Chapter 6

SOLAR CELLS

Introduction

In our fast-growing world, alternative energy sources are quickly becoming a concern. It was shown in the early 1990s that dye-sensitized solar cells (DSSCs) are a very promising technology toward alternative energy conversion[71]. These cells involve coating nanocrystalline TiO_2 with a dye capable of absorbing sunlight and sensitizing the semiconductor. The dye absorbs photons of visible light, promoting electrons into the excited state. The electrons are injected into the conduction band of TiO_2, leaving an oxidized dye and reduced semiconductor. The injected electron is then free to pass to the back electrode and go around a circuit to do work. The oxidized dye is reduced by an ion pair in solution, which in turn is reduced to its original state at the counter electrode, completing the circuit[71].

One of the best dyes currently known for these solar cell applications is Ru(4,4'-dicarboxylic acid-2,2'-bipyridine)$_2$(NCS)$_2$, more popularly know as the N3 dye. While it is not entirely known why this compound performs so much better than others, it has shown that in developing dyes for DSSCs, two important factors must be considered. The potential dye must have strong absorption bands in the visible spectrum, and the dye must be able to bind to the TiO_2 surface. Quick inspection of the absorption spectra of corroles shows that they do indeed satisfy this first requirement. As well, the sulfonate groups of corroles derived from **2** can provide the binding ability called for in the second factor. Therefore, a portion of this work was spent looking at the ability of corroles to act as the dyes in DSSCs.

2-Ga versus Ruthenium Dyes

Initial work started on corrole-TiO_2 systems started with **2-Ga**, with some preliminary work having also been performed with **2** and **2-Sn** as well. The first experiments were to qualitatively determine if the corroles could in fact bind to the TiO_2 surface.

Slides prepared in lab were soaked in an ethanol solution containing **2-Ga** for approximately 24 hours to ensure maximum adsorption onto the TiO_2 surface. After the 24 hour soaking period the dyes are ready for use in a working solar cell with a 0.5M LiI, 0.05M I_2, 20mM pyridine, 20mM pyridinium triflate, and acetonitrile electrolyte. It can also been seen after this soaking period that the dye has indeed bound to the surface, as the slide takes on the green color of the dye (see figure 6.1). By running current-voltage curves on the coated slides, the efficiency can be determined with equation 6.1:

$$E = (J_{sc} \text{ x } V_{oc} \text{ x ff})/I_s \qquad \text{(eq. 6.1)}$$

In this equation E is the efficiency of the cell, J_{sc} is the short circuit current (the amount of current at zero applied voltage), V_{oc} is the open circuit potential (the potential at zero current), ff is the fill factor (a measure of the shape of the curve, see figure 6.2), and I_s is the power of the sun (100 mW/cm^2). Comparison of the curve obtained for **2-Ga** to those

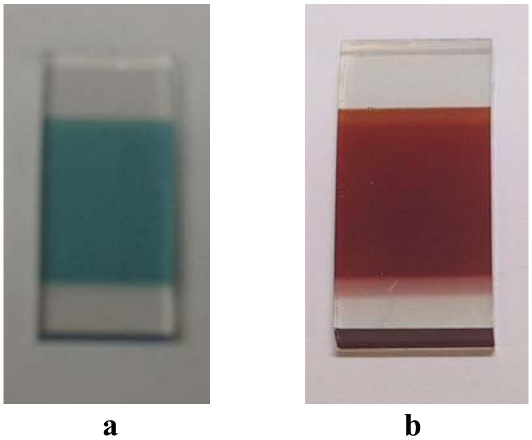

Figure 6.1. TiO_2 slides coated with a) **2-Ga** and b) N3. In both cases the colored area is 1 x 1.5 cm.

