

Corrole-sensitized TiO₂ solar cells

Don Walker^a, Shlomit Chappel^b, Atif Mahammed^c◇, Bruce S. Brunshwig^{*a}, Jay R. Winkler^a, Harry B. Gray^a, Arie Zaban^{*b} and Zeev Gross^{*c}◇

^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

Received 24 July 2006

Accepted 18 September 2006

ABSTRACT: We are investigating the properties of corrole-sensitized TiO₂ solar cells. The TiO₂-adsorbed free base and Ga^{III} corroles display cell efficiencies under AM 1.5 illumination that are about half that of a standard N3-sensitized cell (N3 = *cis*-bis(4,4'-dicarboxy-2,2'-bipyridine)dithiocyanato ruthenium(II)), while that of the Sn^{IV}-based cell is much lower. The properties of the corrole-TiO₂ 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 TiO₂ conduction band. Copyright © 2006 Society of Porphyrins & Phthalocyanines.

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 bacteriopheophylls, 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

[H₃(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 H₃(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 H₃(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 TiO₂ electrodes were immersed

◇SPP full member in good standing

*Correspondence to: Bruce S. Brunshwig, email: bsb@its.caltech.edu, Arie Zaban, email: zabana@mail.biu.ac.il, Zeev Gross, email: chr10zg@tx.technion.ac.il

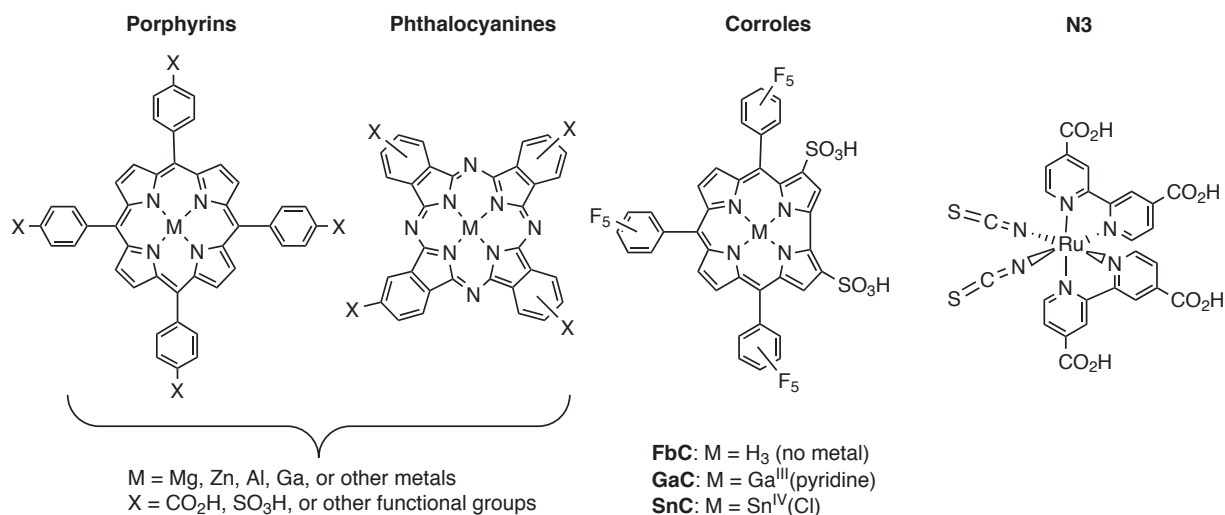


Chart 1.

