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## Remarkable synergistic effects in a mixed porphyrin dye-sensitized TiO<sub>2</sub> film

Attila J. Mozer

University of Wollongong, attila@uow.edu.au

Gordon G. Wallace

University of Wollongong, gwallace@uow.edu.au

David L. Officer

University of Wollongong, davido@uow.edu.au

Matthew Griffith

University of Wollongong, mjg48@uow.edu.au

Pawel W. Wagner

University of Wollongong, pawel@uow.edu.au

*See next page for additional authors*

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## Remarkable synergistic effects in a mixed porphyrin dye-sensitized TiO<sub>2</sub> film

### Abstract

A remarkable 300% efficiency enhancement driven by a matching increase in the short circuit current was observed in a mixed porphyrin dye-sensitized solar cell constructed from two dyes in a 3:1 ratio.

Absorbed photon-to-current conversion efficiency measurements indicate an improved charge injection yield for both dyes in the mixture. Several possible origins for the observed performance enhancement are discussed.

### Keywords

Remarkable, synergistic, effects, mixed, porphyrin, dye, sensitized, TiO<sub>2</sub>, film

### Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

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### Authors

Attila J. Mozer, Gordon G. Wallace, David L. Officer, Matthew Griffith, Pawel W. Wagner, Klaudia K. Wagner, George Tsekouras, Shogo Mori, and Ying Dong

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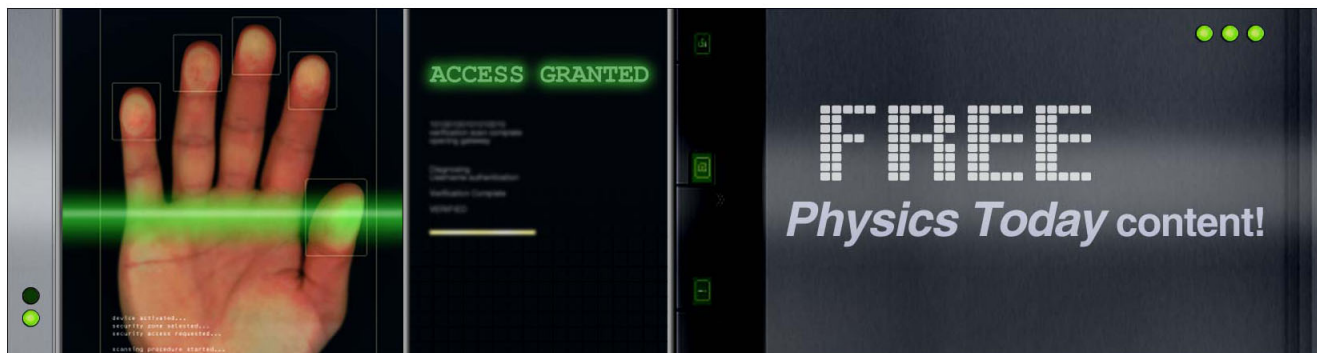
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## ADVERTISEMENT



## Remarkable synergistic effects in a mixed porphyrin dye-sensitized TiO<sub>2</sub> film

Matthew J. Griffith,<sup>1,a)</sup> Attila J. Mozer,<sup>1</sup> George Tsekouras,<sup>1,b)</sup> Ying Dong,<sup>1</sup> Pawel Wagner,<sup>1</sup> Klaudia Wagner,<sup>1</sup> Gordon G. Wallace,<sup>1</sup> Shogo Mori,<sup>2</sup> and David L. Officer<sup>1,a)</sup>

<sup>1</sup>ARC Centre of Excellence for Electromaterials Science and Intelligent Polymer Research Institute, AIIM Facility, Innovation Campus, University of Wollongong, New South Wales 2522, Australia

<sup>2</sup>Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan

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A remarkable 300% efficiency enhancement driven by a matching increase in the short circuit current was observed in a mixed porphyrin dye-sensitized solar cell constructed from two dyes in a 3:1 ratio. Absorbed photon-to-current conversion efficiency measurements indicate an improved charge injection yield for both dyes in the mixture. Several possible origins for the observed performance enhancement are discussed. © 2011 American Institute of Physics.

