

Connaught Global Challenge Symposium on CO<sub>2</sub> Solutions to Climate Change  
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Poster Abstracts

**1. Metal-ligand cooperative catalysts for the reduction of CO<sub>2</sub>**

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The Morris group specializes in catalyst design for the reduction of polar double bonds.<sup>[1-4]</sup> As this is an important field for the pharmaceutical and fine chemical industries, the emergence of homogeneous CO<sub>2</sub> hydrogenation catalysts has sparked great interest for the energy and sustainability industries.<sup>[5,6]</sup> The Morris group developed a method of hydrogenation using formate as the sacrificial hydrogen source,<sup>[7]</sup> and as hydrogenation reactions are often reversible, we saw a future in iron-based CO<sub>2</sub> hydrogenation catalysts. The Morris group is working towards the design of an iron catalyst by varying our tridentate P-N-P ligands to have appropriate functional groups for activity in CO<sub>2</sub> hydrogenation. The Morris group also has an active interest in replacing air sensitive phosphine ligands with more robust N-heterocyclic carbene based ligands. To this end, an N-C-N pincer ligand with de-aromatizable methyl-pyridyl moieties was designed,<sup>[8]</sup> with inspiration drawn from Milstein's highly active phosphine based Ru-PNN CO<sub>2</sub> reduction catalyst.<sup>[9]</sup> CO<sub>2</sub> activation for the generation of formate has been observed and preliminary catalytic testing at low temperatures and pressures are underway.

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## 2. Enhancement Efficiency of Electrocatalytic Reduction of CO<sub>2</sub> using Immobilized Amino- Cobalt (II) Porphyrin Complexes

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The burning of fossil fuels has a significant impact on climate change<sup>1</sup>. The reduction of carbon dioxide into useful materials is a possible solution in converting this greenhouse gas into an energy source and ultimately lowering the CO<sub>2</sub> concentration in the atmosphere.<sup>2-4</sup> Porphyrin complexes have natural catalytic activities with specific types of metal-organic and covalent-organic frameworks providing greater CO<sub>2</sub> absorption<sup>1</sup>. On the other hand, it has been shown that primary and secondary amines can act as Lewis bases by attacking free CO<sub>2</sub> molecules. Upon porphyrin tuning ability, stability and high efficiency using different electron withdrawing and electron-donating groups, we have decided to introduce amino groups to the porphyrin core, allowing manipulation of absorption and conversion of CO<sub>2</sub>.<sup>5-8</sup> In this contribution, a series of amino porphyrin molecules are presented to increase the capturing of the free CO<sub>2</sub> in two different sides of amino porphyrin molecules. This study has been extended to include an investigation of redox reactions of amino cobalt (II) porphyrins including mono, di, tri and tetra primary amino groups in the para positions, which act as both electron-donating and withdrawing groups in terms of CO<sub>2</sub> reduction. The efficiency for the entire synthesized molecules will be reported in the current report as well.

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### 3. Quantifying the Efficiency of CO<sub>2</sub> Capture by Lewis Pairs

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A microfluidic strategy has been used for the time- and labour-efficient evaluation of the relative efficiency and thermodynamic parameters of CO<sub>2</sub> binding by three Lewis acid/base combinations, where efficiency is based on the amount of CO<sub>2</sub> taken up per binding unit in solution. Neither *t*Bu<sub>3</sub>P nor B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> were independently effective at CO<sub>2</sub> capture, and the combination of the imidazolin-2-ylidene-amino-substituted phosphine (N*i*Pr)<sub>3</sub>P and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was equally ineffective. Nonetheless, an archetypal frustrated Lewis pair (FLP) comprised of *t*Bu<sub>3</sub>P and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was shown to bind CO<sub>2</sub> more efficiently than either the FLP derived from tetramethylpiperidine (TMP) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or the highly basic phosphine (N*i*Pr)<sub>3</sub>P. Moreover, the proposed microfluidic platform was used to elucidate the thermodynamic parameters for these reactions.

