Corrole-sensitized TiO$_2$ solar cells

Don Walker$^a$, Shlomit Chappel$^b$, Atif Mahammed$^c$$^\circ$, Bruce S. Brunschwig$^a$$^*$, Jay R. Winkler$^a$, Harry B. Gray$^a$, Arie Zaban$^b$ and Zeev Gross$^c$$^\circ$

$^a$ Beckman Institute, California Institute of Technology, Pasadena 91125, USA
$^b$ Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel
$^c$ Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel

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ABSTRACT: We are investigating the properties of corrole-sensitized TiO$_2$ solar cells. The TiO$_2$-adsorbed free base and Ga$^{III}$ corroles display cell efficiencies under AM 1.5 illumination that are about half that of a standard N$_3$-sensitized cell (N$_3$ = cis-bis(4,4′-dicarboxy-2,2′-bipyridine)dithiocyanatoretanium(II)), while that of the Sn$^{IV}$-based cell is much lower. The properties of the corrole-TiO$_2$ solar cells, along with results obtained with electrodes of lower conduction band energies clearly reveal that the reducing power of the singlet excited states of the free base and Ga$^{III}$ corrole, but not of the Sn$^{IV}$ derivative, is sufficiently high for efficient injection into the TiO$_2$ conduction band.

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KEYWORDS: corroles, sensitizers, solar cells.

INTRODUCTION

Dye-sensitized solar cells (DSSCs) show great promise as devices that can efficiently convert solar energy to electricity [1]. Of the many dyes that have been investigated as sensitizers, the most popular are derivatives of Ru$^{II}$ bipyridines and porphyrinoids (porphyrins, phthalocyanines, chloro- and bacteriophylls, extended porphyrins) [2, 3]. The latter are attractive because their photophysical properties can be readily tuned by selective substitutions on their molecular frameworks and/or via variation of the central metal ion. Recent advances in the synthetic availability of triarylcorroles and the subsequent elucidation of their photophysical properties suggest that they might be particularly good sensitizers in DSSCs [4, 5] since their frontier orbitals are at higher energy than those of analogous porphyrins [4f]. We chose 5,10,15-(pentafluorophenyl)corrole[H$_3$(tpfc)] and its metal complexes for initial study, as these exceptionally robust derivatives [4c,f, 5a] exhibit strong absorptions over a wide range of the visible spectrum. Also of importance is our finding that H$_3$(tpfc) and its closed-shell metal derivatives are intensely fluorescent, a feature that becomes less prominent in complexes in which the central-atom spin-orbit coupling is very large [6]. In addition, selective sulfonation of the framework H$_3$(tpfc) carbon atoms provides ready access to derivatives with substituents that are known to bind to metal oxide surfaces [7].

The structures of a number of porphyrinoid dyes and the most commonly used ruthenium dye are shown in Chart 1, along with corroles that possess two sulfonic acid groups directly attached to the corrole skeleton. The choice of two anchoring groups was made, based on investigations of the binding interactions of Ru$^{II}$ dyes that perform well as sensitizers in DSSCs [8, 9].

RESULTS AND DISCUSSION

Nanoporous TiO$_2$ electrodes were immersed...
overnight in dry 0.5 mM solutions (ethanol or acetonitrile) of FbC, GaC, or SnC (Chart 1). The electronic spectra of the adsorbed corroles are similar to those in solution (a Soret band around 400 nm and Q-band(s) around 600 nm), suggesting that little if any self-aggregation of the dye occurs. The incident photon to current efficiency (IPCE) spectra of the corroles on nanoporous TiO$_2$ (Fig. 1) reveal substantial differences in the efficiencies of the dyes, with GaC > FbC >> SnC. The results obtained for GaC may be compared with those for N3 under identical conditions (Table 1).

