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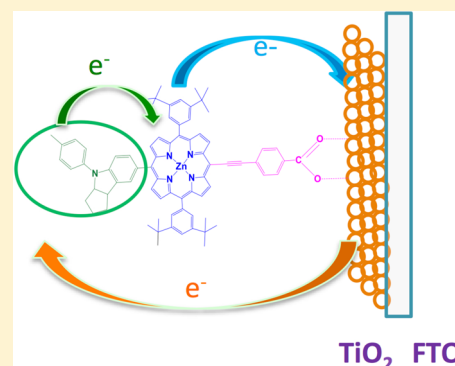
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Supporting Information

ABSTRACT: Dye-sensitized solar cell (DSC) devices were fabricated using a novel donor-(π bridge)-acceptor (D- π -A) porphyrin sensitizer, VC-70, in which an indoline is linked directly to the porphyrin core and functions as the donor group. The best efficiencies of VC-70 and reference YD2-o-C8 devices were found to be 7.31 and 7.60%, respectively, and AMG 1.5 illumination and device properties were fully characterized using transient absorption, charge extraction, and transient photovoltage techniques. A notable effect on TiO₂ conduction band energetics and electron lifetime was observed following light soaking of VC-70 devices under AMG 1.5 illumination. Upon cosensitization of VC-70 with the organic dye D205 an improved efficiency of 8.10% was obtained.



INTRODUCTION

The emergence of dye-sensitized solar cells (DSCs)¹² based on organic sensitizers is evident in the recent literature.³⁴⁵⁶ The development of porphyrin sensitizers with donor-(π bridge)-acceptor (D- π -A) structure in which the porphyrin ring core constitutes the π -bridge has led to efficiencies which rival the best Ru(II) polypyridal dyes employing the iodide/tri-iodide (I⁻/I₃⁻) electrolyte.⁷⁸⁹¹⁰ For such structures the best acceptor has been found to be carboxylic acid providing optimal electronic contact with the nanocrystalline TiO₂.¹¹ Donor groups have included triphenylamine,⁸ diphenylamine,⁶⁷ pyrene,¹⁰ and bulky fluorenyl groups,¹² among others. In this work, for the first time an indoline group as the donor is incorporated into a D- π -A porphyrin, VC-70 (Scheme 1). Indoline has been used in several recent studies as a donor in D- π -A organic sensitizers.¹³¹⁴¹⁵ In agreement with a recent study by this group on a related indoline D- π -A organic dye,¹³ the efficiency of DSCs fabricated with VC-70 was found to increase with post fabrication light soaking.