#### **4. Analytical Modelling of Halbach Array based Linear Generator for Ocean Wave Energy Harvesting**

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Almost 70% of the earth is covered by the ocean that has enormous energy to be exploited. Ocean wave can provide a more consistent and powerful clean energy comparing to wind energy and solar energy, etc. Halbach magnetic array based linear generator provides one possible solution to harvest this clean energy from the ocean. Halbach magnetic array is a special arrangement of permanent magnet to strengthen the magnetic field distribution on one side and eliminate the field on opposite side. This arrangement is used to improve the efficiency of the linear generator. A complete analytical model is critical to the design and optimization, however, there is not any generalized analytical model for the generator. Thus, our main objective is to develop an analytical model of linear generators using Halbach Magnetic for ocean wave energy harvesting. In this work, initially, using Fourier decomposition, the magnetization components of Halbach arrays are determined. Then, the expression of the magnetic distribution is derived using the magnetic scalar potential method based on the boundary conditions of the slotted linear generator for the first time. In addition, a generalized dynamic model is developed combined with the magnetic model to predict the behavior of the generator. This model is validated by finite element analysis. At the end, an experiment is conducted to further proof the correctness of the developed model.

## 5. Electrocatalytic Transfer Hydrogenation for Carbon Dioxide (CO<sub>2</sub>) Activation and Utilization

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Liquid fuels derived from fossil resources have provided humankind a remarkable opportunity that has both spawned and sustained the industrial revolution and is now the basis of modern economies. However, this model has proven to be unsustainable. The combustion of fossil fuels has had deleterious consequences to our climate, yet, the energy-efficient conversion of chemical fuels into useful forms of energy is critical to our energy future. The aim of our work is to develop electrocatalysts that can mediate both the energy-efficient oxidation of alcohols to carbon dioxide (CO<sub>2</sub>), and the reverse, the electrochemical reduction of CO<sub>2</sub> to regenerate an energy storage medium in the form of chemical fuels. It is our opinion that the energy-efficient removal of high free-energy electrons stored in chemical fuels is a key challenge in converting chemical energy into work. We are developing catalysts that perform transfer hydrogenation as a potential transformative approach to activating CO<sub>2</sub> via "electrohydrogenation", which reduces CO<sub>2</sub> via electrochemically generated metal-hydride (M–H) species, avoiding energetically costly single-electron transfer steps. The success of this approach would provide the scientific basis for solving one of the key technological hurdles in a renewable carbon-based energy cycle.

## 6. Synthesis and Characterization of Nanomaterials towards Heterogeneous Catalytic Synthesis of Ammonia

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Ammonia is an important molecule as it is necessary for fertilizer used in agriculture to sustain the global population and is being considered as an energy storage material.<sup>1,2</sup> However, the Haber-Bosch Process that is currently responsible for the majority of ammonia production is energy intensive (operating at 400-600°C and 20-40 MPa), consuming at least 1% of energy generated worldwide.<sup>3,4</sup> Moreover, the Haber-Bosch Process being powered by fossil fuels is incredibly greenhouse gas intensive: the global production of NH<sub>3</sub> is 150 Mega Tonne with a CO<sub>2</sub> footprint of 2 Giga Tonne. Thus it is important to design more energy efficient catalysts. Many ammonia synthesis catalysts are composed of metal particles on a supporting material. The precise mechanism by which supporting materials promote the synthesis of ammonia by metal catalysts is generally not well understood, however recent research efforts have yielded clues as to what key features to keep in mind.<sup>5,6,7</sup> Given our research group's success with studying metal oxides as important actors in CO<sub>2</sub> reduction with hydrogen, we began to investigate if design concepts relating to surface acidity/basicity and reactivity towards H<sub>2</sub> could be translated into the rational design of materials toward ammonia synthesis. An overview of the synthesis, morphology and performance of some of these systems is presented.