The absorbed photon to current efficiency (APCE) plots, which correct for the amount of light absorbed by each corrole, are shown in Fig. 2. Because the APCEs of the corroles are in the same order as their IPCEs, the variation in efficiencies of these dyes is apparently not due to differences in light absorption. Rather, the data of Table 1 suggest that the low efficiency of the SnC-DSSC results from the inability of the excited state to inject electrons into the TiO$_2$ film. Since the reduction potential of the SnC$^{+0}$ couple is over half a volt more positive than those of GaC$^{+0}$, FbC$^{+0}$, and N3$^{+0}$ [10-12], the SnC excited state is not nearly as potent a reductant as GaC$^{+0}$ and FbC$^{+0}$. We conclude that the driving force for electron injection from electronically excited SnC into the conduction band of TiO$_2$ is well below values that would lead to rapid reduction of Ti$^{IV}$ centers [13-16].

In follow-up experiments, we investigated the APCEs of corroles adsorbed on three electrodes that differ in conduction band energies: pure TiO$_2$; SnO$_2$ coated with a thin TiO$_2$ layer; and pure SnO$_2$. The flat band potentials of the conduction bands of the latter two materials are approximately 200 and 450 mV more positive than that of pure TiO$_2$ [17, 18].

![Chart 1.](chart1.png)

**Table 1. Properties of corrole-sensitized TiO$_2$ solar cells**

<table>
<thead>
<tr>
<th></th>
<th>FbC</th>
<th>GaC</th>
<th>SnC</th>
<th>N3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{oc}$ (mV)$^a$</td>
<td>444</td>
<td>524</td>
<td>348</td>
<td>556</td>
</tr>
<tr>
<td>$J_{sc}$ (mA/cm$^2$)$^b$</td>
<td>2.83</td>
<td>4.55</td>
<td>0.58</td>
<td>9.76</td>
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<tr>
<td>fill factor</td>
<td>0.65</td>
<td>0.66</td>
<td>0.60</td>
<td>0.58</td>
</tr>
<tr>
<td>efficiency (%)</td>
<td>0.8</td>
<td>1.6</td>
<td>0.1</td>
<td>3.1</td>
</tr>
<tr>
<td>$E^\circ_p$ (V)$^c$</td>
<td>0.8</td>
<td>0.7</td>
<td>1.4</td>
<td>0.8</td>
</tr>
<tr>
<td>$E^{0}$ (eV)$^d$</td>
<td>$-1.9$</td>
<td>$-2.0$</td>
<td>$-1.9$</td>
<td>$-1.8$</td>
</tr>
<tr>
<td>$E^{0\circ}_{ox}$ (V)$^e$</td>
<td>$-1.1$</td>
<td>$-1.3$</td>
<td>$-0.5$</td>
<td>$-1.1$</td>
</tr>
</tbody>
</table>

$^a$ 0.5M LiI, 0.4 M iodine, 20 mM pyridine, 20 mM pyridinium triflate.
$^b$ Open circuit voltage. $^c$ Short circuit photocurrent density. $^d$ Reduction potential of the corrole radical cation in the indicated complex vs Ag/AgCl in acetonitrile/0.1 M TBAP. $^e$ Estimated for the singlet excited state. $^f$ Estimated reduction potential of the singlet excited state.
differences in APCE values for FbC and GaC are approximately within the experimental error of the measurement. Quite strikingly, however, the APCE of SnC increases from < 0.1 (almost no injection) for pure TiO$_2$ to 0.4-0.5 (virtually identical with the values obtained for FbC and GaC) when bound to electrodes with lower energy conduction bands.

CONCLUSION

We have demonstrated that certain selectively substituted corroles perform well as components of DSSCs, displaying cell efficiencies under AM 1.5 illumination up to half that of an N3-sensitized solar cell and larger than typical values for cells with other tetrapyrrolic sensitizers [2, 3]. The results reveal factors that if optimized could dramatically enhance the performance of corrole-based DSSCs. The driving force for electron injection is one critical factor: corroles (and also other porphyrinoids) with excited-state reduction potentials substantially more positive than roughly -1.0 V will likely not perform well in DSSCs based on TiO$_2$. Work now in progress involves tuning excited-state potentials and other photophysical properties by modification of anchoring groups as well as by metal-ion and corrole-framework substitutions. One challenge is to devise experiments that will help us to understand why the corrole APCEs are only about 50%, less than the roughly 90% for N3.

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REFERENCES