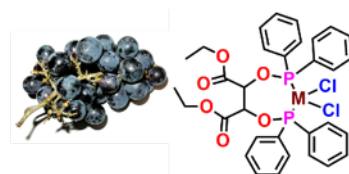


**One Day Symposium on
Recent Trends in Inorganic Chemistry**
in honour of Prof. A. G. Samuelson

Date: 17-07-2021

Venue: Online-MS teams



Biographical Sketch of Ashoka G. Samuelson



Professor Ashoka G Samuelson, well known in the Indian academic circuits as "AGS" and fondly called as "Ashoka" by his friends, is a leading researcher in the domain of Inorganic and Organometallic Chemistry in India. In an illustrious career spanning over 40 years and continuing, he has significantly contributed to the evolution of chemical systems that connect the realms of transition metal and bioinorganic Chemistry. His key research contributions cover the areas of small molecule transformations, organometallics, bioinorganic, and catalysis.

He was born in Madurai, India, in 1956 and grew in various parts of Tamilnadu. He obtained his Bachelor's (B.Sc.) from the St. Joseph's College Trichy and Master's (M.Sc.) degrees in chemistry from IIT-Chennai (then Madras). Soon after, in 1978, he joined the Ph.D. program at the Cornell University, NY, USA, in the research group of Prof. Barry K Carpenter, who is a pioneer of modern physical organic chemistry. During his doctoral research at Cornell, he was involved in the study of kinetic isotope effects and organo-transition metal compounds. He returned to India in 1983 and briefly served as CSIR-pool officer in the Department of Chemistry IIT-Madras. In 1983, he joined the faculty of the prestigious Inorganic and Physical Chemistry Department at the Indian Institute of Science, Bangalore, India as a lecturer and rose to the rank of a full Professor in the year 1999. He served as the head of the Inorganic and Physical Chemistry Department for about 5 years during 2009–2014.

During the early stages of his independent research, he worked on the chemistry of copper (I) compounds involving the synthesis of phenolate complexes of copper(I) and study their reactivity with molecular oxygen to see whether phenol can be converted (hydroxylated) to *ortho*-catechol under aerial oxidation conditions. His group established that the reaction of

phenolate complexes of copper(I) with CS₂ gave the orthocarbonates C(OPh-R)₄, which were not easy to prepare prior to their method. The structures and conformations of orthocarbonates were even fascinating in terms of an anomeric effect. Latter, the emphasis of Samuelson's group, has primarily been on Structure-Reactivity and Structure-Property relationships in Coordination and Organometallic chemistry. One such objective was to develop asymmetric catalysts based on the design of complexes with the potential for weak interactions. For this purpose, specialized phosphinites and phosphines based on diols obtained from natural chiral pool which can have specific interactions with the substrate/reagents were utilized. This design is based on the fact that asymmetric catalysis requires only a difference of few kilocalories between the diastereomeric transition states for effective asymmetric catalysis. This could be easily provided by hydrogen bonding and other weak interactions. Specialized bisphosphine/bisphosphinite ligands with tailorable control on the interactions with the substrate / reagents via weak interactions such as hydrogen bond donors or acceptors, C-H— π interactions were developed to tilt the reaction in favor of one enantiomer. Since early 2000, Samuelson also studied several organic transformations that are mediated by group (IV) metal alkoxides. The reactivity is based on the basic nature of alkoxide group, Lewis acidic nature of the group (IV) metals, insertion of unsaturated molecules into the M-OR bond and the reduction of M(OR)₄ to low valent species. Between 2000-2010, the Samuelson group demonstrated several interesting results based on the insertion reactions and the reductive and metathetic coupling reactions mediated by group (IV) metal alkoxides.