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Dye-sensitization of nanocrystalline metal oxides has emerged as an attractive pathway for various technologies, including gas sensors, electrochromic displays, and photoelectrochemical energy conversion.<sup>1</sup> The majority of these devices employ a single photosensitizer, however, optimizing the performance of most single dyes to achieve high efficiencies is difficult. This is because the desirable properties for efficient electron injection (good electronic coupling between dye and oxide, a high density of states in the semiconductor, and a moderate free energy driving force from the dye excited state to the oxide conduction band) and dye regeneration (moderate free energy driving force between dye and redox mediator) are often incompatible with those required for broad visible and near-IR absorption (low dye bandgap).<sup>2</sup> A mixed dye system in which these different functions are distributed between the various constituents presents an interesting concept for device design. However, combining dyes also creates several new potential photo-physical pathways, including energy transfer between dyes,<sup>3</sup> electron or hole injection from one dye to another,<sup>4</sup> and chemical reactions between the dyes.<sup>5</sup> These interactions can be harnessed in a synergistic fashion to improve injection,<sup>6</sup> light harvesting,<sup>7</sup> or to limit recombination. However, most previous attempts to improve multiple device functions by direct cosensitization have failed.

In this letter we report an unexpected significant improvement in the performance of inefficient porphyrin photosensitizers when simultaneously anchored to the TiO<sub>2</sub> electrode of a dye-sensitized solar cell (DSSC). Using absorbed photon-to-current conversion efficiency (APCE) measurements, we demonstrate an increased charge generation yield for both dyes when they are present as a mixture. This exciting result demonstrates the potential for achieving similar enhancement effects using a wide range of alternative sensitizers.

Current density-voltage curves for the individual dyes and the mixture with the highest performance (76% ZnNC on TiO<sub>2</sub> or ~3:1 ZnNC:FbC) are shown in Fig. 1. The solar-

to-electrical power conversion efficiency of each mixture surpassed those of either dye individually, increasing from 0.4% for FbC and 0.7% for ZnNC to 2.1% for the best mixture. The mixture efficiency exceeds the sum of the two individual dyes, exhibiting an increase of ~300%. Efficiency values for the individual dyes are limited by poor electron injection for these dyes,<sup>8</sup> most likely due to the poor overlap of the dye lowest unoccupied molecular orbital (LUMO) with TiO<sub>2</sub> conduction band states.

The optimized mixture ratio was determined from measured DSSC efficiency and short circuit current densities ( $J_{sc}$ ) for devices sensitized with dye mixtures in various ratios (Fig. 2 inset). Efficiency enhancements are driven by a matching increase in the  $J_{sc}$ , improving from 0.95 mA cm<sup>-2</sup> for FbC and 1.37 mA cm<sup>-2</sup> for ZnNC to 3.75 mA cm<sup>-2</sup> for the 3:1 mixture. The open circuit voltage ( $V_{oc}$ ) of the mixed DSSCs also increased, from 580 mV for FbC and 650 mV for ZnNC to 685 mV for the best mixture. The simultaneous improvement in  $J_{sc}$  and  $V_{oc}$  for a cosensitized DSSC could have a significant impact on future device design.

Figure 2 also compares the incident photon-to-current conversion efficiency (IPCE) spectra of the dyes alone and in a 3:1 ZnNC:FbC mixture. The IPCE increases equally across all wavelengths for the mixed dye device. Significantly, both dyes display improved performance in the mixture compared to their performance as individual sensitizers.

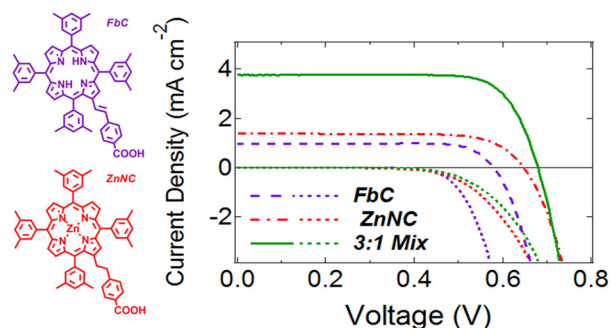


FIG. 1. (Color online) Chemical structures for the dyes employed in this study and current density-voltage curves under AM 1.5 solar illumination for devices sensitized with ZnNC (dash-dot), FbC (dashed), and a 3:1 ZnNC:FbC mixture (solid). Dark curves are shown as dotted lines.