EXPERIMENTAL SECTION

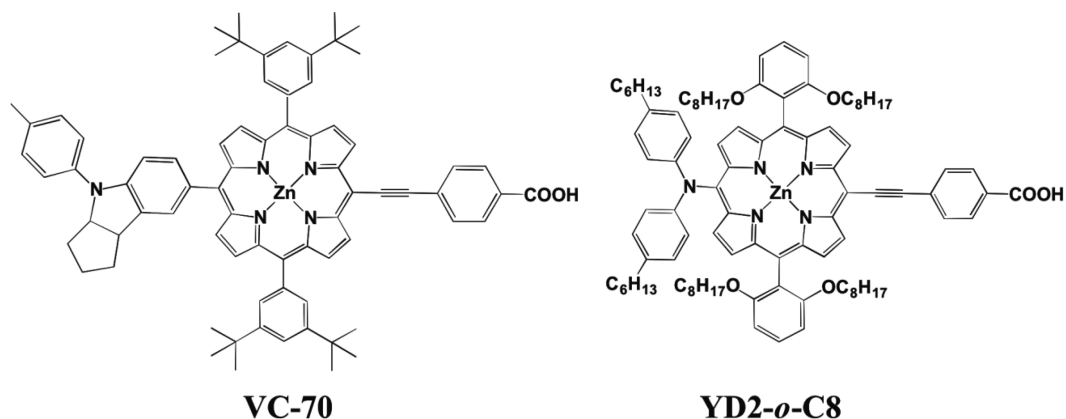
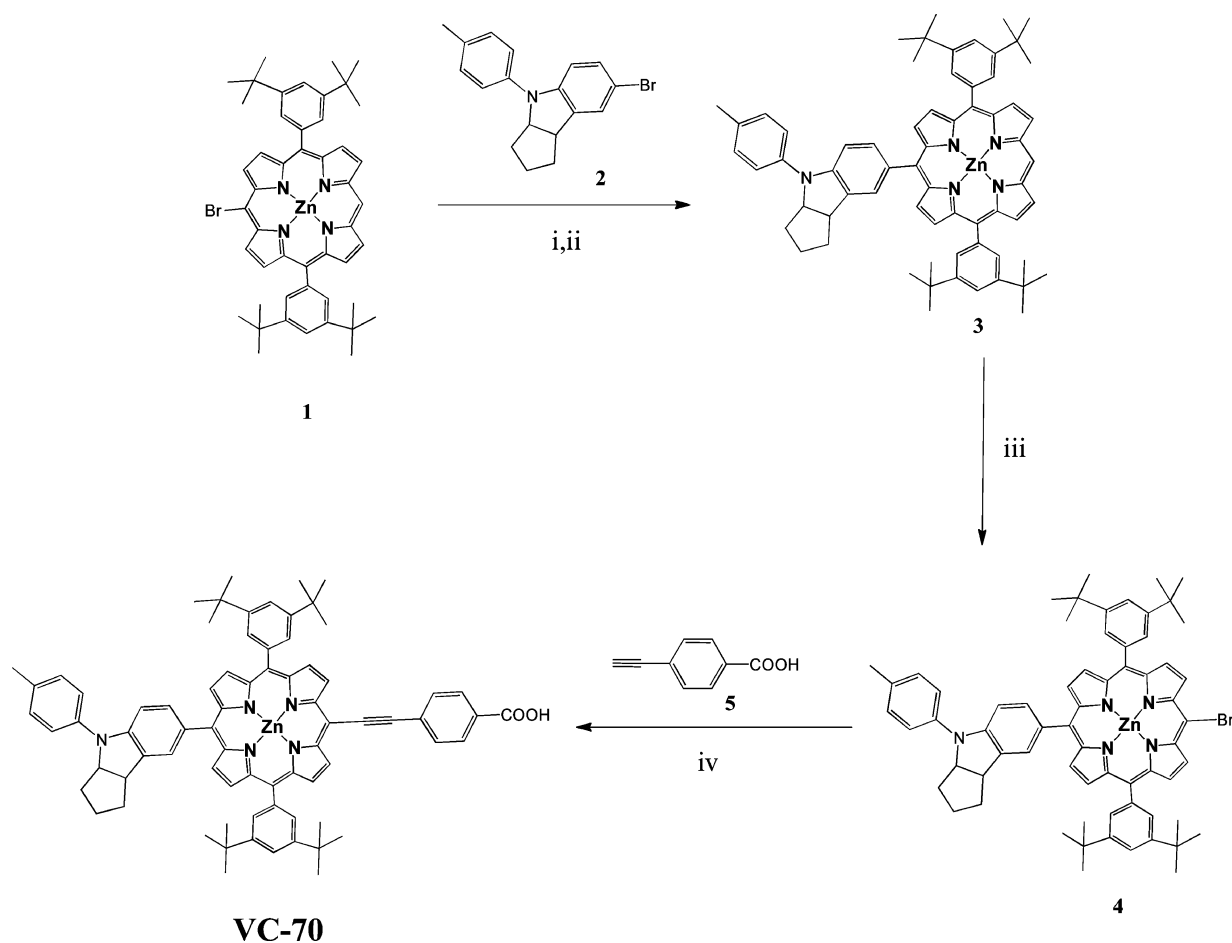
Device Preparation. The working and counter electrodes consisted of TiO₂ and thermalized platinum films, respectively, and were deposited onto F-doped tin oxide (FTO, Pilkington Glass Inc., with 15 Ω sq⁻¹ sheet resistance) conducting glass substrates. Two different types of TiO₂ films were utilized depending on the measurements being conducted. Highly transparent thin films (4 μ m) were utilized for laser transient absorption spectroscopy (L-TAS) measurements, and efficient DSC devices were made using 13 μ m thick films consisting of 20 nm TiO₂ nanoparticles (Dyesol paste) and a scattering layer