Prof. A. G. Samuelson's research group primarily focused on the structure and activity relationship between organometallic/coordination compounds and asymmetric catalysis for three decades. He recognized the importance of copper complexes in various biological activities. His group found that the copper(I) complexes of phosphine ligands showed comparable cytotoxicity to that of the well-known anticancer drug Adriamycin over a range of cancer cells. To gain insight into the cytotoxicity, various biochemical studies at the cellular level and molecular modeling approaches were investigated, particularly on DNA. The encouraging results thus led to the synthesis of many novel metal complexes of potential anticancer activity. A series of organometallic Ru(II) half-sandwich complexes with hydrogen bond acceptor ligands, developed in his research group, showed remarkable cytotoxicity against several cancer cell lines. However, the poor water solubility posed by pure phosphine ligands limit the efficacy of these complexes in spite of having excellent antimetastatic properties. His group adopted the anchoring strategy to combine cytotoxic Ru(II) complexes and water-soluble dendrimers with cancer cell-targeting agents like folic acid and biotin to circumvent these issues. Cellular studies hinted that these complexes enter the nucleus, which triggered further biological studies with nuclear components like DNA and TOPO II α isomerase. Besides the synthesis of metal complexes of anticancer activity, the group was also interested in visualizing the localization of metal complexes inside cells. A new class of bis(thiosemicarbazone) ligands and their copper and zinc complexes were synthesized. The inherent fluorescence nature of zinc bis(thiosemicarbazone) were utilized to visualize the distribution of complexes inside cells; nevertheless, the copper complexes showed remarkable cytotoxicity both *in vitro* and *in vivo*.

Apart from all these research accomplishments, Professor Samuelson was extensively involved in teaching activities, starting from the introductory organometallics courses to advanced research-oriented courses. In addition, he took up various administrative positions right

through his career. At IISc-Bangalore, he served as and dean of faculty affairs (2019–2021). He served as a member of the International Advisory Board of several chemistry journals.

We deem it a great pleasure and privilege to dedicate this one-day symposium on "Recent Trends in Inorganic Chemistry" to Professor Ashoka Samuelson on the occasion of his superannuation. We thank him for his contributions to our Department, Indian Institute of Science and more generally, to Inorganic, Organometallic, and Bioinorganic Chemistry. We are aware that he is writing some books and we are sure that these books would be of enormous value to the students and practitioners. We wish him a happy, healthy, and peaceful life ahead.

Scientific Program

Time	Speaker	Title
<u>Session 1: 9:00 am – 10:25 am</u> Chairs: Prof. V. Krishnan and Profs. A. R. Chakraborty, IPC, IISc		
09:00 – 09:05	Prof. E. Arunan <i>Indian Institute of Science, Bangalore</i>	Welcome
09:05 – 09:35	Prof. Alan. S. Goldman <i>Rutgers University, USA</i>	Catalytic transformations of hydrocarbons by pincer-Iridium complexes: New approaches, new reactions
09:35 – 10:00	Prof. N. Narasimha Murthy <i>Indian Institute of Technology, Madras</i>	Ligand controlled structure, spectroscopy and oxidation reactions of 3d-metal complexes
10:00 – 10:25	Prof. J. B. Baruah <i>Indian Institute of Technology, Guwahati</i>	Reactivity and in-situ transformations of selected nitrogen donor ligands and their first row transition metal complexes
<u>Break</u> (password: rticags)		
<u>Session 2: 11:00 – 12:40</u> Chairs: Prof. S. S. Krishnamurthy and Prof. K. L. Sebastian, IPC, IISc		
11:00 – 11:30	Prof. Kumaravel Somasundaram <i>Indian Institute of Science, Bangalore</i>	Cancer stem cells: understanding tumor hierarchy and heterogeneity
11:30 – 11:50	Prof. C. Sivasankar <i>Pondicherry University, Pondicherry</i>	Copper in nitrogen and carbene chemistry: Catalysts or co- catalysts
11:50 – 12:10	Prof. Akshai Kumar <i>Indian Institute of Technology, Guwahati</i>	Synthesis of speciality chemicals via catalytic transformations by pincer-metal complexes
12:10 – 12:40	Prof. Gernot Frenking <i>Philipps-Universität Marburg, Germany</i>	Chemical bonding and valence
<u>Lunch Break</u> (password: rticags)		
<u>Session 3: 14:00 – 16:10</u> Chairs: Prof. E. D. Jemmis and Prof. S. Vasudevan, IPC, IISc		
14:00 – 14:30	Prof. Felix Tuczek <i>Christian-Albrechts- Universität zu Kiel, Germany</i>	A Chatt-type catalyst with a Single Coordination Site for Dinitrogen Reduction to Ammonia