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## **7. Nanoscale Building Blocks: Plasmonic Metal and Photoelectrochemically Active Metal Oxide Nanoparticles for Renewable Energy Applications**

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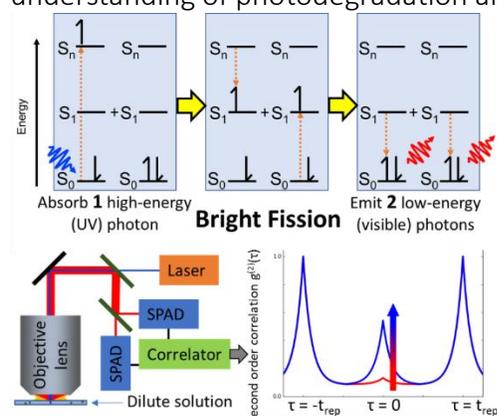
Size- and shape-uniform nanoparticles and nanostructures can serve as well-defined nanoscale building blocks (NBBs) for a variety of applications. Convenient tailoring of NBB composition, surface chemistry, size-dependent functional properties and self-assembly enables versatile design of novel materials using NBBs. With respect to renewable energy applications, plasmonic metal nanoparticles can enhance sunlight absorption with a wavelength conveniently tunable by the NBB dimensions. Photoelectrochemically active metal oxide NBBs, such as hematite and manganese (III,IV) oxides, are effective in oxygen evolution. We will present our work on well-defined NBBs at Laurier.

## 8. Two-colour $g^{(2)}$ photon correlation in solution: Towards a measurement of *bright singlet fission*

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Advances in techniques for fluorescence spectroscopy continually reveal novel electron dynamics in excited state molecules, with potential applications in solar technologies and photocatalysis. Recently, Beyler (Bawendi) developed a technique using photon counting and second-order correlation analysis ( $g^{(2)}(\tau)$ ) to extract the probability of multi-photon emission events from an ensemble of colloidal nanocrystals in solution.<sup>1</sup> Here we propose and demonstrate an epifluorescence apparatus for two-colour solution-phase  $g^{(2)}$  measurements to investigate the hypothesized process of ‘bright’ singlet fission in multichromophoric assemblies of organic molecules. Bright fission involves the rapid evolution of a single, highly-excited state ( $S_n$ ) into two *emissive* excitations on neighbouring chromophores (Fig. 1),<sup>2</sup> giving it potential impact in photocatalysis and fluorescence down-conversion applications. Although bright fission has not yet been experimentally validated, the speed of singlet-singlet annihilation—the reverse process—suggests that the rate of bright fission could compete with thermal relaxation. Our research will offer a window into the dynamics of highly excited states, furthering our understanding of photodegradation and photocatalytic processes.



**Fig. 1. (Top)** Energy diagram of the bright fission process, followed by incoherent two-photon emission. **(Bottom-left)** Epifluorescence microscope used to measure emitted photons from organic aggregates in solution. **(Bottom-right)** Expected result of second-order correlation analysis ( $g^{(2)}(\tau)$ ) on the fluorescence from a sample with efficient bright fission/two-photon emission – excitation with high-energy photons (blue trace) enlarges the center peak compared to the background signal from multi-photon absorption (red trace: low-energy excitation).

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## 9. Manufacturing from CO<sub>2</sub>: Acetic Acid Synthesis on Mars

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The motivation for this work stems from the desire of in situ production of useful products such as biopolymers, food, fuels, or pharmaceuticals from carbon dioxide the accomplishment of such a system would drastically reduce extraterrestrial mission costs. Our team collaborated with advisors from NASA to develop a proof-of-concept model of such a system through the Multidisciplinary Capstone Design Course at the University of Toronto. In order to reach the ultimate useful product, the design team chose to focus on the physicochemical production of an acetic acid intermediate as it can be easily metabolized by downstream biological systems to produce the useful products the industry desires. Two reaction pathways were combined that would first convert carbon dioxide to methanol via methanol synthesis, followed by methanol carbonylation to produce acetic acid. The first reactor system to produce methanol is an Integrated Micro Packed Bed Reactor-Heat Exchanger with a heterogeneous Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. This reactor is capable of operating at a carbon monoxide conversion of 29.5%, maintained at a pressure of 80 bar and temperature of 528 K. The second reactor system to convert methanol to acetic acid is a plug flow reactor with a fixed-bed, heterogeneous, iridium catalyst. This reactor is capable of operating at a methanol conversion to acetic acid of 46.3%, maintained at a pressure of 17.2 bar and temperature of 513 K. Kinetic and equilibria data was utilized to assess the system's operating set point in terms of its distance from equilibrium operating conditions. NASA's Equivalent System Mass (ESM) methodology was implemented to evaluate system costs based on key design parameters such as mass, volume, and power requirements, which provided optimization guidelines during the design development process.