of 4 μ m of 400 nm TiO₂ particles (Dyesol paste). Prior to the deposition of the TiO₂ paste, the conducting glass substrates were immersed in a solution of TiCl₄ (40 mM) at 70 °C for 30 min and then dried. The TiO₂ nanoparticle paste was deposited onto a conducting glass substrate using the screen-printing technique. The TiO₂ electrodes were gradually heated under an airflow at 325 °C for 5 min, 375 °C for 5 min, 450 °C for 15 min, and 500 °C for 15 min. The heated TiO₂ electrodes were immersed again in a solution of TiCl₄ (40 mM) at 70 °C for 30 min and then washed with ethanol. The electrodes were heated again at 500 °C for 30 min and cooled before dye adsorption. The active area for devices was 0.16 cm². The counter electrode was made by spreading a 5 mM solution of H₂PtCl₆ in isopropyl alcohol onto a conducting glass substrate containing a small hole to allow the introduction of the liquid electrolyte using vacuum, followed by heating at 390 °C for 15 min. Films were sensitized in 0.1 mM VC-70 solutions in ethanol containing 0.5 mM chenodeoxycholic acid overnight at room temperature. For cosensitized devices, films were first sensitized for 3 h in a 0.5 mM solution of D205 in acetonitrile/*tert*-butanol (1:1) containing 1 mM chenodeoxycholic acid followed by 3 h sensitization in the VC-70 solution. Finally, the working and counter electrodes were sandwiched together using a thin thermoplastic (Surlyn) frame that melts at 100 °C. The electrolyte for all devices measured consisted of 0.5 M 1-butyl-3-methylimidazolium iodide (BMII), 0.1 M lithium iodide, 0.05

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Scheme 1. Molecular Structures of VC-70 and YD2-*o*-C8Scheme 2. Synthetic Route of VC-70^a

^aReaction conditions: (i) *n*-BuLi, THF, B(OCH₃)₃, −78 °C; (ii) Pd(PPh₃)₄, 2 M K₂CO₃ aqueous solution, THF, 6 h, 80 °C; (iii) NBS, DCM, pyridine, room temperature; (iv) Pd₂(dba)₃, AsPh₃, dry THF, NEt₃, reflux 6 h.

73 M iodine, and 0.5 M *tert*-butylpyridine in a mixture of
74 acetonitrile/valeronitrile (85:15).

75 **Characterization Techniques.** UV–vis absorption spectra
76 were measured in a 1 cm path-length quartz cell using a
77 Shimadzu model 1700 spectrophotometer. Steady state
78 fluorescence spectra were recorded using a Spex model
79 Fluoromax-3 spectrofluorometer using a 1 cm quartz cell. ¹H
80 NMR spectra were recorded at 300 MHz on a Bruker 300
81 Avance NMR spectrometer with X-WIN NMR software. ¹H

spectra were referenced to tetramethylsilane. MALDI mass
82 spectra were recorded on a Water Quattro micro (Water Inc.,
83 USA). Cyclic voltammetric experiments were carried out with a
84 PC-controlled CH instruments model CHI620C electro-
85 chemical analyzer.
86

The IV characteristics of cells were measured using a Sun
87 2000 Solar Simulator (150 W, ABET Technologies). The
88 illumination intensity was measured to be 100 mW/m² with a
89 calibrated silicon photodiode. The appropriate filters were 90

91 utilized to faithfully simulate the AM 1.5G spectrum. The
92 applied potential and cell current were measured with a
93 Keithley 2400 digital source meter.

94 Transient photovoltage and charge extraction measurements
95 were carried out on a system described elsewhere.¹⁶ In charge
96 extraction, white light from a series of light-emitting diodes
97 (LEDs) was used as the light source. When the LEDs are
98 turned off the cell is immediately short-circuited, and the charge
99 is extracted allowing electron density in the cells to be
100 calculated. By changing the LED intensity the electron density
101 can be estimated as a function of cell voltage. In transient
102 photovoltage measurements, in addition to the white light
103 applied by the LEDs, constant background voltage is applied to
104 the cells, and again, a diode pulse (660 nm, 10 mW) is then
105 applied to the sample inducing a change of 2–3 mV within the
106 cell. The resulting photovoltage decay transients are collected,
107 and the τ values are determined by fitting the data to the
108 equation $\exp(-t/\tau)$.

109 Laser-transient absorption spectroscopy measurements were
110 carried out using a system described previously.¹⁶ Kinetics were
111 recorded in a blank electrolyte consisting of 0.5 M *tert*-
112 butylpyridine in acetonitrile and the iodide/tri-iodide electro-
113 lyte used for optimized 0.16 cm² devices.

114 ■ RESULTS AND DISCUSSION

115 The synthetic route of porphyrin dye VC-70 is depicted in
116 Scheme 2. An ethyne bridge provides a well-defined and rigid
117 structural arrangement, and for this reason ethynyl benzoic acid
118 was selected as the electron acceptor and the anchoring group.
119 The synthesis of the target dye VC-70 was achieved using a
120 convergent synthetic strategy on the basis of Suzuki coupling of
121 indoline borate with bromo porphyrin (1) in the presence of
122 Pd(PPh₃)₄ and K₂CO₃ in dry tetrahydrofuran (THF), and a
123 simple bromination was performed on the reactive porphyrin
124 unit (4). The ethynyl benzoic acid group was attached to the
125 *meso* position via catalyzed Sonagashira coupling. The
126 important intermediates and the targeted dye VC-70 were
127 well characterized by ¹H NMR, ¹³C NMR, and matrix-assisted
128 laser desorption/ionization (MALDI) mass spectroscopy.