Time	Speaker	Title
14:30 – 14:55	Prof. J. K Bera <i>Indian Institute of Technology, Kanpur</i>	Ligand Electronic Asymmetry in Organometallic Catalysis
14:55 – 15:20	Prof. S. Ramakrishnan <i>Indian Institute of Science, Bangalore</i>	Strategies for reducing length scales of microphase separation and more
15:20 – 15:40	Dr. S. Dinda <i>Schrödinger Inc., Hyderabad</i>	Catalyst Design using molecular modelling and data-driven approach
15:40 – 16:05	Prof. P. K. Das <i>Indian Institute of Science, Bangalore</i>	The story of ferrocene
16:05 – 16:10	Prof. P. Thilagar <i>Indian Institute of Science, Bangalore</i>	Vote of thanks
Break (password: rticags)		
Session 4: 16:30 – 18:30 Felicitations of Prof. A. G. Samuelson		
Break		
Session 5: 19:00 – 21:00 Social Gathering at Gather-Town (password: rticags). Please finds instruction here .		

Abstract

Catalytic Transformations of Hydrocarbons by Pincer-Iridium Complexes. New Approaches, New Reactions

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Abstract

Iridium complexes have played a leading role in the organometallic chemistry of alkanes and unreactive C-H bonds since the inception of the field 30 years ago. We have found that “PCP”-pincer-ligated iridium complexes are particularly effective for the dehydrogenation of alkanes and have incorporated this reaction into tandem systems for several catalytic transformations based on dehydrogenation. A closely related class of reactions that we are exploring is dehydrogenative coupling. More recently we have turned attention to iridium Phebox complexes. Although the (PCP)Ir and (Phebox)Ir units are formally isoelectronic, the former operates via C-H activation by Ir(I) while the latter effects dehydrogenation via Ir(III) (as an acetate complex) and possibly Ir(V) intermediates. Such a high-oxidation-state catalytic cycle offers advantages for many potential applications of dehydrogenation. In parallel, we have found fundamentally new approaches, including high oxidation-state routes, to C-H activation and dehydrogenation by (PCP)Ir and related catalytic fragments.

1. Gao, Y.; Guan, C.; Zhou, M.; Kumar, A.; Emge, T. J.; Wright, A. M.; Goldberg, K. I.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2017**, *139*, 6338–6350.
2. Wilklow-Marnell, M.; Li, B.; Zhou, T.; Krogh-Jespersen, K.; Brennessel, W. W.; Emge, T. J.; Goldman, A. S.; Jones, W. D. *J. Am. Chem. Soc.* **2017**, *139*, 8977-8989.
3. Goldberg, K. I.; Goldman, A. S. *Acc. Chem. Res.* **2017**, *50*, 620-626.
4. Kumar, A.; Bhatti, T. M.; Goldman, A. S. *Chem. Rev.* **2017**, *117*, 12357-12384.
5. Gao, Y.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2018**, *140*, 2260-2264.

