecyl-3,4-dihydroisochromen-1-one. We also report on the isomerization of monoene anarcadic acid to crystalline isoanarcadic acid, (E)-2-hydroxy-6-(pentadec-1-enyl)benzoic acid as a major product and a desired isomer for synthesis of a kairomone, 3-propyl phenol or a monomer for polymerisation, 3-hydroxystyrene. Both isomerization reactions were achieved using 1,2 Bis(ditertiarybutylphosphinomethyl)benzene modified palladium catalyst. Other functional materials prepared from cashew nut shell liquid will also be highlighted.

Sustainable natural aroma chemical production by biotechnology

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Keywords: biotechnology, natural, aroma chemical, biological synthesis.

Traditionally aroma chemicals for use in the flavour and fragrance industry are produced either by chemical syntheses, or by extractive methods from plant material sources (typically essential oils), yielding synthetic and natural aroma chemicals respectively. Although the bulk of flavouring materials used world wide are still of the synthetic kind, which includes the definition "nature identical" for aroma compounds manufactured by classical chemical routes that have the exact same chemical structure as their natural counterparts, there is a growing market demand for natural flavouring substances¹. However, production of natural aroma chemicals from agricultural sources is not always sustainable, environmentally friendly, or even possible on a large scale. Low product yields, food security considerations, climate change, agricultural practices, political instabilities, labour issues and rising energy costs often severely impact production of aromatic materials from agricultural sources, especially in cases where the desired product cannot be obtained from an agricultural product processing waste stream.

Due to the above-mentioned factors, and the fact that EU and FDA (US) food legislation classifies microbiologically or enzymatically derived aroma compounds as natural, the flavour and fragrance industry has in recent years seen a definite shift towards sustainable and large scale natural aroma chemical production with biotechnological methods. These are currently termed as "cultured" or "synthetic biology" products².

Aroma chemical production by biotechnological means is by no means a new concept. Processes for the manufacture of aroma compounds have often inadvertently taken place for millennia in many traditional food preparation processes. Think of mould cheese production with various *Penicillium* fungi, or the production of Soy sauce with *Aspergillus oryzae*/ *Saccharomyces rouxii* and various lactobacilli, to name but a few. Substances present in the raw material (e.g. milk fat, soy protein) are typically partially converted into a range of aroma active components (e.g. methyl ketones, furanones/mercaptans) by enzymatic processes. The same principle applies when micro-organisms or isolated enzymes are employed for the production of aroma chemicals. The only



difference being that the required product formation is specifically targeted and optimized to maximize yields, and is not just incidental to the food preparation process³.

An important added benefit to the use of biotech methods for natural food flavouring production is that the over-all carbon footprint is in most cases but a fraction of what it is when traditional extractive methods from dedicated agricultural sources are employed.

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Building your business on Biobased Chemicals

Head of Corporate Sustainability, Prof. Dr. Claus Stig Pedersen

Corporate Sustainability, Novozymes A/S, Denmark, e-mail: clsp@novozymes.com

Keywords: Novozymes, Enzymes, Business building, Sustainability.

Novozymes is the world largest manufacturer of enzymes and microbes for industrial appliances. Annual turnover approximately 2 Bn USD, headquartered in Denmark and more than 6000 employees globally. Claus Stig Pedersen is leading sustainability globally for the Group and will share how sustainability and Green Chemistry perspectives increasingly are becoming an integrated element of how the company operates and grow its business. Sustainability and Green Chemistry perspectives are integrated in sourcing, R&D, production, sales, marketing, public affairs, communication, investor relations, corporate and employer branding. See www.novozymes.com for more information.

Tuesday 26 August

Venue: Think Tank

Organocatalysis, a precious metal free approach to reaction discovery.

David W. Lupton

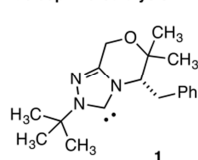
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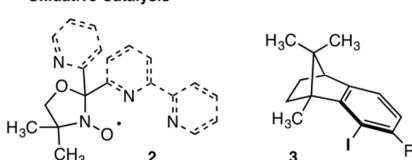
Keywords: organocatalysis, *N*-heterocyclic carbene, hypervalent iodine, nitroxide, chemical synthesis.

Catalysis can play a central role in allowing chemical synthesis to be achieved in a sustainable fashion.¹ While discoveries in precious metal homogeneous catalysis have enabled new transformations, this creates potential problems with the depletion of valuable elements. To address this challenge organocatalysis can replace existing technologies, and fuel new reaction discoveries. In this presentation I will focus on our recent studies in organocatalysis which have examined nucleophilic catalysts (such as **1**)² and oxidation catalysts (such as **2** and **3**),³ to enable chemical synthesis.

Nucleophilic Catalysis



Oxidative Catalysis



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Recyclable organocatalysts for asymmetric synthesis

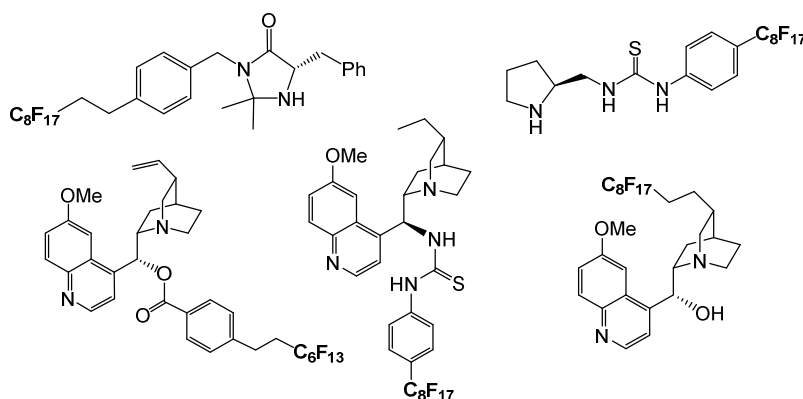
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Keywords: organocatalysis, asymmetric synthesis, fluorination, one-pot reaction, green synthesis

Organocatalysis has advantages of toxic heavy metal-free, mild reaction condition, novel mode of activation, and good structural amenability. It is a green technology for asymmetric synthesis. However, organocatalysis requires high catalyst loading and separation of organocatalysts is not an easy task. The development of fluorinated organocatalysts provides an efficient way to address the issue.¹ In addition to phase-tag separation,² the stereoelectronic effect of the fluorinated chain can be used to modify the reactivity and selectivity of the catalysts. This presentation highlights our recent effort on the development of fluorinated organocatalysts for asymmetric synthesis including Diels-Alder reaction,³ α -chlorination of aldehydes,⁴ fluorination,⁵ Michael addition,⁶ Robinson annulation,⁷ and one-pot synthesis of multiple chiral centers.



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Tailoring Solid Acid Catalysts for Biomass Conversion

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Keywords: Solid acid, Green Chemistry, Lignocellulose, Biodiesel, Platform Chemicals.