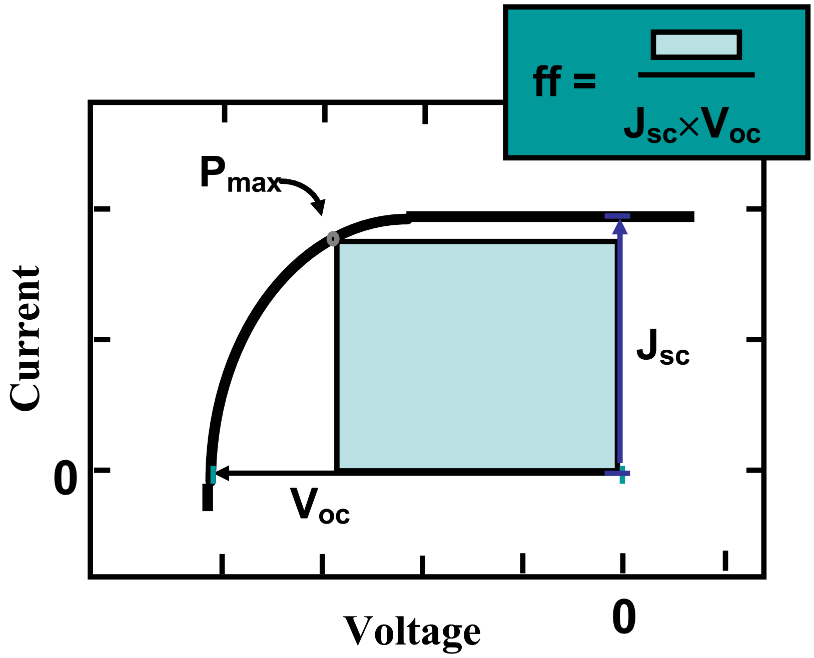

Figure 6.2. Model diagram of current-voltage curve showing important parameters for calculating efficiency. P_{max} is the maximum power from the cell. The remaining terms are defined in the text.

obtained from various ruthenium-diimine dyes (figure 6.3) shows that the corrole based slide has similar parameters to various ruthenium dyes studied, falling in between the best dye, N3, and the worst dye studied, a ruthenium tris(bipyridine) based dye. The overall efficiency of the corrole slide was 1.56%, about half of that found for N3 (3.14%), but more than twice that of the poorest dye (0.69%) (see table 6.1).

2, 2-Ga, and 2-Sn Dyes versus N3

Work was then done to introduce other corrole compounds into the solar cells as well, namely **2** and **2-Sn**. Interestingly, it was found that the free-base performed slightly worse than **2-Ga**, at 0.82% efficiency; however, both were significantly better than **2-Sn** at 0.12% efficiency (see figure 6.4, table 6.2). The reasons behind these differences are still under investigation.

One important factor to consider in the adsorption of these dyes to the TiO_2 cells is whether or not the dye is being changed upon adsorption. However, as seen in figure 6.5, the overall absorption spectrum of the dyes when bound to the surface shows the same typical shape of a corrole spectrum, and the shift in band position seen is similar to that seen with ruthenium-based dyes.

Another experiment performed in characterization of these dyes was incident photon-to-current conversion efficiency (IPCE) measurements. As seen in figure 6.6, the conversion efficiencies of **2-Ga** and **2** rival that of the N3 dye in their Soret and Q-band regions, while

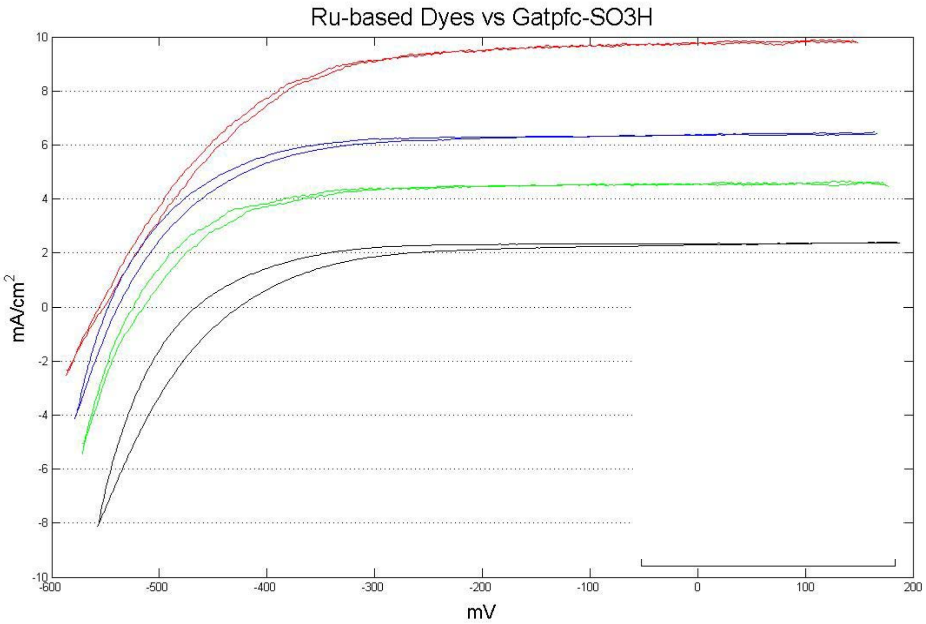

Figure 6.3. Current-voltage curves for N3 dye (red), a ruthenium-diimine dye (blue), **2-Ga** (green), and the poorest ruthenium-diimine dye used in this study (black).