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Alan Goldman received his B.A from Columbia University in New York in 1980 and his Ph.D. from Columbia in 1985, studying the mechanisms of photoinduced organometallic reactions in the laboratory of Prof. David R. Tyler. He then took an IBM Post-doctoral Fellowship in the lab of Prof. Jack Halpern at the University of Chicago. Goldman began his independent career as an assistant professor at Rutgers University in 1987 where he is currently Distinguished Professor of Chemistry. His research focuses on the development and mechanistic study of transition-metal-catalyzed transformations of small molecules and relevant fundamental chemistry. Goldman has received an Alfred P. Sloan Fellowship, a Dreyfus Teacher-Scholar Fellowship, the inaugural ACS Catalysis Lectureship Award for the Advancement of Catalytic Science, the 2019 ACS Award in Organometallic Chemistry, and the 2020 Royal Society of Chemistry Sir Geoffrey Wilkinson Award

Ligand controlled structure, spectroscopy and oxidation reactions of 3d-metal complexes

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Ligand plays multiple roles in regulation of the structure, self-assembly of polynuclear aggregates, control of coordination geometry, stability, dynamics, binding, activation and catalysis in both natural and synthetic transition metal centers. The active-sites of natural metalloproteins containing Fe, Co, Ni, and Cu metal-ions, responsible for O₂ activation and oxidation catalysis, have attracted remarkable recent attention. The tripodal tri- and tetradentate N,O-chelating picolylalkylamine ligands have served as excellent platforms to support and mimic the above bioactive-site features. Currently, there is a tremendous interest to modify these commonly employed N-ligands to further the metal active-site intermediates and functions. We have employed the simple biphenyl-substituted (2-pyridylalkyl)amine bi- and tridentate ligands, linked by alkyl tethers to control the coordination geometry and unique spectroscopic signatures of 3d-metal (Fe, Ni, Cu and Co) ion complexes [1-2]; also, they control the self-assembly of polynuclear iron and cobalt aggregates [3]. On the other hand, cobalt complexes of simple tridentate 2-pyridylalkylamine ligands having dissimilar alkyl tethers exhibit isomerism, structural dynamics in solution and impart an uncommon oxidative conversion of the ligand secondary-amine to the imine, in the presence of O₂ as oxidant. By contrast, an analogous cobalt complex with ligand having symmetrical alkyl tethers gives simple metal-centered oxidation product [4]. Likewise, iron and cobalt complexes of analogous tetradentate N-ligand having an anisole-append give clean oxidative O-demethylation of anisole to phenol in the presence of TBHP as an oxidant; while, milder oxidant O₂ provides simple metal-centered oxidation products [5-6]. Results of these investigations, highlighting the role of on the structure, geometry, self-assembly, dynamics, spectroscopy, and ligand/metal-centered oxidation reactions will be highlighted.

References

- [1] Divya, S.; Ramkumar, V.; Murthy, N. N. *ACS Omega*, **2017**, 2474.
- [2] Ramanaiah, K.V.; Ramkumar, V.; Murthy, N. N. *Inorg. Chimica Acta*, **2017**, 197.
- [3] Nisha, C.; Ramkumar, V.; Murthy, N. N. *Polyhedron*, **2019**, 241.
- [4] Anjana S. S., Donring S., Sanjib P., Varghese B., Murthy, N.N. *Dalton Trans.*, **2017**, 10830.
- [5] Anjana S. S.; Varghese, B.; Prasad, E.; Murthy, N.N. *Eur. J. Inorg. Chem.* **2018**, 972.
- [6] Anjana S. S.; Varghese, B.; Murthy, N.N. *Dalton Trans.*, **2020**, 3187.

Reactivity and in-situ transformations of selected nitrogen donor ligands and their first row transition metal complexes

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In general, the reactivity of a ligand with a metal ion is an important issue in successful synthesis of stable metal complexes. Many stoichiometric reactions become essential to develop catalysts once reactivity of a substrate is delineated under appropriate reaction conditions with or without an additional reactant. Thus, the reactivity of different metal complexes by variations of solvent, pH and many other reaction conditions are routinely studied.