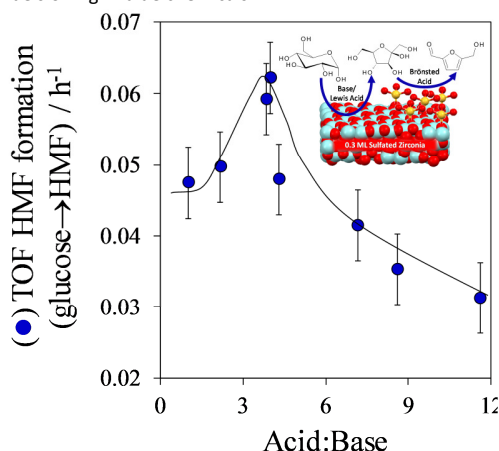
Concerns over dwindling oil reserves and CO₂ emissions coupled with associated climate change is driving the urgent need for clean, renewable supplies of fuels and chemical feedstocks. Biomass, derived from waste materials or non-food crops, offers the most



UCT Chemistry



easily implemented and low cost solution for transportation fuels, and the only non-petroleum route to organic molecules for the manufacture of bulk, fine and speciality chemicals necessary to secure the future needs of society.¹ However, to facilitate such a transition requires innovations in catalyst and process design for the selective conversion of these hydrophilic, bulky feedstocks into fuels or high-value chemicals.



This presentation will highlight how the activity and selectivity of solid acid catalysts for biomass conversion can be tailored by tuning the hydrophobicity, acid strength or pore architecture. Case studies will demonstrate how increased hydrophobicity in sulfonic acid functionalised silicas can be readily achieved by co-derivatisation with inert octyl groups and is found to impart a striking enhancement in both acid strength and turnover frequency in esterification reactions.ⁱⁱ The effects of pore architecture and acid strength will also be illustrated for free fatty acid esterification in biodiesel synthesis^{iii,v} and terpene isomerisation.^{iv} The role of bi-functional catalysts with tuneable acid-base properties will finally be demonstrated in the conversion of glucose to the important platform chemicals 5-HMF and levulinic acid. Bi-functional catalysts based upon zirconia doped with sub-monolayer SO₄ coverages are found to offer the ideal balance of basic and Lewis/Brønsted acid sites required to respectively isomerise glucose to fructose, and subsequently dehydrate fructose to 5-HMF (Figure 1). Such bi-functional catalysts capable of effecting one-pot telescopic syntheses in aqueous media will become increasingly critical to achieve atom-economical, selective transformations of bio-derived molecules for sustainable chemicals and fuels.

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Introduction of the Key Laboratory of Green Chemistry and Technology (MOE of China) in Sichuan University

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Keywords: green chemistry, technology, laboratory.

Green chemistry embodies the concept of sustainability. With the spring up of green chemistry in the world, a Cross-Discipline Center of Green Chemistry and Technology was founded in Sichuan University in 1998. It developed into the Key Laboratory of Green Chemistry and Technology in Sichuan province in 2001, and then the Key Laboratory of Green Chemistry and Technology in Ministry of Education of China in 2003. It is one of the pioneer laboratories aiming at the development of principles and technology of green chemistry in China.

The research work carried out in the key laboratory is focused on the greening of starting material, the greening of chemical reaction process, and the greening of target product. The main research areas include the following:

- 1) Methodology of green synthesis. It deals with the construction of chemical methodology that stresses the sole product and increases the atom economy of the chemical reaction. It develops versatile catalysts system for the asymmetric synthesis. It develops novel organic functional materials for the direct functionalization of aromatic heterocyclic C-H bonds.
- 2) Biological catalysis and biomimetic catalysis. It develops novel hydrolytic enzyme systems for specific, nonspecific, and corresponding cascade reactions.
- 3) Catalytic transformation of biomass. It focuses on the use of benign, recyclable and renewable biomass-based raw materials (including monomers such as fructose, glucose, fatty acids; components of raw biomass materials such as cellulose, hemicellulose, lignin; and raw biomass such as pubescen, algae etc.) to synthesize fine chemicals.



4) Chemistry and technology for green process. It deals with the engineering aspects and/or industrial application of the basic achievements in green chemistry and technology.

During the past five years, 818 papers have been published in SCI cited journals, and 47 patents have been authorized.

From Plants to polysaccharides: Green technologies for Elemental Recovery and Sustainability

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Keywords: Porous materials, phytoremediation, elemental recovery, separation, sustainability.

Over the last several years there has been a growing awareness of the criticality of elements we utilize in chemical products and also consumer goods. The reserves of these elements are depleting at a rapid rate and are being quickly dispersed throughout our environment [1]. Many of these important unique elements have low recycling rates and recapture is both challenging and costly. As such, it is essential to develop new sustainable routes for the use and recovery of these elements [1,2]. Herein, two such routes highlight the importance of adopting a sustainable, holistic and multi-disciplinary approach to the recovery of all elements.

Recently it has been demonstrated that plants can accumulate metals in nanoparticulate forms through phytoextraction [3]. We demonstrate the use of plants to recover metals and their transformation into supported metal nanoparticle based catalysts, for use in a wide range of applications [4]. The effective production of such materials by plants could open new doors in catalyst development and present solutions to critical element availability.

Polysaccharides including starch are non-toxic, biodegradable, possess polyfunctionality and are found in nearly every geographical location on the planet. The development of tunable, nano-structured and mesoporous carbon monoliths derived from waste polysaccharides will open new doors to adsorbents. The surface chemistry, functionality and surface polarity of these materials can be controlled through varying the temperature of preparation, thus making them ideally suited for the recovery of a wide variety of elements. These materials have been demonstrated to not only adsorb metals but also offer an effective method for separation and selective elemental recovery.

Acknowledgments

The authors would like to acknowledge the G8 Research Councils Initiative on Multilateral Research Funding and the EPSRC for their financial contribution.

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Immobilization of Platinum Group Metal (PGM) Catalysts: Applications in Green Catalysis

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Keywords: biopolymers, dendrimers, synthesis, catalysis, hydroformylation.

The immobilization of transition metal catalysts has been well-explored in an attempt to recover and reuse expensive and diminishing available resources. Amongst the approaches employed in efforts to address this problem is the immobilization of homogeneous catalysts on solid supports such as polymers, dendritic scaffolds, metal oxides and mesoporous materials.[1] This practice has also seen a concomitant increase in activity and selectivity of the metal catalysts.

In recent years, researchers have looked to biopolymers such as chitosan to immobilize transition metal catalysts due to its appealing abundance in nature, renewability, biodegradability and non-toxicity. [2] This material has shown encouraging potential as a solid supported for the immobilization of transition metal catalysts owing to its affinity for metal ions and high thermal stability. In addition, dendritic catalysts which constitute a class of well-defined hyperbranched polymers, maintain high activity and selectivity and in certain cases, can be separated from reaction mixtures by nano- or ultrafiltration. The immobilisation of transition metal catalysts on dendritic supports offers several advantages in that they facilitate recycling of the catalysts to avoid environmental toxicity and makes purification of products easier. It is for this very reason that they are considered to be at the interface between homogeneous and heterogeneous catalysis.