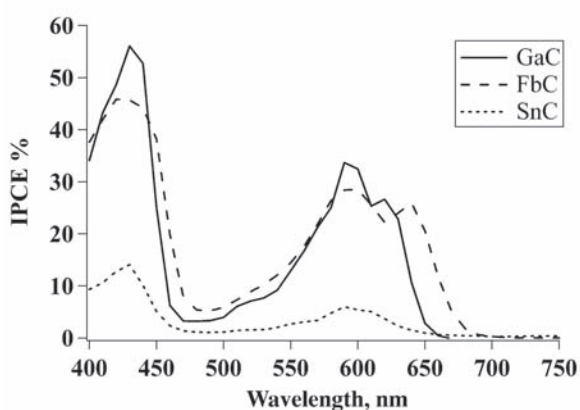


Fig. 1. IPCE spectra of corroles adsorbed to TiO₂ electrodes

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 TiO₂ (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 TiO₂ 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 TiO₂ 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 TiO₂; SnO₂ coated with a thin TiO₂ layer; and pure SnO₂. 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 TiO₂ [17, 18]. The

Table 1. Properties of corrole-sensitized TiO₂ solar cells^a

	FbC	GaC	SnC	N3
V _{oc} (mV) ^b	444	524	348	556
J _{sc} (mA/cm ²) ^c	2.83	4.55	0.58	9.76
fill factor	0.65	0.66	0.60	0.58
efficiency (%)	0.8	1.6	0.1	3.1
E _{gs} ⁰ (V) ^d	0.8	0.7	1.4	0.8
E ⁰⁰ (eV) ^e	~1.9	~2.0	~1.9	~1.8
E _{ex} ⁰ (V) ^f	-1.1	-1.3	-0.5	-1.1

^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.

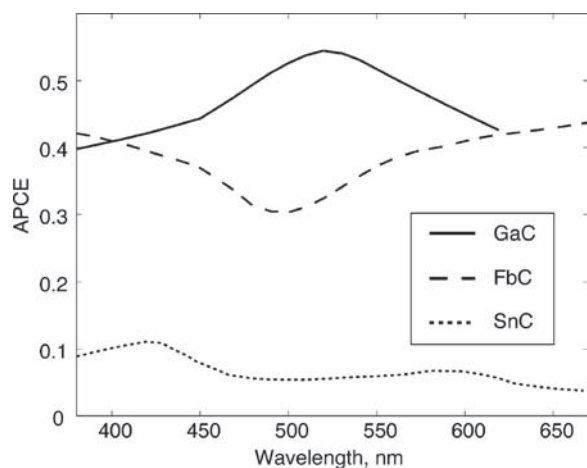


Fig. 2. APCE spectra of corroles adsorbed to TiO₂ electrodes

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 TiO₂ 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 TiO₂. 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**.

Acknowledgements

This work was supported by the Israel Ministry of Infrastructures (AZ); BP and NSF (JRW, BSB, and HBG); and the US-Israel Binational Science Foundation (BSF: ZG and HBG).

