

## Project 07: Enhanced Efficiency Dye-Sensitized Solar Cell

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### Background

There are three broad classes of photovoltaic (PV) materials that are currently available for converting sunlight into electric energy. The *first generation* of PV materials includes conventional crystalline and multicrystalline silicon p-n devices, which can generate conversion efficiencies ( $\eta$ ) up to *ca.* 26%, but are hindered by the high temperatures and vacuum conditions required for wafer production. *Second generation* “thin-film” devices overcome these high fabrication costs (often at the expense of performance) because of the lower quantity of material required, but typically rely on metals that are highly toxic or not found in abundance in the earth’s crust. A *third generation* of solar cell technologies has surfaced over the past two decades exploring different mechanisms for achieving high PV performance at a lower cost. Among the myriad of options in this broad class of PV materials (*e.g.*, organic bulk heterojunction devices, multiple-exciton generation devices), the most mature technology is the “**dye-sensitized solar cell**” (DSSC).<sup>1</sup> Not only has the DSSC demonstrated the highest power conversion efficiencies ( $\eta > 12\%$ ) within this class of PV materials,<sup>2</sup> it also offers numerous advantages over conventional silicon and thin-film solar cells in that it does not require high purity materials and is amenable to lower-cost processing techniques. The first commercial DSSC product was introduced in 2009 by G24i (Europe). The current phase of commercialization involves the production of solar cells for small consumer products, such as cell phones and laptops. The next phase of development will inevitably involve the implementation of the DSSC as a built-in photovoltaic (BIPV) application. There are a number of factors that support the possibility of this occurring in the near term, including the insensitivity of the performance of the DSSC to the angle of incident radiation, clouds, and temperatures up to 80 °C. On this basis, a host of international companies are now fully dedicated to the commercialization of the DSSC, including 3GSolar (Israel), Dyesol (USA/Australia) and Daunia Solar Cell (Italy); however, none currently exist in Canada.

### Challenge & Opportunity

There are two main practical factors hampering the implementation of DSSCs in commercial applications:<sup>3</sup>

1) *Device stability.* While there have been modeling studies on test cells that forecast minimal cell deterioration over two decades, most DSSC products degrade within two years; and

2) *Low efficiencies.* The use of materials that are stable under practical operating conditions are typically confined to lower performance parameters.

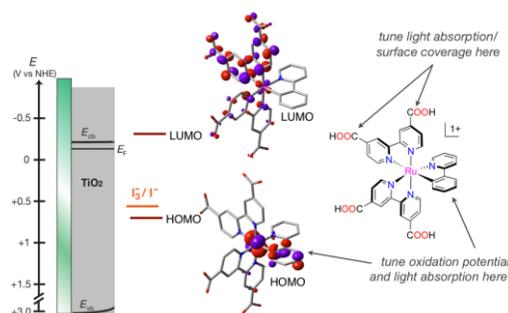
The team of Bender and Berlinguette will address said limitations through the rational design, synthesis and engineering of novel materials/compositions of matter. Berlinguette will develop a robust class of high performance Ru-based and organic dyes, for conventional DSSC devices. Bender will develop non-volatile and stable triarylamine liquid electrolytes for the DSSC over the entire phase of the project. In the short-term, the Berlinguette group will make test cells with dyes and electrolytes to screen combinations that are viable for scale-up. Longer term goals of the project involve the development of upconversion dyes as a means of harvesting lower-energy photons and enhancing photovoltages, and the development of solid-state DSSCs through the optimization of electrolytes developed in the Bender labs to match the specific dye structures from the Berlinguette labs. Each of these goals will be successively improved through numerous feedback loops between the two groups.