	N3	$[Ru(H_2L')_2(CN)_2]^{2+}$	$[Ru(H_2L')L_2]^{2+}$	**2-Ga**
V_{oc} (mV)	556	548	466	524
J_{sc} (mA)	9.76	6.36	2.34	4.55
Fill Factor	0.58	0.64	0.63	0.66
Efficiency	3.14	2.13	0.69	1.56

Table 6.1. Efficiency parameters for **2-Ga** slides vs. Ru-diimine dyes.

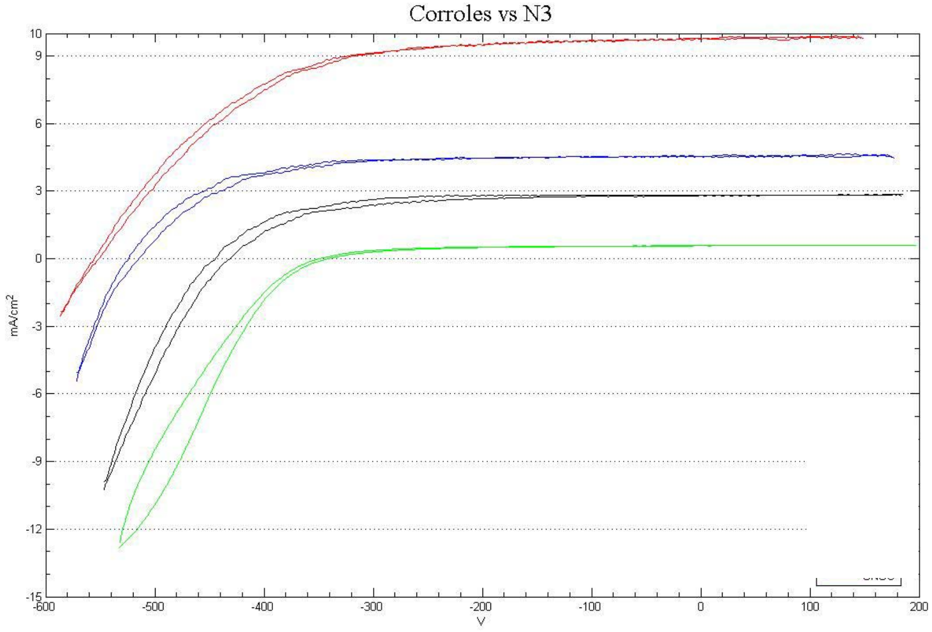

Figure 6.4. Current-voltage curves of N3 (red), **2-Ga** (blue), **2** (black), and **2-Sn** (green).

	N3	**2-Ga**	**2-Sn**	**2**
V_{oc} (mV)	556	524	348	444
J_{sc} (mA)	9.76	4.55	0.58	2.83
Fill Factor	0.58	0.66	0.60	0.65
Efficiency	3.14	1.56	0.12	0.82

Table 6.2. Efficiency parameters for corrole dyes vs. N3.