A strategy to replace expensive and potentially harmful organic solvents with less noxious media such as water has also emerged as a viable alternative to immobilise catalysts. Water is widely regarded as an environmentally safe solvent, being nontoxic, readily available, stable and easy to handle.[3] Aqueous biphasic catalysis therefore combines the advantages of homogeneous and heterogeneous catalysis consisting of an aqueous phase in which the catalyst is dissolved, and the organic phase containing the substrate. At the end of the reaction the organic phase containing the products can be decanted from the immobilized aqueous catalyst, which can then be recycled into further catalytic reactions.

This presentation will highlight the use of biopolymers and dendrimers as scaffolds for homogeneous catalysts. Particular attention will be given to their synthesis, coordination chemistry and structure. In addition, this overview will focus on selected catalytic data illustrating the activity of the complexes in aqueous Green Chemistry.

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A progress report on a roadmap for Green Chemistry Education

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Keywords: green chemistry, education, roadmap, university

The mission of the ACS Green Chemistry Institute® (ACS GCI) is to catalyze and enable the implementation of green chemistry and engineering throughout the global chemical enterprise. This includes advocating for progress in green chemistry education and communication. We believe that there needs to be a new way of thinking about chemistry education that helps prepare students to implement new approaches to chemistry and that lead to a more sustainable world. But how far down the road are we to incorporating ideas about more sustainable and greener chemistry into chemistry education today? In 2005, the National Academies hosted a workshop to discuss the tools available for teaching green chemistry, barriers to implementation in the curriculum, and the degree of incorporation of green chemistry principles into chemistry education. Over the past year, the ACS GCI conducted an independent analysis of the progress made in these areas since the 2005 workshop. This presentation will describe progress and the current state of green chemistry education in the US.

Wealth from Waste through Indian Green Chemistry Network Centre : Real World Cases

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Keywords: green chemistry, wealth, waste, real world cases.

Green Chemistry Network Centre (GCNC), established under the recommendation of a panel of world leaders headed by Professor Paul Anastas (known as father of Green Chemistry) is working in India for sustainable and socio-economic solutions for the problems associated with the generated waste. The presentation will describe a case study related to industry, which has been identified as the biggest metal pollutant across the country by Department of Environment, Government of India. It will also focus on various pioneering achievements and contributions of GCNC via exploration of innovative and socially accepted approaches using green chemistry principles. Few real world cases and successful implementation of a newly designed reactor for large scale, online, efficient and fast extraction of heavy metals from various environmental wastes using chelating polymer will also be discussed. The Green Chemistry Network Centre is involved in educating industries and chemists by sharing best practice, promoting green technology transfer and providing data to show that adoption of Green Chemistry can provide cost benefits for industry. The presentation shall also include a real world case of Indian Pharmaceutical Industry, which proves that the Industries have to adopt Green Chemistry because, it will not be only beneficial for the society and the environment, but will make companies economically competitive

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CO₂ related chemistry

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Keywords: carbon dioxide, cyclic carbonate, sustainable catalysis, halide-free, green solvent.

Carbon dioxide is a cheap, abundant and non-toxic sustainable carbon source for chemical industries. Therefore, the development of new catalytic processes that use carbon dioxide as feedstock has generated great attention in recent years [1]. Among these processes, the reaction of epoxides **1** and carbon dioxide can afford either polycarbonates **2** or cyclic carbonates **3** and is a 100% atom-economic transformation (Scheme 1). Cyclic carbonates are the thermodynamic product of the reaction and have many applications including as electrolytes for lithium ion batteries, solvents and chemical intermediates [2].

Scheme 1: Synthesis of poly- and cyclic carbonates.

The reactions shown in Scheme 1 do not occur spontaneously and require the use of a catalyst. In this lecture, the development of a bimetallic aluminium(salen) complex and Bu₄NBr as a catalyst system for the synthesis of cyclic carbonates at room temperature and pressure will be described. Recent kinetic studies on the synthesis of glycerol carbonate at temperatures of 25-100 °C, carbon dioxide pressures of 1-100 bar and catalyst loadings of 0.1-2.5 mol% have shown that there is an optimal carbon dioxide pressure (50 bar) for the reaction. Under these conditions, the bimetallic aluminium(salen) complex is catalytically active in the absence of a cocatalyst. To demonstrate the utility of this process, eight cyclic carbonates have been prepared from terminal epoxides and carbon dioxide under solvent free conditions. The importance of these results is that they simplify the catalyst system and avoid the cost, corrosion and purification issues associated with the use of ammonium halide or basic cocatalysts.

Cyclic carbonates make excellent polar aprotic solvents with the potential to replace nitrogen and sulfur containing solvents such as DMF, NMP and DMSO. The use of ethylene and propylene carbonate as solvents for proline catalysed, asymmetric aldol reactions will be presented, including the use of enantiomerically pure propylene carbonate as a chiral solvent.

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Posters

A multi-level perspective on solvent substitution: A case study on biocatalysis in the pharmaceutical industry

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Keywords: Solvent, bio-based, enzymatic catalysis, sustainability.

Solvents are ubiquitous with industrial chemical manufacture and the majority of materials input for chemical synthesis are associated with the solvent used within the reaction. With climate change and peak oil crises making headlines with increasing intensity over the past decade, solutions are being sought to lessen our dependence on oil. Unfortunately, there is a serious problem! The vast majority of solvents still used worldwide today are derived from petrochemical sources. Using renewable solvents derived from biomass, which do not compete with food applications, go a long way towards satisfying both consumer and legislative demands with regards to sustainability. As nation's move towards a more bio-derived focused manufacturing base and further legislation is developed, the opportunities for new and bio-derived solvents are only expected to increase.

Replacing conventional process solvents, many of which are increasingly targeted by chemicals regulation [1], with a greener bio-based alternative is a complex issue. The decision impacts on both upstream and downstream businesses, and faces different drivers and barriers at different levels of the firm's decision-tree.

A holistic approach to solvent substitution is herein presented and applied to the use of organic solvents in enzymatic catalysed esterifications [2]. This is pursued through four phases that develop from reaction and process chemistry to management and behavioural analysis.

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Acetals: A New Masked Chemotype for Carbonyl Enantioselective α -Amination

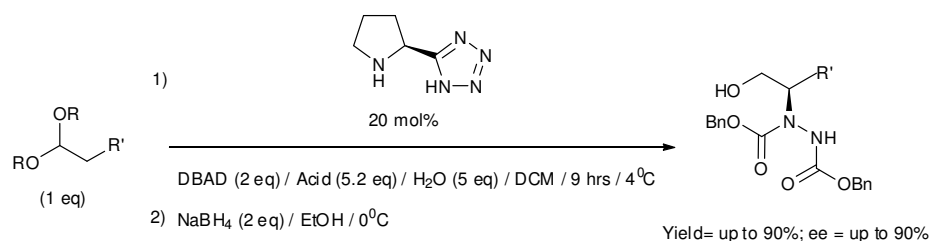
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Keywords: organocatalysis, acetals, α -amination.