The present talk will discuss examples from (a) In situ transformations of some selected C-N bonded ligands to prepare various metal complexes, (b) Promotional reactivity by coordination polymer in functional group transformations, (c) Changes in the courses of reactions by electronic effects. (c) Changes in the detection ability of anions by metal complexes through electronic effects,

Cancer stem cells: understanding tumor hierarchy and heterogeneity

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Inter- and Intra-tumoral genetic heterogeneity is a well-documented phenomenon and complicates cancer diagnosis and treatment. It is now well established that cancer stem-like cells (CSCs), also known as tumor-initiating cells (TICs) or tumor-propagating cells (TPCs), evolve through genetic and epigenetic alterations. Like normal stem cells, CSCs can self-renew and possess long-term growth potential but are not subject to regular controls that limit growth. The CSCs have a dichotomous division pattern, as they can self-renewal and give rise to the differentiated cells that form the bulk of the tumor. CSCs alone can initiate a tumor even though they are present in negligible proportions in a tumor. In contrast, the differentiated tumor cells form the bulk of the tumor, yet they cannot initiate a tumor. The massive imbalance in the proportions of CSCs and differentiated bulk tumor cells raises several interesting questions. The differentiated bulk tumor cells: do have any specific essential functions, or they are there to make up the tumor mass. The talk will present some of our recent findings demonstrating the importance of bulk cells in supporting the tumor growth.



Kumar Somasundaram is a Professor and Chair at the Department of Microbiology Cell Biology, Indian Institute of Science, Bangalore, India. He obtained his Veterinary Medicine degree (1985) from Madras Veterinary College, Masters in Biotechnology (1987), and Ph.D. in bacterial genetics (1993) from Madurai Kamaraj University, Madurai, India. Subsequently, he did his post-doctoral training at Northwestern University and the University of Pennsylvania in Cancer Biology before moving to the Indian Institute of Science (1999). The primary focus of his laboratory is the genetics of glioma, the most common primary adult cancer.

Copper in nitrogen and carbene chemistry: Catalysts or co- catalysts

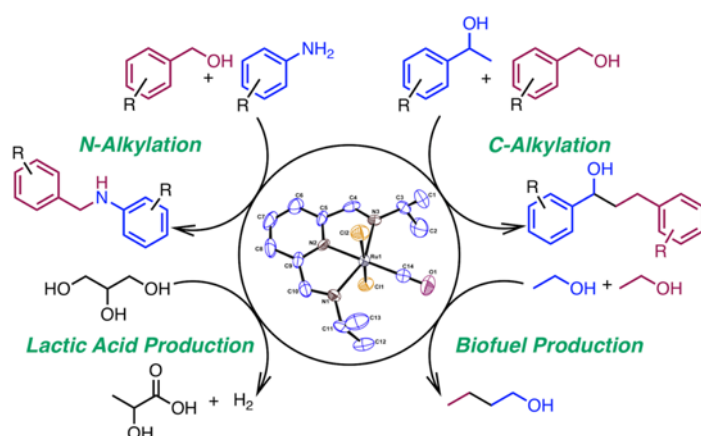
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Synthesis of Specialty Chemicals Via Catalytic Transformations by Pincer-Metal Complexes

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Ever since the first report by Moulton and Shaw in 1976, the chemistry of pincer metal complexes have witnessed an explosive growth and have found wide spread utility.¹ The rigidity of the pincer framework along with the high thermal stability that it imparts allows pincer-metal systems to operate at temperatures not normally accessible to other homogeneous systems. In addition, the modularity of the pincer complex allows for an

plethora of possible modifications not only to the three coordinating groups but also to the ligand backbone, thereby, facilitating excellent ligand tuning. In the recent past, pincer-metal complexes have been used in a myriad of applications promoting stoichiometric and catalytic transformations relevant to fuels, commodity chemicals and fine chemicals.² The current talk would shed light on the efforts carried out in our lab in utilizing pincer- ruthenium complexes³ based on *bis*(imino)pyridine & 2,6-*bis*(benzimidazole-2-yl) pyridine ligands in accomplishing valuable transformations that include but are not limited to *N*-alkylation,⁴ *C*-alkylation,⁵ biofuel⁵ and lactic acid⁶ production.