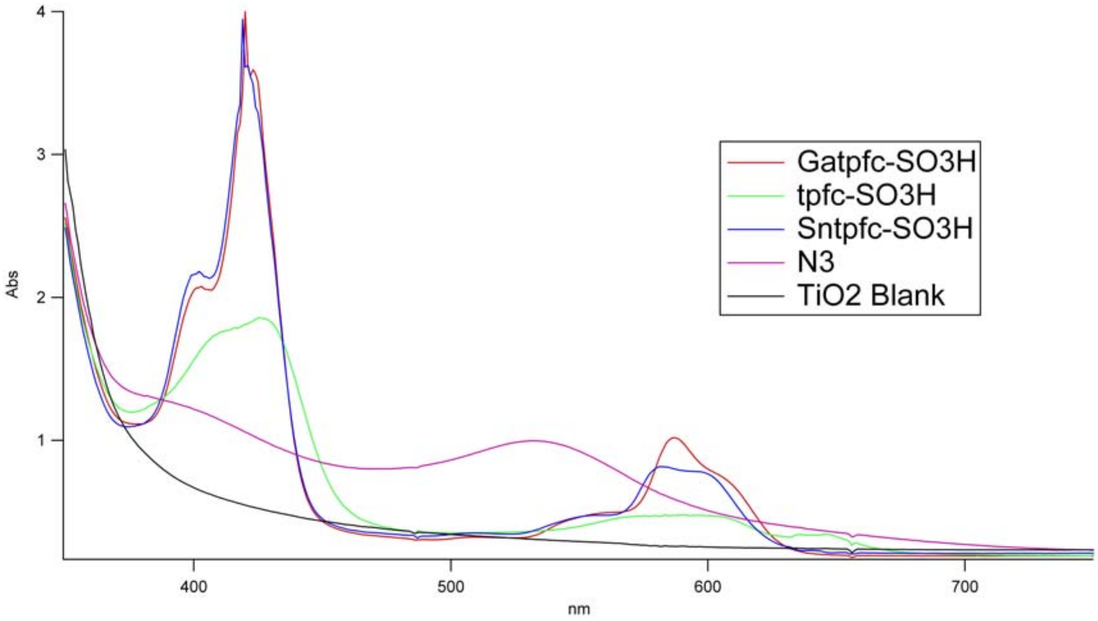

Figure 6.5. Absorption spectra of N3 (purple), **2-Ga** (red), **2** (green), **2-Sn** (blue), and TiO_2 blank (black). Corroles show slight blue shifting of Q-bands. Soret of **2-Ga** shows ~9 nm blue shift; Sorets of **2** and **2-Sn** show 2-3 nm red shifts. These shifts are similar to those seen for ruthenium-diimine dyes.

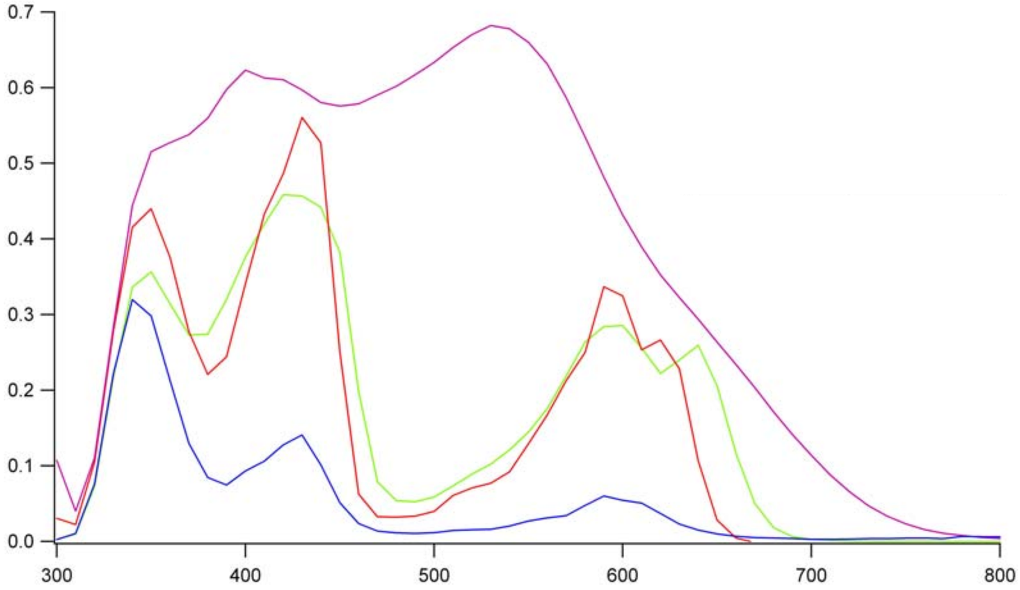

Figure 6.6. IPCE curves of N3 (purple), **2-Ga** (red), **2** (green), and **2-Sn** (blue).

2-Sn shows relatively poor conversion efficiency across the board in comparison with the other dyes.

Conclusions

The corrole based dyes used in this work show great promise for making efficient solar cells and have demonstrated good binding to the TiO_2 surface. However, the kinetics of the cell processes with corroles dyes is not fully understood, and future work will be devoted to elucidating these events. As well, it has been seen qualitatively that the corrole dyes do fall off the surface of the solar cells, and over time the cell loses its color. Research is also being planned toward developing new types of corroles with different binding groups, such as carboxylic acids or phosphonate groups, with the goal of providing stronger overall binding to the surface and making a more robust cell.