Project 07: Project Scientific Progress – Fall 2012 to Fall 2015

The Berlinguette group synthesized a series of stable, ruthenium dyes for the dye cell, and the Bender group synthesized a series of solid electrolytes for the DSSC. The funding period was successful in enabling us to access both classes of materials, and future work will look towards merging these materials together to form a stable cell configuration.

A series of ruthenium dyes capable of hole transfer to terminal aryl amine units were synthesized as originally intended. The electrolytes took a longer period of time to scale up than anticipated, but were completed before the end of the study. Future studies will test the compatibility of the dyes and the electrolytes. In the meantime, the dye compounds of interest were tested for hole transport properties and intermolecular bonding interactions.

Project Objectives.

Berlinguette and Bender discussed the project goals at the start of the project, and final objectives

An intriguing finding we have made, in a collaboration with Gerald J. Meyer (Johns Hopkins, now at UNC-Chapel Hill), is that the large molecular dipole that arises with these molecules has a profound affect on the voltage. Moreover, it was found that charge recombination was not affected by an intramolecular hole transfer event. (*J. Am. Chem. Soc.* **2012**, 134, 8352-8355.)

Consequently, the major thrust of the project to date has been to place insulating spacers between the triarylamine and the ruthenium complex to slow down undesirable recombination and thus to enhance the voltage and the photocurrent of the cells. These results have yielded interesting findings and will be will be submitted to Nature Chemistry in late 2015. These dyes will then be amalgamated with the redox active electrolytes in the Bender group (starting in early 2016)

<u>Bender Laboratory (see Project 07 Description for details of overall project):</u>

During the first 1.5 quarters of this project we have been focused on two major objectives (identical to the project plan):

- Train new personnel to prepare and purify silicone triarylamines
- Assessment of Silyl Ethers (triarylamines containing silyl ethers)

Due to the start date of the project, we were only able to assign an existing graduate student (B.K.) to the project. Therefore training of new personnel was not an issue. However, B.K. will take up a training role as new graduate student(s) come onto the project.

Given the short duration to date, we have been solely focused on the determination/consideration/assessment of what an ideal 'silicone-ized triarylamine' (triarlyamine containing discrete silicone molecular fragments made using our novel Piers-Rubinsztajn conditions) for application in a dye sensitized solar cell would look like.

We have previously published the synthesis and characterization of a number of model silicone-ized triarylamines (Figure 1, *J. Org. Chem.*, **2012**, *77* (4), 1663–1674.). In each case, the generic class is representative of a known general class of triarylamines know to function well in organic electronics device, albeit most primarily applied in organic light emitting diodes (OLEDs). The representative classes are: phenylene diamines, TPDs, NPBs, spiro-TADs, dendritic (dendrites) and carbazoles. Each class was synthesized so as to contain either 'MM' or 'MDM' units (shown).

In our assessment, we only considered triarylamines with suitable electrochemistry (suitable being defined as reversible oxidation events over multiple cycles). After that, in order to assess the triarylamines we have established three desirable physical properties or parameters which are desirable; each of which are linked to a potential way to process silicone-ized triarylamines into a dye sensitized solar cell.

(1) Neat viscosity – We have a desired to explore the neat processing (neat infusion) of a silicone-ized triarylamine into partially constructed dye sensitized solar cells. In other words, apply the triarylamine as a neat liquid to dye treated TiO_2. Neat processing is foreseen as a green processing method. By contrast the standard KI/I_2 electrolyte system is volatile, corrosive and toxic. In order to facilitate neat processing the silicone-ized triarylamine must be a liquid a room temperature and that liquid must have a suitable viscosity (low viscosity) for easy infusion.

(2) Liquidity – We have set the two different conditions for liquidity. We are unsure until we study the silicone-ized triarylamine in a DSSC which is more desirable or would result in better performance.

(a) The silicone-ized triarylamine remains a liquid over the entire range of what we term 'terrestrially accessible temperatures' (TATs). We could loosely define that range to be -40 °C to +50 °C.

(b) The silicone-ized triarylamine is a liquid at a processing temperature exceeding TATs and a solid at TATs.

By comparing a contrasting (a) and (b) we will be able to determine whether molecular motion (for example in the liquid of (a)) is a performance advantage or disadvantage.

(3) Solubility in inert environmentally benign solvent – hexamethyldisiloxane (HMDS) – if processing of the triarylamines neat is not successful then the next best thing would be to process them in an inert benign solvent such as HMDS. The choice of HMDS is not arbitrary (see below).

Based on the data presented in our paper (*J. Org. Chem.*, **2012**, *77* (4), 1663–1674.) we can conclude several things regarding the most appropriate class(es) of molecules for application in dye sensitized solar cells. The first is that the 'MDM' group is far more able to impart liquidity to the triarylamine that can the 'MM' unit. The second observation is that our silicone-ized triarylamines are for the most part soluble in hexamethyldisiloxane (HMDS). As stated above HMDS is an environmentally benign solvent with low toxicity. However, based on criteria 1-3 outlined above, none of our previously reported silicone-ized triarylamines are suitable. Therefore our activities have focused on exploratory synthesis and considerations of molecular design toward a second generation of silicone-ized triarylamines which meet criteria 1-3. This work is ongoing and will be further detailed in the next report, 6 months hence.

Over the next quarter we are also aiming to supply some silicone-ized triarylamines of the TPD class to the Berlinguette lab for initial testing and evaluation in DSSCs. To that end, we have begun scale up considerations with an aim at producing >10 g of material.

In early 2016 we are aiming to supply some silicone-ized triarylamines of the TPD class to the Berlinguette lab for initial testing and evaluation in DSSCs now that we have successfully scaled up the reaction.