<sup>a)</sup>Electronic addresses: mjg48@uow.edu.au and davido@uow.edu.au. Tel.: +612 4298 1457. FAX: +612 4221 3114.

<sup>b)</sup>Present address: School of Chemistry, University of St Andrews, North Haugh, St Andrews, Fife, KY16 9ST, Scotland, United Kingdom.

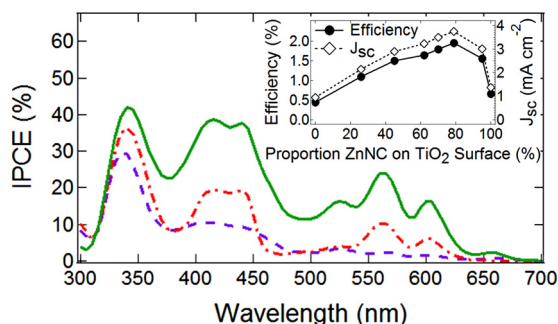


FIG. 2. (Color online) Incident photon-to-current efficiencies (IPCEs) for devices sensitized with ZnNC (dash-dot), FbC (dashed), and a 3:1 ZnNC:FbC mixture (solid). The inset shows variation in DSSC efficiencies (solid) and  $J_{sc}$  (dashed line) for mixed devices with various dye ratios.

APCE spectra of thin-film ( $\sim 2 \mu\text{m}$ ) DSSCs, shown in Fig. 3, were calculated from measured IPCE curves (details in SI) to further investigate the origin of the mixture enhancements. Assuming negligible charge collection losses for thin films, APCE spectra are determined by the charge generation yield of the dyes under operating conditions. Measured diffusion lengths indicate this assumption is valid for ZnNC and the mixture, however, FbC most likely experiences some recombination, meaning the internal quantum efficiency is probably higher than the APCE. The individual dyes show low APCE values of  $\sim 2\%$  for FbC and  $\sim 7\%$  for ZnNC. In comparison, an N719 reference exhibits an APCE of  $\sim 100\%$ , in agreement with reported injection values for this dye.<sup>9</sup> The APCE of the 3:1 mixture is  $\sim 24\%$ , significantly higher than either individual dye. The mixture APCE is enhanced in the absorption regions of both dyes, indicating injection yields for both dyes are enhanced in the mixture. The mixture APCE is also  $\sim 350\%$  higher than that of ZnNC, closely correlating with the magnitude of the  $J_{sc}$  and efficiency enhancements and also exhibiting similar mixture ratio dependence (Fig. 3 inset). This provides clear evidence that an improvement in the charge generation yield of both dyes produces the enhancements in the  $J_{sc}$ .

A number of physical phenomena could be responsible for enhanced performance in the mixture, such as closer packing of the dyes on the  $\text{TiO}_2$  resulting in reduced recombination, prevention of porphyrin aggregation or enhanced dye electronic coupling to  $\text{TiO}_2$ . A comparison of the total dye surface coverage measured from desorbed dye solutions shows minimal differences, with coverages of  $(6.5 \pm 0.5)$

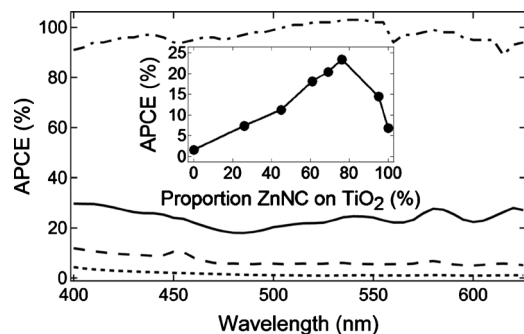


FIG. 3. APCEs for devices sensitized with ZnNC (dashed), FbC (dotted), the 3:1 ZnNC:FbC dye mixture (solid) and N719 (dashed-dotted). The inset displays average mixture APCEs as a function of the amount of ZnNC present on the  $\text{TiO}_2$ .

$\times 10^{-9} \text{ mol cm}^{-2} \mu\text{m}^{-1}$  determined for FbC, ZnNC, and each of the different dye mixtures (see Table III, Ref. 10). Therefore, combining the dyes has very little effect on the packing density on  $\text{TiO}_2$ .