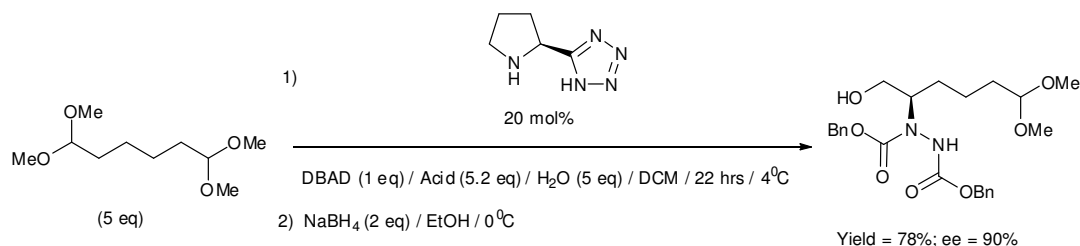
Research into organocatalysed asymmetric reactions has been a rapidly growing and competitive field in recent times, wherein aminocatalysis is widely used for the asymmetric functionalization of carbonyl compounds.¹ Since its simultaneous publication by List² and Jorgensen,^{3,4} the organocatalysed α -amination reaction has become a key method for asymmetric heteroatom functionalization of carbonyl compounds.⁵ Herein we report the first application of this methodology to acetals.

Following extensive optimisation, acidic reaction conditions for the reaction were established as shown in Scheme 1, in which dibenzyl azodicarboxylate (DBAD) was used as the aminating agent and (S)-(-)-5-(2-pyrrolidinyl)-1H-tetrazole as the preferred organocatalyst. The desired aminated products were obtained in high yields and enantioselectivities.



Scheme 1: α -Amination reaction of an acetal.

The above reaction can also be used for the chemoselective amination of a diacetal (Scheme 2), a feat not achieved with the more reactive dicarbonyl analogue.



Scheme 2: Chemo- and stereoselective amination of a diacetal.

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Influence of textural properties of Starbons® on adsorption of polycyclic aromatic hydrocarbons

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Keywords: mesoporous, Starbon, adsorption

Potential applications of the new class of carbonaceous porous materials, Starbons®, developed in the Green Chemistry Centre of Excellence of University of York, have been growing, and include water treatment, catalysis and solid phase extractions. The material is produced from renewable and widely available polysaccharides, such as starch, alginic acid and pectin obtainable from agricultural and food industry wastes, and through process optimization the large-scale route to these materials is becoming solvent and energy efficient, and therefore more economically viable.

The characteristic trait of Starbons® is their mesoporosity, greater pore volume and tunability (through carbonization temperature) of the surface chemistry corresponding to faster adsorption diffusion rates and potential for selective adsorption. Since physical adsorption is reversible and is in equilibrium with desorption, greater pore volume also offers increased desorption diffusion rate. Chemical contamination of water is a growing concern due to the negative environmental impact of chemicals and deterioration of water quality leading to demanding purification, activated carbons dominate the market of adsorbents for water treatment. Previously, mesoporous Starbons® showed an advantage over microporous activated carbons in adsorption of textile dyes and this superior performance was attributed to mesoporosity.[2] In this work, a range of Starbons® (Table 1) was tested for adsorption of a range of common industrial organic pollutants (phenolics and polycyclic aromatic hydrocarbons) in order to establish a link between textural properties (surface area, pore volume, pore size) and adsorption isotherms, kinetics and thermodynamics. A number of interesting trends and correlations were observed that shed light on the mechanism of adsorption of given pollutants on Starbons®. This information would help in choosing Starbons® with appropriate textural properties for adsorption of given chemical pollutants.

Table 1. Physical properties of Starbons® and a representative activated carbon

Material	BET Surface Area, m ² /g	Mesopore volume, cm ³ /g	Micropore volume, cm ³ /g	Average pore diameter, nm
Activated carbon	921	0.12	0.40	4.5
1_Starbon®, 800 °C	565	1.72	0.17	13.9
2_Starbon®, 800 °C	565	1.46	0.16	23.5
3_Starbon®, 800 °C	428	0.86	0.11	22.9

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A new OPEC- Orange Peel Exploitation Company

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Keywords: waste, orange peel, valorisation, biorefinery, microwave.

Food supply chain waste (FSCW) has appreciable potential as a resource for the production of marketable chemicals.¹ By volume, citrus peel represents an important type of FSCW around the globe, with at least 40% of orange fruit being grown for processing. It has been estimated that just under 10 million metric tonnes of waste orange peel were produced for the 2012/2013 harvesting season, as a by-product of the juicing operations, by the world's top five producers of orange fruits (i.e. Brazil, U.S.A., the E.U., China and Mexico).² The main challenge to its implementation as a biorefinery feedstock is in the development of an efficient process allowing for the recovery of a maximum number of valuable components from waste citrus peel.³ Ideally the process should be integrated, avoid any pre-treatment steps, limit/avoid the use of acid or additives and employ predominantly food grade solvents.

An acid-free microwave-assisted hydrothermal process was developed to recover both *D*-limonene and pectin from the waste citrus peels. In addition, the process also allows for the recovery of some highly valuable polymethoxylated flavonoids, hesperidin and fermentable sugars. A range of parameters such as the water/peel ratio, temperature (100-140 °C) were optimized and also the influence of the microwave power density was investigated. The obtained yields of *D*-limonene and pectin are respectively between 1-1.5% and 5-20% depending on the operational conditions used. Both these products meet the standard industrial specifications. The microwave-extracted pectin was found to gel at pH 2 using a 70 wt% sucrose solution. Its molecular weight was found to be comparable to pectin extracted using classic HCl-mediated hydrolysis (251,917 vs. 232,250 respectively). The polydispersity is ~1.68 which is higher than the one of pectin obtained by acid hydrolysis (1.17). All chemicals have been characterised using ¹H and ¹³C NMR, ESI, HPLC-MS and/or ATR-IR. The process demonstrates the use of a scalable technology for the recovery of marketable chemical compounds achieving a key milestone for the implementation in industry of the clean conversion of FSCW for the production of chemicals, materials and fuels.

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Direct Synthesis of Pd Nanoparticles on Alginic Acid & Seaweed Supports

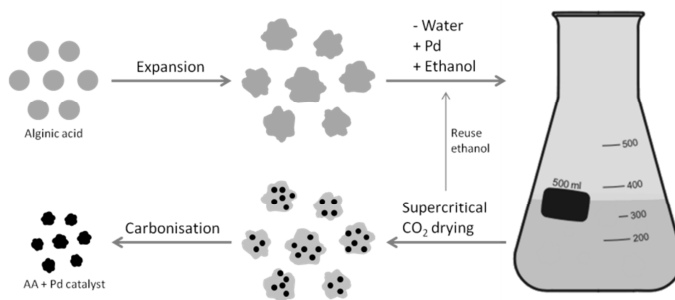
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Keywords: elemental sustainability, catalysis, Heck reactions.