## 10. Nanotip-defined high local electric fields accelerate CO<sub>2</sub> reduction heterogeneous catalysts

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The electrochemical reduction of carbon dioxide (CO<sub>2</sub>) provides a promising path towards the storage of renewable energy and to the sustainable synthesis of carbon-based chemical feedstocks. A key challenge for such a process is the low activity and selectivity of the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR). It is intensely desired to reduce CO<sub>2</sub> at low overpotentials, generating desired products at high current densities over extended periods, and reacting selectively without the formation of undesired byproducts. However, CO<sub>2</sub>RR today is hindered by the low local concentration of CO<sub>2</sub> in aqueous electrolytes, in which more kinetically favorable reduction of protons to H<sub>2</sub> often outcompetes CO<sub>2</sub>RR, eroding reaction selectivity. We developed a field-induced reagent concentration (FIRC) method to enhance the CO<sub>2</sub>RR process. Through shaping electrodes into arrays of nanoneedles, we generated a high local electric field even when using low applied overpotentials. The high field concentrates electrolyte cations, and the cations bring with these a high local concentration of CO<sub>2</sub> to the active CO<sub>2</sub>RR surface. Simulations revealed that 10-fold higher electric fields can be achieved on nanometrically sharp tips compared to that of quasi-planar regions. Utilizing bottom-up synthesized gold nanoneedle electrodes, record-low onset potential and record-high geometric current density at the low potential of -0.35 V with nearly quantitative (>95%) Faradaic efficiency (FE) for CO<sub>2</sub> reduction to CO conversion were achieved (1). This current density surpasses by an order of magnitude the performance of the best previously-reported gold nanorods, nanoparticles, and oxide-derived noble metal catalysts. The nanoneedle electrodes exhibited robust continuous reactions over 8 hours in an inorganic aqueous electrolyte. The FIRC concept has also been leveraged to build other metal nanoneedles and metal or metal sulfide covered gold nanoneedles. These electrodes exhibit much enhanced CO<sub>2</sub> to hydrocarbon conversion efficiencies, proving the wider application of the FIRC concept.

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## 11. Structural modulation of tris porphyrin molecules for electrochemical reduction of carbon dioxide

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The burning of fossil fuels has a significant impact on climate change<sup>[1]</sup>. Carbon dioxide emissions, from the burning of fossil fuels, are proposed to be the leading cause of global warming, with global emissions predicted to reach 36.4 billion tons by 2020<sup>[1]</sup>. This has entailed increasing incidence of extreme weather events and ocean acidification, among other adverse environmental effects<sup>[1,2]</sup>. The reduction of carbon dioxide into useful material is a possible solution in converting this greenhouse gas into an energy source and ultimately lowering the CO<sub>2</sub> concentration in the atmosphere<sup>[3,4,5]</sup>. A seemingly feasible way of countering this growing issue is the conversion of CO<sub>2</sub> into useful compounds that are not environmentally damaging<sup>[2]</sup>. This task has proven to be a challenge, due to the nature of this species in terms of its low reactivity<sup>[1]</sup>. Two of the popular metalloporphyrins are cobalt and iron-based porphyrins, which have demonstrated effectiveness as electrocatalysts in the formation of these multi-electron transfer products<sup>[1,6]</sup>. One reason is likely due to the fact that iron and cobalt both have active d orbital electrons, which are believed to be able to energetically facilitate bonding between the metal centre and the CO<sub>2</sub> desorption of the reduction product(s)<sup>[7-9]</sup>. In the current research, we have designed a series of symmetric and nonsymmetrical porphyrin complexes on meso-positions. The synthesis and electrochemical behavior of a novel porphyrin trimer (**Figure 1**) in terms of CO<sub>2</sub> reduction will be presented.