REFERENCES

- Robertson N. *Angew. Chem., Int. Ed.* 2006; **45**: 2338-2345.
- Gratzel M. *Chem. Lett.* 2005; **34**: 8-13.
- a) Campbell WM, Burrell AK, Officer DL and Jolley KW. *Coord. Chem. Rev.* 2004; **248**: 1363-1379. b) Wang Q, Campbell WM, Bonfantani EE, Jolley KW, Officer DL, Walsh PJ, Gordon K, Humphry-Baker R, Nazeeruddin MK and Gratzel M. *J. Phys. Chem. B* 2005; **109**: 15397-15409.
- a) Nardis S, Monti D and Paolesse R. *Mini-Rev. Org. Chem.* 2005; **2**: 355-372. b) Koszarna B and Gryko DT. *J. Org. Chem.* 2006; **71**: 3707-3717. c) Geier GR, Chick JFB, Callinan JB, Reid CG and Auguscinski WP. *J. Org. Chem.* 2004; **69**: 4159-4169. d) Gryko DT, Fox JP and Goldberg DP. *J. Porphyrins Phthalocyanines* 2004; **8**: 1091-1105. e) Paolesse R, Marini A, Nardis S, Froiio A, Mandoj F, Nurco DJ, Prodi L, Montalti M and Smith KM. *J. Porphyrins Phthalocyanines* 2003; **7**: 25-36. f) Gros CP, Barbe JM, Espinosa E and Guilard R. *Angew. Chem. Int. Ed.* 2006; **45**: 5642-5645.
- a) Ding T, Aleman EA, Modarelli DA and Ziegler CJ. *J. Phys. Chem. A* 2005; **109**: 7411-7417. b) Ventura B, Degli Esposti A, Koszarna B, Gryko DT and Flamigni L. *New J. Chem.* 2005; **29**: 1559-1566. c) Poulin J, Stern C, Guilard R and Harvey PD. *Photochem. Photobiol.* 2006; **82**: 171-176. d) Gross Z and Gray HB. *Comm. Inorg. Chem.* 2006; **27**: 61-72.
- a) Gross Z, Galili N and Saltsman I. *Angew. Chem., Int. Ed.* 1999; **38**: 1427-1429. b) Gross Z, Galili N, Simkhovich L, Saltsman I, Botoshansky M, Blaser D, Boese R and Goldberg I. *Org. Lett.* 1999; **1**: 599-602 c) Bendix J, Dmochowski IJ, Gray HB, Mahammed A, Simkhovich L and Gross Z. *Angew. Chem., Int. Ed.* 2000; **39**: 4048-4051. d) Mahammed A. and Gross Z. *J. Inorg. Biochem* 2002; **88**: 305. e) Weaver JJ, Sorasaene K, Sheikh M, Goldschmidt R, Tkachenko E, Gross Z and Gray HB. *J. Porphyrins Phthalocyanines* 2004; **8**: 76-81. f) Stavitski E, Berg A, Ganguly T, Mahammed A, Gross Z and Levanon H. *J. Am. Chem. Soc.* 2004; **126**: 6886-6890. g) Wagnert L, Berg A, Stavitski E, Berthold T, Kothe G, Goldberg I, Mahammed A, Simkhovich L, Gross Z and Levanon H. *Appl. Magn. Reson.* 2006; in press.
- a) Mahammed A, Goldberg I and Gross Z. *Org. Lett.* 2001; **3**: 3443-3446. b) Saltsman I, Mahammed A, Goldberg I, Tkachenko E, Botoshansky M and Gross Z. *J. Am. Chem. Soc.* 2002; **124**: 7411-7420.

8. Hagfeldt A and Grätzel M. *Acc. Chem. Res.* 2000; **33**: 269-277.
9. Kilså K, Mayo EI, Brunschwig BS, Gray HB, Lewis NS and Winkler JR. *J. Phys. Chem. B* 2004; **108**: 15640-15651.
10. Simkhovich L, Mahammed A, Goldberg I and Gross Z. *Chem. Eur. J.* 2001; **7**: 1041-1055.
11. Nazeeruddin MK, Kay A, Rodicio I, Humphry-Baker R, Muller E, Liska P, Vlachopoulos N and Gratzel M. *J. Am. Chem. Soc.* 1993; **115**: 6382-6390.
12. Sauve G, Cass ME, Coia G, Doig SJ, Lauermann I, Pomykal KE and Lewis NS. *J. Phys. Chem. B* 2000; **104**: 6821.
13. Ferrere S, Zaban A and Gregg BA. *J. Phys. Chem. B* 1997; **101**: 4490-4493.
14. Asbury JB, Hao E, Wang YQ, Ghosh HN and Lian TQ. *J. Phys. Chem. B* 2001; **105**: 4545-4557.
15. Van De Lagemaat J, Park NG and Frank AJ. *J. Phys. Chem. B* 2000; **104**: 2044-2052.
16. Bisquert J, Ruhle S, Cahen D, Hodes G and Zaban A. *J. Phys. Chem. B.* 2004; **108**: 8106-8118.
17. Chappel S, Chen SG and Zaban A. *Langmuir* 2002; **18**: 3336.
18. Kalyanasundaram K and Gratzel M. *Coord. Chem. Rev.* 1998; **177**: 347-414.