Biosorption is a popular alternative to existing methods of metal recovery, for example, hydrometallurgical and chemical routes.^[1] Compared to these methods biosorption offers many advantages including: high efficiency, low operating costs and minimal waste.^[2] The mechanisms of biosorption are generally based on physio-chemical interactions between the adsorbate metal ions and functional groups of the biomass adsorbent. Functionalities commonly implicated in such interactions are carboxylate, hydroxyl and amine groups.^[3] Alginic acid contains both carbonyl and hydroxyl groups which are excellent for the anchoring of metals.^[4] It is also a highly abundant biomaterial with up to 39,000 tons extracted annually worldwide.^[5] However, this naturally occurring polymer has so far captured very little attention for precious



metal biosorption despite presenting these attractive properties. In this work alginic acid-derived materials are investigated for the adsorption of palladium.

As a result of biosorption of palladium by alginic acid it was noted that palladium nanoparticles (PdNPs) were been formed on the support. Characterisation and subsequent catalytic testing of the materials showed that the supported PdNPs were catalytically active. By varying the heating rate during catalyst preparation, materials with a range of different surface areas and porosities have been produced in order to determine the effect this has on catalytic activity, rate of reaction and palladium leaching. In the interest of sustainable chemistry and the aim of reducing the number of chemical steps required for the production of supported catalyst, the direct impregnation of seaweed with palladium was also investigated. Seaweed consists of approximately 25% alginic acid and therefore if it could be used as a successful catalyst it would eliminate the many steps necessary to extract alginic acid.

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Low temperature synthesis of multiwalled carbon nanotubes

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Keywords: low temperature, synthesis, Non-equilibrium PECVD, green, nanoparticles.

Solar energy is one of the most useful renewable and green energy resource. In solar energy, the photovoltaic effect converts light to electrical energy. The organic solar cells (OSC) provide solar-to-electric energy conversion in portable, light-weight packages, at extremely low cost and environmentally friendly way. Multiwalled carbon nanotubes (MWCNTs) have great potential in solar cells. Most methods often involved in MWCNTs synthesis often violate green chemistry principles.

MWCNTs are typically synthesised by several methods such as laser ablation and various types of chemical vapour deposition (CVD). The floating catalyst CVD is the most commonly used synthetic method. In this method several solvents are involved in catalyst synthesis, purification and in dissolving the catalyst prior to injection into the reactor during MWCNTs synthesis. Furthermore, the method employs very high temperatures, 500-1100 °C [1] which go against "green chemistry" principles. In this work we describe our recent efforts to produce MWCNTs using a tailor made non-equilibrium plasma enhanced chemical vapour deposition (PECVD) technique. In this method a lower temperature of 200 °C was employed in the production of MWCNTs. Such low temperatures enables easy deposition of MWCNTs onto various substrates such as indium tin oxide (ITO) with minimum use of solvents.

Nanoparticles used in the synthesis of MWCNTs and as-synthesised MWCNTs were characterised using scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX) and Raman spectroscopy. Mono-dispersed nanoparticles with dimensions between 1-10 nm were synthesized and used in MWCNTs synthesis. Typical hollow tubular structures of MWCNTs were observed using TEM. These observations correlated morphology from SEM which showed the absence of amorphous carbon. Raman spectroscopy showed typical MWCNTs bands, G band and D band due to graphitic carbon vibrations and defects respectively. Non equilibrium PECVD, a "greener synthetic method," was used to produce MWCNTs using LPG and Acetylene.

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Green chemistry approach towards sustainable energy

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Keywords: dye sensitized solar cells, sol-gel, chemical vapour deposition, green, carbon nanotubes, titania.

The use of fossil fuels is causing various forms adversity to the environment such as air pollution from the release of NO_x, CO and SO₂, and water pollution. In this study dye sensitized solar cells (DSSCs), a green chemistry approach towards energy production, that incorporate titanium dioxide and multi-walled carbon nanotubes (MWCNTs) were designed. The immediate attribute is the fact that solar energy is renewable and that metal-free natural dyes are substituting the well documented ruthenium-based dyes. Solar energy has no gas emissions or health-related hazards associated with its harvesting and use.

The work takes advantage of the bridging ability of nanotechnology between macro molecules and solid state in solving potential energy crises in a "greener approach." MWCNT-titania nanocomposites were synthesized from titania precursors and acid-treated MWCNTs by means of two synthetic methods, namely, sol-gel and chemical vapour deposition (CVD). The CVD method, greener approach, involves less use of solvents because MWCNTs and a titanium precursor are simply mixed *via* grinding and then loaded into a reactor. Physical and chemical properties of the mesoporous composites were investigated using Raman spectroscopy, thermo-gravimetric analysis, Fourier transformation infra-red spectroscopy, scanning electron microscopy, transmission electron microscopy, textural characteristics, inductively coupled plasma-optical emission spectroscopy and X-ray diffraction analysis.

A gel state electrolyte employing polyvinyl acetate that inhibits I₃⁻/I⁻ liquid electrolyte system from drying was successfully synthesized [1]. DSSC devices were fabricated using doctor's blade method to deposit nanocomposites slurry on ITO glass, sintering, dipping in eosin B, electrolyte addition and aluminium coated on ITO glass was used as counter electrode. A solar simulator was used in voltage-current characterization of the PV devices. MWCNTs in nanocomposites by the CVD method had fewer defects, highly thermally stable and more uniformly coated, more crystalline, more porous, had smaller surface areas and were 90 % more efficient than sol-gel prepared. The work suggest that green chemistry approaches can be applied in material synthesis for greener energy production.

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Effectiveness of cobalt ferrite/doped carbon nanotubes for the adsorption of rhodamine B from aqueous solutions

Oluwaseun A. Oyetade, Vincent O. Nyamori, Bice S. Martincigh and Sreekanth B. Jonnalagadda

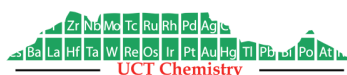
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Keywords: multiwalled carbon nanotubes, cobalt ferrite nanoparticles, adsorption, remediation, rhodamine B.

The efficiency of cobalt ferrite (CoFe₂O₄) nanoparticles, acid-functionalized multiwalled carbon nanotubes, (MWCNT-COOH) and carbon nanotube - cobalt ferrite nanocomposites (CNT-CoFe₂O₄) for the removal of the dye, rhodamine B (RhB) by adsorption, from simulated aqueous solutions was investigated by carrying out a series of batch adsorption experiments. The adsorption capacity and percentage efficiency were evaluated at varying pH conditions, contact times, adsorbent doses, initial dye concentrations and temperatures. The effect of increasing the percentage of MWCNT-COOH in the nanocomposites was also studied.

The adsorption capacity was lowest in CoFe₂O₄ (5.12 mg g⁻¹), and highest with MWCNT-COOH (42.68 mg g⁻¹). For the nanocomposites, an increase in adsorption capacity was obtained with increase in the amount of MWCNT-COOH. The adsorption was pH dependent, and an increase in the removal efficiency was noticed as the pH of the solution was increased. The optimum pH was obtained at 7 and equilibrium was reached after 360 min for all adsorbents used in this study. Adsorption efficiency increased and tends towards 100 % as the dose of the adsorbent was increased from 30 mg to 400 mg. The kinetics of adsorption was fitted to the pseudo-first order, pseudo-second order, Elovich, and intraparticle diffusion models. The pseudo-second order model best described the kinetics data showing the lowest values for the sum of squared residuals.