- (a) Moulton, C. J.; Shaw, B. L., Transition metal–carbon bonds. Part XLII. Complexes of nickel, palladium, platinum, rhodium and iridium with the tridentate ligand 2,6-bis[(di-*t*-butylphosphino)methyl]phenyl. *J. Chem. Soc., Dalton Trans.* **1976**, (11), 1020-1024; (b) Arora, V.; Narjinari, H.; Nandi, P. G.; Kumar, A., Recent advances in pincer–nickel catalyzed reactions. *Dalton Trans.* **2021**, 50 (10), 3394-3428.
- (a) Gunanathan, C.; Milstein, D., Bond Activation and Catalysis by Ruthenium Pincer Complexes. *Chem. Rev.* **2014**, 114 (24), 12024-12087; (b) Kumar, A.; Bhatti, T. M.; Goldman, A. S., Dehydrogenation of Alkanes and Aliphatic Groups by Pincer-Ligated Metal Complexes. *Chem. Rev.* **2017**, 117 (19), 12357-12384.
- (a) Nandi, P. G.; Jadi, P. K.; Das, K.; Prathapa, S. J.; Mandal, B. B.; Kumar, A., Synthesis of NNN Chiral Ruthenium Complexes and Their Cytotoxicity Studies. *Inorg. Chem.* **2021**, 60 (10), 7422-7432; (b) Das, K.; Dutta, M.; Das, B.; Srivastava, H. K.; Kumar, A., Efficient Pincer-Ruthenium Catalysts for Kharasch Addition of Carbon Tetrachloride to Styrene. *Adv. Synth. Catal.* **2019**, 361 (12), 2965-2980.
- (a) Arora, V.; Dutta, M.; Das, K.; Das, B.; Srivastava, H. K.; Kumar, A., Solvent-Free *N*-Alkylation and Dehydrogenative Coupling Catalyzed by a Highly Active Pincer-Nickel Complex. *Organometallics* **2020**, 39 (11), 2162-2176; (b) Das, K.; Nandi, P. G.; Islam, K.; Srivastava, H. K.; Kumar, A., *N*-Alkylation of Amines Catalyzed by a Ruthenium–Pincer Complex in the Presence of in situ Generated Sodium Alkoxide. *Eur. J. Org. Chem.* **2019**, 2019 (40), 6855-6866.
- Das, K.; Yasmin, E.; Das, B.; Srivastava, H. K.; Kumar, A., Phosphine-free pincer-ruthenium catalyzed biofuel production: high rates, yields and turnovers of solventless alcohol alkylation. *Catalysis Science & Technology* **2020**, 10 (24), 8347-8358.

6. Dutta, M.; Das, K.; Prathapa, S. J.; Srivastava, H. K.; Kumar, A., Selective and high yield transformation of glycerol to lactic acid using NNN pincer ruthenium catalysts. *Chem. Commun.* **2020**, 56 (68), 9886-9889.

Chemical Bonding and Valence

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A Chatt-type catalyst with a Single Coordination Site for Dinitrogen Reduction to Ammonia

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Molybdenum complexes play a prominent role in synthetic nitrogen fixation.[1] In search of a single-site molybdenum phosphine complex catalyzing dinitrogen protonation and reduction we have developed the pentadentate tetrapodal phosphine (pentaPod) ligand P2 MePP2 Ph .[2] The derived molybdenum complex, [Mo(N₂)(P2 MePP2 Ph)], generates 26 equivalents of ammonia from N₂, employing SmI₂ as reductant and H₂O as proton source.[3] Analogous Mo(0)-N₂ complexes supported by a combination of bi- and tridentate phosphine ligands are catalytically inactive under the same conditions. The catalytic activity of the title complex is due to the strong activation of N₂ and the unique topology of the pentaPod ligand. By protonation with HBARF in ether, the analogous hydrazido(2-) complex [Mo(NNH₂)(P2 MePP2 Ph)](BARF)₂ is generated and characterized by NMR and vibrational spectroscopy. Importantly, it is catalytically active as well. Along with the fact that the structure of the title complex precludes dimerization this demonstrates that the corresponding catalytic cycle follows a mononuclear pathway. The implications of these results on the area of synthetic nitrogen fixation and further prospects of the pentaPod concept are discussed.[4]

[1] N. Stucke, B. M. Flöser, T. Weyrich, F. Tucek, *Eur. J. Inorg. Chem.* 2018, 1337.