As in previous work,<sup>11</sup> no evidence for porphyrin aggregation was observed. The absence of aggregates for both dyes was confirmed by adding chenodeoxycholic acid, a cosensitizer used to disrupt aggregation,<sup>12</sup> to sensitizing solutions of ZnNC and FbC. Neither dye displayed an improvement, indicating aggregation is not a limiting factor for these dyes. The formation of heteroaggregates or a complex between the dyes was also discounted since the UV-vis and IPCE spectra were unchanged, with the absorption spectrum of the optimal mixture closely reconstructed from a linear combination of the individual dye spectra (Fig. S1).<sup>10</sup>

Combining dyes could also alter the surface adsorption environment, increasing dye coupling to  $\text{TiO}_2$ . To examine this,  $\text{TiO}_2$  binding modes for individual dyes and the 3:1 mixture were analyzed. The carboxylate peaks were unchanged for both individual dyes and the mixed system (Fig. S4).<sup>10</sup> Peak positions, determined by analyzing  $\text{TiO}_2$  sensitized with a benzoic acid linker (Fig. S4 inset),<sup>10</sup> were located at  $1387$  and  $1527 \text{ cm}^{-1}$  for ZnNC, FbC, and the 3:1 mixture, indicative of bridging bidentate binding modes for both dyes and the mixture as in previous studies.<sup>13</sup>

Energy or electron transfer from ZnNC to FbC is one possible explanation for the improved injection yield of ZnNC. Such photoinduced excited state interactions could affect the charge generation yield through two key processes; either injection into the  $\text{TiO}_2$  conduction band, or the degree of asymmetry between the rates for dye ground state regeneration and recombination of conduction band electrons. Energy transfer from ZnNC to FbC is possible due to the spectral overlap between ZnNC emission and FbC absorption,<sup>9</sup> and could allow ZnNC to inject through a more efficient conjugated pathway. The theoretical quantum yield for this process was calculated as 85% assuming an isotropic dipole orientation, donor fluorescence yield of 0.05, and an intermolecular spacing of  $16 \text{ \AA}$  (pp. S6, SI). This value neglects deactivation of excited ZnNC by electron injection, providing an upper limit on the energy transfer yield.<sup>14</sup> Measurements of emission and photoluminescence excitation spectra (at FbC emissions) for the dye mixture adsorbed onto  $\text{ZrO}_2$  (a high band gap semiconducting oxide which prevents electron injection) were inconclusive, however, IPCE measurements in which FbC is replaced with a noninjecting free base analog suggest the free base dye is responsible for a much larger proportion of the mixture photocurrent than its fractional absorbance would allow, thus supporting the concept of energy (or electron) transfer. We note however that to increase the injection yield for ZnNC, the internal quantum efficiency for FbC must also be increased simultaneously.

Charge transfer interactions could also affect injection yields in the mixture. ZnNC has higher highest occupied molecular orbital and LUMO energies compared to FbC, enabling hole transfer (HT) from  $\text{FbC}^+$  to neutral ZnNC (Fig. S3).<sup>10</sup> Similar processes between zinc and free base porphyrins have been previously observed on picosecond timescales.<sup>15</sup> Such HT may lead to an improved charge generation yield for FbC if  $k_{\text{HT}} \gg k_{\text{EDR,FbC}} \gg k_{\text{DR,FbC}}$ , where  $k_{\text{EDR,FbC}}$  is the rate constant for charge recombination between  $\text{TiO}_2$  electrons and  $\text{FbC}^+$ , and  $k_{\text{DR,FbC}}$  is the rate constant for dye regeneration of FbC. Transient absorption mea-

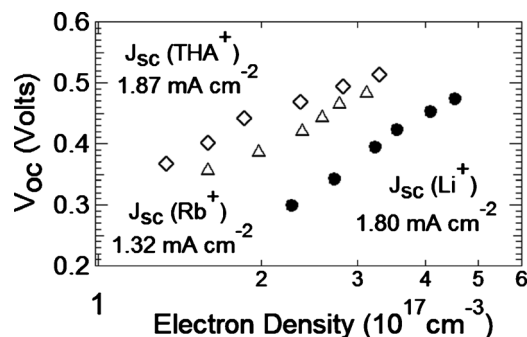


FIG. 4. Open circuit voltage plotted as a function of electron density in the  $\text{TiO}_2$  for DSSCs sensitized with a 3:1 ZnNC:FbC mixture containing either  $\text{Li}^+$  (circles),  $\text{Rb}^+$  (triangles), or  $\text{THA}^+$  (diamonds) cations in the electrolyte.