Among the various adsorption isotherms tested, the Langmuir isotherm provided the best fit to the equilibrium data obtained. The thermodynamic parameters, ΔH°, ΔS° and ΔG°, were obtained over a temperature range of 20 °C – 45 °C. The thermodynamic studies showed that adsorption was spontaneous, endothermic and entropy-driven, except for one of the doped nanocomposites for which adsorption was exothermic. A good desorption of RhB from the loaded adsorbents was obtained using either acetone or ethanol with a desorption efficiency in the range of 62 – 95%.



The adsorbents used in this study proved to be good materials for the remediation of wastewater polluted with the dye, rhodamine B. They were also recyclable without much loss of activity.

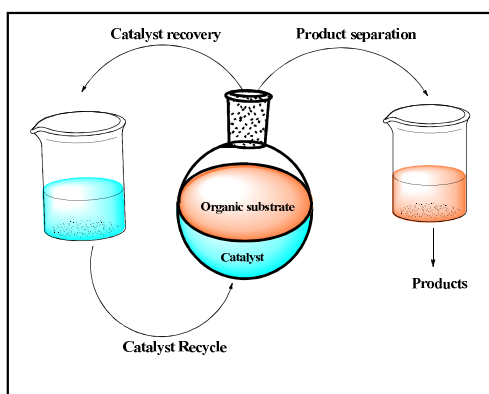
Water as a green solvent for aqueous biphasic catalytic transformations using Rh(I) catalysts precursors

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Keywords: Water-soluble, Recycle, Green Chemistry, Aqueous Biphasic.

Homogeneous catalysts are usually preferred due to their high activity and selectivity since they remain in the same phase as the substrate¹. However, it often requires tedious procedures to separate the catalysts from the products²⁻³. Heterogeneous catalysts can be easily separated from the products but these do not usually have excellent activity and selectivity as compared to homogeneous catalysts. There is therefore a need to bridge the gap between homogeneous and heterogeneous catalysis. Developing aqueous biphasic systems can be a key because it enables easy separation whilst the catalyst remains 'heterogenised' with respect to the organic products. This is in line with some of the principles of Green Chemistry which encourage reuse of resources and the use of water which is non-toxic, odourless and readily available in good quality. The design of hydrophilic ligands with suitable electronic and steric properties is vital in achieving highly active water-soluble complexes for aqueous biphasic hydroformylation.



Herein, we describe the synthesis and characterisation of sulfonated water-soluble *N,O*-chelating ligands and a series of water-soluble Rh(I) complexes. Results from the aqueous biphasic hydroformylation of 1-octene will be presented. Recovery and recyclability of these catalysts will also be presented.

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Fluorous Biphasic Rh(I) Catalyst Precursors for the Hydroformylation of Higher Olefins

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Keywords: biphasic, hydroformylation, rhodium, green catalysis.

Hydroformylation has been widely used in industry for the production of aldehydes since its discovery in 1938. The most commonly used catalysts for this reaction are based on Rh complexes due to its high activity and selectivity at milder conditions. However, the practical application of homogeneous hydroformylation systems in industry has been limited by problems associated with separation of the catalyst/product mixture.^{1a-b}

Researchers have looked to fluorous biphasic catalysis (**Figure 1**) which combines the advantages of homogeneous and heterogeneous catalysis. This type of system involves the presence of two phases in one reactor such that at the end of the reaction the organic phase, now containing the products, can be decanted from the immobilized fluorous catalyst, which can then be recycled into further catalytic reactions.^{2a-b}

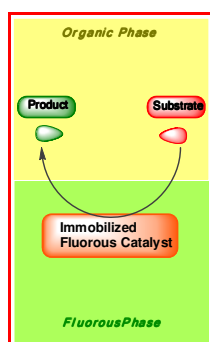


Figure 1. Illustration of fluorous biphasic catalysis.

Herein we report the synthesis and characterization of Rh(I) fluorous catalyst precursors. These systems are then employed in the fluorous biphasic hydroformylation of higher olefins.

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Nitrogen-doped carbon nanotubes as supports for Pd catalysts

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Keywords: catalysis, green chemistry, Pd, N-CNTs

Catalytic reactions uphold the principles of green chemistry by increasing the efficiency of producing chemicals in industries. It is therefore necessary to develop sustainable and selective catalytic systems that optimize the synthesis of industrial chemicals. To accomplish this, an efficient metal catalyst system with a high surface-to-volume ratio, a high degree of particle dispersion and good metal-support interactions, among other properties, is necessary [1].

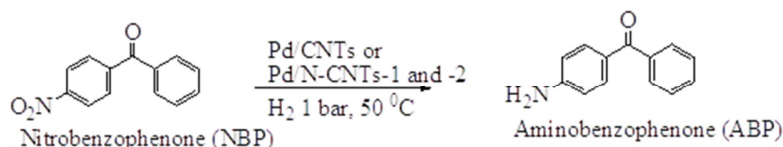
Nitrogen doped carbon nanotubes (N-CNTs) are carbonaceous materials exhibiting the afore-mentioned properties, making them attractive materials for use as metal catalyst supports [2]. Pd catalysts supported on N-CNTs is postulated to show high catalytic activity in diverse reactions. In this study we aimed at synthesizing N-CNTs and applying them as supports for Pd nanoparticle catalysts used in hydrogenation reactions.



Aligned nitrogen-doped carbon nanotubes (N-CNTs) containing 2.5-4.4% of nitrogen were synthesized using chemical vapour deposition (CVD) method and used as supports for Pd nanoparticles. The catalysts were characterized using transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA) and Raman spectroscopy.

From the SEM and TEM images, it was evident that Pd nanoparticles were mainly located along the defect sites of N-CNTs. This implied that the defect sites consisted of electron rich functional groups which enhanced the electronic interaction between Pd nanoparticles and N-CNTs.

The synthesized catalysts were used in the liquid phase hydrogenation of nitrobenzophenone (scheme 1). The catalyst were observed to increase the product yield within a shorter reaction time thus upholding some of the principles of green chemistry.



Scheme1: Hydrogenation of nitrobenzophenone.

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Facile pathway toward bio-based furanic monomers from lignocellulosic biomass via 5-acetoxymethyl-2-furfural (AMF)

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Keywords: lignocellulosic biomass, furanic monomers, 5-acetoxymethyl-2-furfural (AMF), 5-chloromethyl-2-furfural (CMF), alkylammonium acetates

Current issues of energy and environment prompt us to replace fossil-based resources with renewable and sustainable ones. Biomass-derived carbohydrates photosynthesized from atmospheric carbon dioxide attract much attention due to their abundance and availability. Up to now, a large number of efforts have been made to transform biomass-derived carbohydrates into fuels and value-added chemicals.