[2] S. Hinrichsen, A. Kindjajev, S. Adomeit, J. Krahmer, C. Näther, F. Tucek, *Inorg. Chem.* 2016, 55, 8712.

[3] T. A. Engesser, A. Kindjajev, J. Junge, J. Krahmer, F. Tucek, *Chem. Eur. J.* 2020, 26, 14807.

[4] J. Junge, T. A. Engesser, J. Krahmer, C. Näther and F. Tucek, *Z. Anorg. Allg. Chem.* 2021, 647, 822

Ligand Electronic Asymmetry in Organometallic Catalysis

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Two donor modules in a ligand with different sigma and pi-bonding characteristics offer prospect for uniting and managing different substrates on a metal center. In this talk, I will provide an orbital perspective on the origin of electronic asymmetry. A Pd(II)-catalyzed Wacker-type oxidation of olefins and proton/hydride management at the ligand/metal assembly for reductive amination of aldehyde and alkylation of ketones will be discussed.

References

1. ACS Catal., **2020**, 10, 11385–11393
2. Organometallics, **2020**, 39, 3849-3863
3. Chem. Eur. J., **2021**, 27, 0000.

Strategies for reducing length scales of microphase separation and more ...

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Creating smaller and smaller domains of one polymer in another, with controlled shape and distribution, has drawn a great deal of interest because of the potential for applications in many fields, such as nanofiltration membranes, composites, solar cells, lithography, etc. Achieving small domain sizes by blending two polymers is generally not possible, as they will phase separate; and the domain sizes are more process dependent rather than thermodynamically controlled. Hence, researchers have resorted to using block copolymers, wherein two immiscible polymers are covalently linked and therefore are forced to occupy adjacent domains, which in turn permits the sizes of domains to be controlled by the size of each block. However, this strategy also has its limits due to a factor, namely the segregation strength (χN), where χ is the Flory interaction parameter and N reflects the size of the block copolymer; for microphase separation to occur, χN should exceed 11.5. Since, χ is an intrinsic property of a polymer-pair, this value cannot be increased dramatically and consequently, for readily accessible polymer block pairs, the value of N cannot fall below a critical threshold, thereby imposing a lower size limit for the domains, which is typically around 50 nm. Several strategies have been adopted in the literature to bring the sizes down to below 10 nm; we too have developed one such strategy using periodically grafted amphiphilic copolymers (PGACs) and have shown that the zigzag folding of the chain occurs to generate lamellar morphologies with lengths scales less than 10 nm. I will discuss some salient examples during my talk.

“And more...” reflects the many ideas that were experimentally challenging and hence we were unable to realize them; they have remained *gedanken* experiments. Since, traditionally we are inclined only to discuss successful experiments, I thought I would deviate and speak a little about our failed attempts at *what I thought would have been neat experiments*; many of these I may have discussed with AGS during our lunch walks. So as a tribute to AGS and his patience to listen to many of my crazy ideas, I shall discuss a few of these, which I really wished had succeeded. By discussing failed ideas, I believe we may promote others to attempt them, if they are indeed as brilliant as the originator may have perceived them to be. 😊