### Project

The sensitization of TiO<sub>2</sub> by conventional dyes, such as **N3** (see Figure 1a), relies on a light-driven metal-to-ligand charge-transfer (MLCT) transition, followed by charge-injection into the TiO<sub>2</sub> anode ( $k_{inj}$ ).<sup>4</sup> The generation of higher photocurrents via chromophore design demands that the MLCT absorbance band be extended to longer wavelengths to better overlap with the solar spectrum. The

conventional approach to achieving this goal is to expand the  $\pi^*$  system of the polypyridyl ligands using conjugated substituents at the  $R_1$  position of **N3** to lower the LUMO of the dye. Departing from this strategy, a major effort within the Berlinguette program involves advancing cyclometalated Ru dyes in the DSSC setting.<sup>3</sup> They have confirmed that the perturbation of the electronic structure by the Ru–C  $\sigma$ -bond is favorable for light-harvesting applications. Not only are the energy levels appropriate for sensitizing  $\text{TiO}_2$ , the replacement of two  $\text{NCS}^-$  ligands with a single  $C^{\wedge}N$  ligand offers the unique opportunity to tune *both* the metal-based HOMO and the ligand  $\pi^*$ -based LUMO. Grätzel *et al.* independently demonstrated that a related Ru( $C^{\wedge}N$ ) dye is capable of generating conversion efficiencies of  $\eta = 10.1\%$ , while Berlinguette has developed a diverse family of dyes with PCEs  $< 8\%$ .<sup>5</sup> Because these dyes are devoid of  $\text{NCS}^-$  ligands, which is the primary cause of cell degradation, the cyclometalated chromophores will be aggressively pursued as a collaborative effort with Bender and various international industry partners (e.g., Daunia, 3GSolar) to make more robust dyestuff.

The Bender group has taken an unconventional approach to replacing the paradigmatic  $\text{KI/I}_2$  electrolyte system by developing non-volatile, liquid triarylamine hole-transport materials (HTMs) that are capable of shuttling charges efficiently.<sup>6-8</sup> Triarylamines are known charge conductors and specifically known to be hole conductors in DSSCs; however, all previous versions have been triarylamines that remain in the solid state (even at high temperatures). By engineering triarylamines to be liquids over the entire terrestrial temperature range, the material can: (i) flow into the pores of the  $\text{TiO}_2$  semiconductor to interact with the Ru-dye; and (ii) allow free orientation of the molecules within the liquid (hole-conduction is known to have a geometric component). The **Bender** lab has found two approaches to the synthesis of liquid triarylamines. Each approach utilizes the unique properties of organosilicon to tailor the physical (viscosity,  $T_g$ ) and electronic ( $E_{1/2,ox}$ ) of the triarylamine and each is amenable to systematic variation. The first uses simple silyl ethers and the second uses Piers-Rubinsztajn conditions ( $(\text{C}_6\text{F}_5)_3\text{B}$  catalysis) to introduce discrete silicones into the triarylamine structure. Using our methods, a crystalline triarylamine (m.p. =  $122\text{ }^\circ\text{C}$ ) can be transformed into a liquid using either a silyl ether ( $T_g = -14\text{ }^\circ\text{C}$ ) or a discrete silicone (c,  $T_g = -45\text{ }^\circ\text{C}$ ). We have preliminary data suggesting our liquid triarylamines function in dye sensitized solar cells (DSSCs) with efficiency  $< 2.4\%$  and that they possess higher charge carrier mobilities than their solid crystalline counterparts.



## Training

Collaboration between the Berlinguette and Bender research groups provides a very powerful and effective means to converge on stable DSSCs. Dye synthesis, and device assembly and characterization, will be performed in the Berlinguette labs, while the HTMs will be synthesized and characterized in the Bender labs. Each student will be trained, at the highest levels of sophistication, in organic/inorganic/materials synthesis and molecular characterization techniques (including numerous electrochemical and spectroscopic methods), as well as experience in measuring standardized test cells under simulated sunlight and as a function of wavelength. The students in Calgary and Toronto will be fully engaged with each other at each stage of the project, including visiting each other's labs as necessary, to efficiently optimize the materials and devices as they move forward.

## References

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