In this study, the facile pathway to furan-based monomers from lignocellulosic biomass via 5-acetoxymethyl-2-furfural (AMF) was developed. As an alternative to 5-hydroxymethyl-2-furfural (HMF), the most-renowned intermediate of furan-based monomers, AMF offers important advantages for industrial production: good stability, easy handling, non-toxicity, and simple separation/purification. AMF was obtained with an optimized yield of 96% under mild conditions (within 1 hour at room temperature) using 5-chloromethyl-2-furfural (CMF) and alkylammonium acetates, both of which could be converted directly from lignocellulosic biomass. Unlike HMF, hydrophobic and less reactive AMF allowed by simple separation/purification method such as recrystallization and vacuum distillation to afford highly pure product up to 99.9% without a significant loss of yields. Heterogeneous reaction using polymer-supported alkylammonium acetates was also successfully performed to give AMF from CMF in 90% yield, which showed the feasibility for continuous process of this pathway. The resulting AMF could be transformed into various furan-based monomers such as 2,5-furandicarboxylic acid (FDCA, 82%), 2,5-furandimethanol (FDM, 92%), 5-hydroxymethyl-2-furanoic acid (HFA, 38% with 43% of FDM) in high yields..

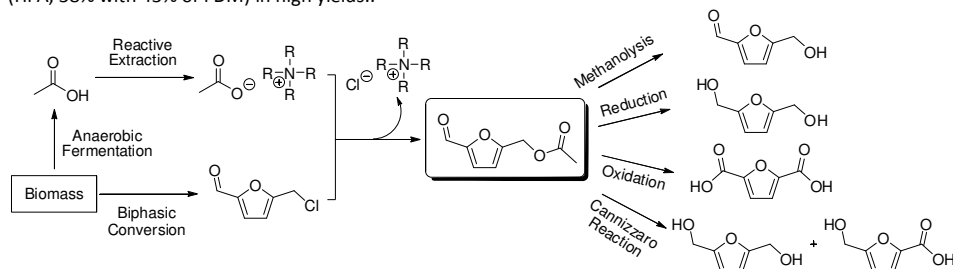


Figure. Pathway toward bio-based furanic monomers from lignocellulosic biomass via 5-acetoxymethylfurfural (AMF).

Catalyst effect on the polymerization of isosorbide-based polycarbonate using various catalysts

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Keywords: isosorbide, biomass, catalyst, isosorbide-based polycarbonate, cesium.

Taking the issues on carbon footprint and depletion of petroleum reservoirs into account, isosorbide is one of the most commercially satisfactory compounds to replace petroleum-based compounds because its starting material, glucose is originated from the most abundant biomass resources on earth. Isosorbide also shows interesting results in optical and thermal properties owing to its wedge-shape fused ring structure. In this regard, isosorbide has been widely used for the synthesis of polyesters, polyurethanes, poly(ester-co-carbonate)s, and polycarbonates. As far as the polycarbonates are concerned, isosorbide is an excellent candidate to replace bisphenol A (BPA), which is derived from petroleum and could induce chronic toxicity. However, isosorbide is highly hydrophilic and its acidity is lower than that of BPA, resulting in the difficult synthesis of isosorbide-based polycarbonates.

In this study, we investigated the effect of catalyst on the synthesis of isosorbide-based polycarbonate using diphenylcarbonate as a carbonate source. Four different catalysts (based on Li, Ti, La, and Cs, respectively) were evaluated here and molecular weights and T_g s of resulting polymers were measured and compared depending on catalyst content. In addition, reaction constant of an initial condensation step was measured for each catalyst using GC-MS. Based on the results we can know that the choice of the catalytic system is really crucial for the success of isosorbide-based polycarbonate polymerization and the most promising catalytic system is a cesium based one.

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Study on miscibility of Isosorbide based polycarbonate/Poly(L-lactic acid) solution blends

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Keywords: bio-based plasitcs, isosorbide based polycarbonate, poly(lactic acid), solution blending

Recently, studies on biomass materials have captured much attention due to the concern about the increase in plastic waste generation. Isosorbide based polycarbonate(Iso-PC) is bio-based plastic, produced from isosorbide monomer. And it is a potential alternative to petroleum-based plastics. Poly(L-lactic acid)(PLA) is a sort of commercial available polyester, which is synthesized by the direct polycondensation of lactide monomer, and has become most widely used as bio-based and biodegradable polymer. However, the applications of PLA as common plastics have been limited owing to some drawbacks, such as brittleness and poor thermal stability[1]. In this study, Iso-PC/PLA blends were prepared by solution blending in order to improve the thermal and mechanical properties of PLA. To evaluate the miscibility of Iso-PC/PLA blends, solution blends were compression-molded. The morphology and glass transition behaviors were analyzed by FE-SEM and DMA, respectively. In overall composition, domain size of several micron was observed in morphology. And Inward shift phenomenon of glass transition temperature was not observed in DMA. The TGA results revealed the improved thermal stabilities of the PLA-rich composition. Finally, we could find Iso-PC/PLA blends need to improve compatibility through compatibilizing system.



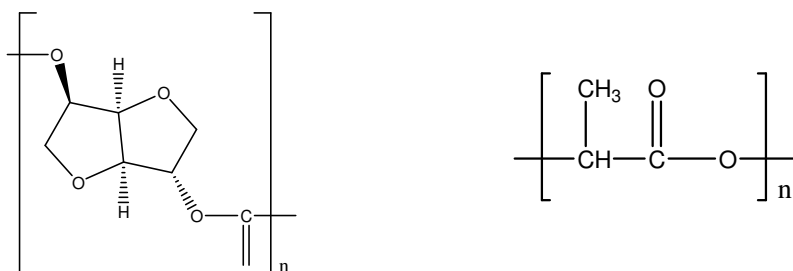


Figure. Structure of Isosorbide based polycarbonate and Poly(L-lactic acid)

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Synthesis of carbohydrate biomass-based furanic compounds bearing epoxide end group(s) and evaluation of their feasibility as adhesives

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Keywords: renewable and sustainable; carbohydrate biomass; furanic compounds; epoxide; cationic photo-curing; tensile-shear strength

Current issues of energy and environment prompt us to replace fossil-based resources with renewable and sustainable ones. In this regard, carbohydrate biomass photosynthesized from atmospheric carbon dioxide attracts much attention due to its abundance and availability. Recently, furanic compounds that can be derived from carbohydrate biomass are highlighted as promising substitutes for aromatic compounds that are totally dependent on petroleum reforming processes. In this article, we report on several carbohydrate biomass-based furanic compounds as alternatives to petroleum-based adhesives. Furanic compounds bearing epoxide end group(s) were synthesized from renewable and sustainable carbohydrate biomass-based compounds (>70% yields). Another bis-epoxy furanic compound with a mimetic structure of bisphenol A (BPA) was also synthesized from xylose-derived 2-furan carboxylic acid and acetone (39% overall yield). In particular, epoxy groups were efficiently introduced to the hydroxymethyl functionality attached by furanic cores under the bi-phasic solvent system using phase transfer catalysis. Cationic photo-curing kinetic profiles of synthetic compounds were investigated in terms of heat flow integrals using photo-DSC. It was found that their half-time values ($t_{1/2}$), representing curing rates, ranged from 0.54 to 1.15 min when irradiated with 40 mW/cm² UV light. When synthetic furanic compounds functionalized by epoxide group(s) were used for bonding polycarbonate by cationic photo-curing, we noted that tensile-shear strength of PC joints bonded with biomass-based furan mono-epoxide having furan ring was greater (4.7 MPa) than that of joints bonded with petrochemical-based phenyl glycidyl ether having phenyl ring (2.6 MPa). When bonded with di-epoxide functionalized furan di-epoxide, tensile-shear strength of PC joint was 3.5 MPa after photo-curing for 3 min at 40 °C. However, bis-furan di-epoxide (bFdE), the mimetic compound of BPA showed lower tensile-shear strength (approximately 1 MPa) due to structural features of bFdE, such as rigidity and hydrophobic property.