measurements designed to detect such a fast recombination component for FbC<sup>+</sup> and examine its possible removal in the mixture are currently being performed. It is also possible that a charge transfer complex could form between the photooxidized and neutral porphyrin dyes which alters their recombination kinetics. The existence of one-electron holes delocalized over metallated and free base porphyrins is well established.<sup>16</sup> Spectroelectrochemical studies of the 3:1 ZnNC:FbC mixture in solution and on  $\text{TiO}_2$  shows some evidence for interaction of the oxidized ZnNC with the neutral FbC (Fig. S5),<sup>10</sup> however the interaction is absent for the dye mixture on  $\text{TiO}_2$  (Fig. S6).<sup>10</sup>

The possibility that mixing the dyes could reduce the barrier potential and/or distance for through-space electron tunneling from the dyes to  $\text{TiO}_2$  was also considered. Given its lower LUMO energy, modifying the  $\text{TiO}_2$  conduction band edge potential ( $E_{\text{CB}}$ ) should affect the injection energetics for FbC more than for ZnNC, which could aid in elucidating injection behavior in the mixture. To examine this, the cation species in the redox electrolyte was altered to reside near the  $\text{TiO}_2$  surface (lithium,  $\text{Li}^+$ ) or outside the dye layer (tetrahexylammonium,  $\text{THA}^+$ ) due to size. Replacing  $\text{Li}^+$  cations with  $\text{THA}^+$  produced a  $\sim 150$  mV negative shift in  $E_{\text{CB}}$  (measured using stepped-light induced photovoltage transients and charge extraction techniques),<sup>17</sup> however, the  $J_{\text{sc}}$  of the device was unaffected (Fig. 4). This result cannot be explained by energy transfer or hole transfer mechanisms since inducing a negative shift in  $E_{\text{CB}}$  by replacing adsorbed  $\text{Li}^+$  ions with bulky  $\text{THA}^+$  cations which cannot approach the  $\text{TiO}_2$  should also reduce the driving force for injection, reducing  $J_{\text{sc}}$  unless the density of available acceptor states is unchanged.<sup>18</sup> An alternative explanation was thus considered; that the local potential profile at the  $\text{TiO}_2$ /dye interface could be altered by mixing the dyes, an effect which is amplified for  $\text{THA}^+$  as the Helmholtz double layer extends beyond the dye layer for this cation and thus does not screen these electric fields. A third electrolyte in which  $\text{Li}^+$  was replaced with rubidium ( $\text{Rb}^+$ ) was employed to examine this concept. Both these cations can approach the surface and create a compact double layer, thus screening of any electric fields will be unaffected. Replacing  $\text{Li}^+$  with  $\text{Rb}^+$  produced a  $\sim 125$  mV negative shift in  $E_{\text{CB}}$ , but also resulted in a 30%  $J_{\text{sc}}$  decrease, confirming purely negative shifts in  $E_{\text{CB}}$  reduce the  $J_{\text{sc}}$ . The unaffected current for  $\text{THA}^+$  devices is therefore consistent with the concept of local electric fields which can aid injection. In this instance the mixture enhancement could arise from a local electric field which develops from an in-

homogeneous double layer when the dyes are combined. This field, present only in the mixture, could improve electron injection from both dyes by aiding charge separation, reducing the barrier height for through-space electron tunneling or altering dipole alignment. The magnitude of such fields and their quantitative impact on injection for these dyes cannot be deduced from these results.

In summary, we have combined two individually poor dyes in a specific 3:1 ratio to create a mixed porphyrin DSSC which exhibits a remarkable simultaneous increase in  $J_{\text{sc}}$  and  $V_{\text{oc}}$ , and consequently overall device efficiency. The enhancement is due to improved charge generation yields for both dyes when present as a mixture. While the reported effect is exciting, there are multiple processes which may contribute to its origin, thus a greater understanding of the mechanism is necessary to extend the principle to alternative sensitizers in the future. Further studies employing transient absorption and luminescence lifetimes measurements to elucidate the exact origin of the mixture enhancement effect remain ongoing.

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