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## 12. Visible and Near Infrared Photothermal Catalyzed Hydrogenation of Gaseous CO<sub>2</sub> over Nanostructured Pd@Nb<sub>2</sub>O<sub>5</sub>

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The reverse water gas shift (RWGS) reaction driven by Nb<sub>2</sub>O<sub>5</sub> nanorod-supported Pd nanocrystals without external heating using visible and near infrared (NIR) light is demonstrated. By measuring the dependence of the RWGS reaction rates on the intensity and spectral power distribution of filtered light incident onto the nanostructured Pd@Nb<sub>2</sub>O<sub>5</sub> catalyst, it is determined that the RWGS reaction is activated photothermally. That is the RWGS reaction is initiated by heat generated from thermalization of charge carriers in the Pd nanocrystals that are excited by inter-band and intra-band absorption of visible and NIR light. Taking advantage of this photothermal effect, a visible and NIR responsive Pd@Nb<sub>2</sub>O<sub>5</sub> hybrid catalyst that efficiently hydrogenates CO<sub>2</sub> to CO is developed. The mechanism of this photothermal reaction involves H<sub>2</sub> dissociation on Pd nanocrystals and subsequent spillover of H to the Nb<sub>2</sub>O<sub>5</sub> nanorods whereupon adsorbed CO<sub>2</sub> is hydrogenated to CO. This work represents a significant enhancement in our understanding of the underlying mechanism of photothermally driven CO<sub>2</sub> reduction and will help guide the way towards the development of highly efficient catalysts that exploit the full solar spectrum to convert gas-phase CO<sub>2</sub> to valuable chemicals and fuels.

### 13. CO<sub>2</sub> reduction on In<sub>2</sub>O<sub>3-x</sub>(OH)<sub>y</sub> nanoparticles via Photo-excited surface frustrated Lewis pairs

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The significant challenge faced by our global society, from issues of climate change to question of energy security could be solved if we can find a champion catalyst that can convert atmospheric CO<sub>2</sub> to carbon based fuels. However, designing catalytic nanostructures that can thermochemically or photochemically convert gaseous CO<sub>2</sub> into fuels is a significant challenge which requires a keen understanding of the physical and chemical properties of complex materials and the processes happening on them at atomic and electronic level. In this context, this work will present our recent advancements in the area of gas phase heterogeneous catalysis achieved by using computational techniques in conjunction with experimental research. Specifically, it will highlight the insights provided by computational analysis into the surface chemistry of CO<sub>2</sub> reduction reaction on In<sub>2</sub>O<sub>3-x</sub>(OH)<sub>y</sub> nanoparticles, in the presence and absence of light. This research resulted in the discovery of a new class of “frustrated Lewis pair (FLP) heterogeneous photocatalysts”, which among many reaction possibilities could enable efficient gas-phase hydrogenation chemistry of CO<sub>2</sub> to fuels and chemicals [1,2].

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## 14. Scaling Renewable Energy GHG Utilization Technologies

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Renewable energy driven conversion of carbon dioxide into useful chemical products provides an opportunity to reduce greenhouse gas (GHG) emissions while simultaneously providing economic benefit. Three key requirements for process success are identified: efficiency, stability, and scalability. While lab-scale fundamental research is quickly reaching the efficiencies and stability expected for industrial application, the question of scalability still remains. At present, the large-scale adoption of renewable energy GHG utilization technologies is hindered by: the availability of a reliable, safe, and sustainable source of hydrogen; the start-up and shut-down dynamics associated with the transient nature of renewable energy sources; and the integration of these processes into existing chemical infrastructure.

Our multidisciplinary research team applies a holistic approach to address these issues in chemical process innovation. By exploring new thermochemical, photochemical and photothermal reactor designs, as well as novel approaches to catalyst design, discovery, and manufacture, we aim to optimize access of renewable energy into the catalyst bed while maintaining an analogue to their conventional fossil-powered industrial counterparts. Further, we explore the prospect of bypassing the need for hydrogen altogether by utilizing an ambient photothermal catalyst cycle that is able to directly reduce gaseous carbon dioxide with water vapor, circumventing the sustainability and safety issues associated with sourcing and using hydrogen. Finally, we bring these components together to conduct detailed process engineering analysis and implementation that integrates renewable energy light and heat components for the production of methanol (chemical feedstock) and dimethyl ether (diesel replacement) from carbon dioxide in a demonstration unit at the University of Toronto.