Synthesis of isosorbide derived polymer and its molecular weight with various catalysts

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Keywords: bio-based polymer, isosorbide monomers, catalyst, degree of polymerization, molecular weight, green house gas (GHG)

We have been studied environmental friendly bio-based polymer materials due to low green house gas (GHG) emission and replacement petroleum resources. Recently we focus on some biopolymers such as furan based polyester, polyurethane and isosorbide based polycarbonate. Generally polycarbonate is well-known material as the most useful thermoplastic polymer. It has used and developed at diverse fields due to special abilities such as heat resistance, flame retardation, high impact strength, high optical transparency and dimensional stability. In this study, we synthesized poly isosorbide carbonate (ISBPC) by melt polymerization in the presence of Cs or La catalyst. In our study we found that molecular weight of ISBPC were affected by kinds of catalyst and their amounts. Molecular weight of ISBPC using Cs catalyst was 33,000 g/mol at 500 ppm (concentration) and another molecular weight of polycarbonate using La catalyst was obtained 33,400 g/mol at 2000 ppm. From this result Cs catalyst influence upon the enhancement of molecular weight of ISBPC compare to La catalyst. Finally we tried to scale up the reactor size from 250ml to 5000ml and carried out polymerization using the same isosorbide monomer and catalyst as well. We found out that similar molecular weight of isosorbide based polycarbonate can be obtained of 35,000 g/mol at large sized reactor.

Evaluation of Water-Soluble Heterobimetallic Complexes in the Aqueous Biphasic Hydroformylation of 1-Octene.

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Keywords: Green Chemistry, Heterobimetallic, Aqueous Biphasic

The continued design of improved catalysts is driven by the need for simple and effective catalysts to facilitate complicated catalytic reactions, such as the aqueous biphasic hydroformylation of higher olefins (Fig. 1).¹⁻⁴ The use of water as a second phase solvent in such reactions is in line with the green chemistry principles since water is environmentally friendly, relatively inexpensive, abundant, non-flammable, non-toxic and is immiscible with a wide range of organic solvents which enables efficient catalyst separation from the product for recycling.⁵ The ease of catalyst separation subsequently solves the difficulty associated with product recovery in biphasic systems when used for the hydroformylation of higher olefins. Moreover, the atom-economical nature of hydroformylation has seen the process being the main synthetic route for the production of linear C₃–C₁₈ aldehydes which can further be processed to plasticisers for PVC plastic, detergents and surfactants, chemical intermediates, solvents and lubricants.⁶

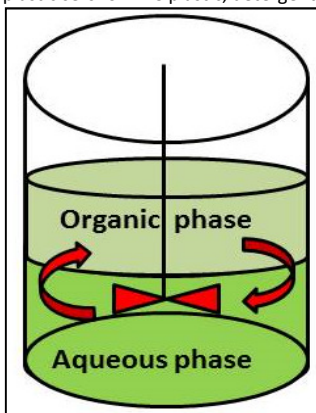


Fig. 1 Diagram illustrating the principle of aqueous biphasic catalysis.

The potential for heterobimetallic species to exhibit cooperative effects between metal centres has prompted studies into application of these systems in catalysis and medicine amongst others. In this work, we describe the syntheses of new water-soluble mononuclear *N, N'* monosodium 5-sulfonatosalicylaldehyde-ferrocenylimine complexes and heterobimetallic Rh(COD)–ferrocenylimine complexes with *N,O*-chelating ligands, as well as the preliminary application of these complexes as catalyst precursors in the aqueous biphasic hydroformylation of 1-octene.

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The Antimicrobial activities of Chitosan and derivatives thereof

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Chitosan (Figure 1) has attracted significant scientific interest with a broad spectrum of applications. Its unique physical properties due to the amino group, its biodegradability and renewable nature, favor chitosan as an alternative 'green' material.

Aim: Chitosan's rigid crystalline structure prevents it from dissolving in most organic and aqueous solvents due to strong intra- and inter-molecular hydrogen bonds. In order to improve chitosan's poor solubility, conjugates bearing various hydrophilic or hydrophobic moieties of chitosan have been prepared. The antimicrobial properties of these polymers alone and in conjunction with silver loading were tested. Selected derivatives were screened for anti-TB activity.

Method: Modified chitosan derivatives were synthesised using various synthetic methodologies. These derivatives have been characterised using $^1\text{H-NMR}$, IR spectroscopy and elemental analysis. The antimicrobial efficacies of these polymers were tested using *E.coli* as a model bacterium.

Result: Certain polymers showed good antimicrobial efficacy against *E.coli* while others displayed moderate activity. The silver loaded polymers displayed promising activity.

Conclusion: Chitosan derivatives and the silver loaded counterparts displayed moderate to good activity against *E.coli*.

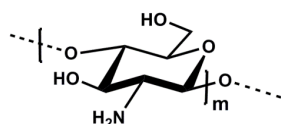


Figure 1: Structure of chitosan

Expedient, metal free synthesis of D-luciferin

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Imaging techniques have become widely used diagnostic tools in chemical and medicinal research.^{1,2} Bioluminescence imaging, which involves the biochemical production of light, has become increasingly popular as it provides extremely high signal-to-noise ratios.³ Synthetically produced luciferins, which are the substrates in luciferase catalyzed light emitting oxidation reactions, forms the core for one of the premier methods in bioluminescence imaging.⁴ Herein, we describe the first one-pot, metal free synthesis of C4-substituted 2-cyanobenzothiazoles from p-substituted-o-brominated anilines, as an advanced intermediate for luciferin



preparation. The synthesis involves the condensation of o-bromoanilines with 4,5-dichloro-1,2,3-dithiazolium chloride (Appel's salt) to generate

N-arylimino-1,2,3-dithiazoles, which undergo cyclization to afford the corresponding 2-cyanobenzothiazoles. The 2-cyanobenzothiazole scaffold is an important synthon in the preparation of light emitting small molecule luciferins, and its use in the synthesis of D-luciferin is also demonstrated. Furthermore, a green controlled monobromination of activated arenes is also described. The controlled monobromination of 1,4-substituted anilines is a necessary requirement for the metal free cyclization.

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