Catalyst Design using Molecular Modeling and Data-Driven Approach

Shrabani Dinda

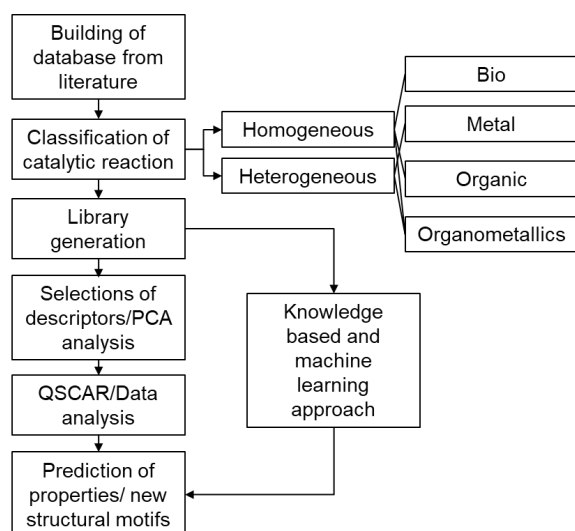
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The availability of a large amount of experimental and simulation data has led us to the fourth paradigm of science over the past few years, called data-driven science. Herein, we attempt to apply molecular modeling, informatics, and data-driven approaches in catalyst design. The application of molecular modeling complements the experiments. It provides critical insights to design a better catalyst, as demonstrated by the example of selective oxidation reactions by metal embedded zeolite and redox-active ligand containing metal catalysts and the prediction of asymmetric enantiomeric excess.¹⁻³

In contrast, building a web portal to showcase the available information on catalysts as a database naturally follows from the first three paradigms of the experiment, theory, and computation/simulation. Development of the Molecular Property Diagnostic Suite (MPDS) of program,⁴ primarily for disease-specific web portals, for catalyst design is aligned in this direction. Initially, we built a catalyst database. The objective is to establish the Quantitative Structure Catalytic Activity Relationship using various machine learning (ML) techniques. The ML models thus outline the important features/descriptors describing the catalysts' electronic and steric properties to predict the more efficient catalysts.

A generic flowchart for computer-aided catalyst design is shown in Scheme 1.



Scheme 1. Flowchart of catalyst design using data-driven approach

References

1. (a) Vummaleti, Kuriakose, Dinda, Wu, Genest, Rösch, *Cat. Sci. Tech.*, **2019**, *9*, 2781–2793; (b) Dinda, Genest, Rösch, *ACS Catal.*, **2015**, *5*, 4869–4880
2. Dinda, *JOC*, **2018**, *83*, 13911–13921
3. Dinda, *JPC C* (under review)
4. Gaur, et al. *J. Chem. Sci.* **2017**, *129*, 515–531

The story of ferrocene and...

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Ferrocene is unique in organometallic chemistry in many ways. It is cheap and can be attached to any molecule either by making a covalent link to the cyclopentadienyl ring or by coordination to the Fe-center. It is rather easy to oxidize or reduce the central Fe-atom to alter the donating or the accepting ability of the ferrocene, in situ. Ferrocene also has a rich uv-vis spectrum which provides an indicator for electronic arrangement inside a molecular architecture containing ferrocene. My life-long collaboration with Ashoke Samuelson started by investigating the second order optical nonlinearity (β) of a series of partially oxidized ferrocenyl complexes and relating their β values to the extent of charge transfer between the ferrocenyl compound and the oxidant which were typically I_2 , DDQ, or TCNQ, etc. In these donor-acceptor complexes the ferrocenyl unit was clearly the donor. In these compounds, the d-d band of ferrocene shifts from 460 nm to 550 nm in the presence of the oxidant/acceptor which enhances the β value by a two-photon resonance mechanism. The two-photon contribution to the second harmonic signal was later determined by a wavelength scan of the detected second harmonic light in the hyper-Rayleigh scattering (HRS) measurement set-up. In a separate publication, ferrocenyl barbituric acid was used in determining the stoichiometry of its H-bonded assembly with ferrocenyl diaminopyridine in solution using HRS. The same ferrocenyl barbituric acid was also used in a lambda-shaped hydrogen bonded heterodimer with bispyridinylbenzenedicarboxamide to enhance molecular nonlinearity by manifold. Most recently, ferrocenyl derivatives of thiophene was oxidized electrochemically to achieve molecular enhancement of β in a ferrocene donor-ferricenium acceptor combination.