129 The absorption and emission spectra of VC-70 and YD2-*o*-
130 C8 in solution are shown in Figure 1, and their photophysical
131 and electrochemical characteristics are collected in Table 1.

132 Both dyes show typical absorption bands associated with
133 porphyrins, namely, an intense Soret band at around 445 nm
134 and a series of lower intensity Q bands at longer wavelength
135 (550–700 nm). It is noticeable that though the molar
136 extinction coefficients of the Q-bands are comparable the
137 Soret band of VC-70 is nearly double that of YD2-*o*-C8 (Figure
138 S3, Supporting Information). Strong emission at around 660
139 nm was observed for both dyes. There is a clear shift of 15 nm
140 in both absorption and emission for VC-70 toward the blue.
141 Cyclic voltammetry studies measured in solution (Figure S4,
142 Supporting Information) show that the ground state oxidation
143 potential (E_{ox}) of VC-70 is 70 mV more positive than that of
144 YD2-*o*-C8. Both photophysical and electrochemical studies
145 suggest that the band gap of VC-70 is larger than that of YD2-
146 *o*-C8. This may be due to a lack of coplanarity between the
147 planar indoline and porphyrin core in VC-70, making the
148 indoline a weaker electron-donating group than the diphenyl-
149 amine of YD2-*o*-C8. This is also indicated by the stronger and
150 more blue absorbing Soret band in VC-70, which has been
151 observed in other D- π -A dyes where no or weakly electron-
152 donating groups have been placed in the *meso*-position opposite

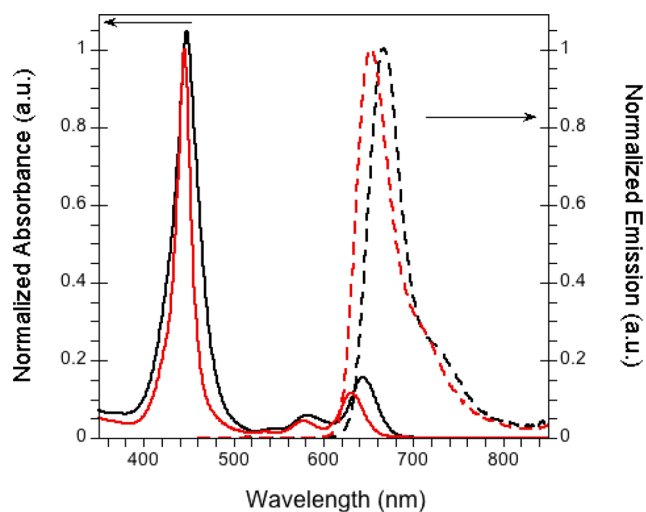


Figure 1. Normalized absorption (solid) and emission (dashed) spectra of YD2-*o*-C8 (black) and VC-70 (red) in THF.

to the anchoring group.¹⁷ It is noted that the *meso*-phenyls in YD2-*o*-C8 are functionalized at the *ortho*-positions with electron-donating dioctyloxy substituents, whereas the *meso*-phenyls in VC-70 contain *tert*-butyl groups. This may also contribute to the differences in photochemical and electrochemical properties observed as noted elsewhere.⁶

The E_{HOMO} and E_{LUMO} values calculated from photophysical and electrochemical data in Table 1 indicate that efficient dye regeneration by the I^-/I_3^- redox electrolyte ($E_{redox} = -4.75$ eV) and also efficient electron injection into the TiO₂ conduction band ($E_{TiO_2} = -4.0$ eV) are energetically favorable for these sensitizers.

YD2-*o*-C8 and VC-70 were used to fabricate DSC solar cells and measured under standard illumination conditions (AM 1.5G 100 mW/m²). Device properties are listed in Table 2. Devices were measured before and after 90 min of continuous illumination to investigate the effect of light soaking on device performance.

The YD2-*o*-C8 device shows an efficiency of 7.60% which compares extremely well with literature values.¹⁴ Upon 90 min light soaking there is little difference in device performance. On the other hand, the efficiency of the VC-70 device increases markedly from 5.59 to 7.31% with light soaking, an increase of 31%. The reasons for this increase will be discussed further on. The much higher V_{oc} for the YD2-*o*-C8 device can be ascribed to the hexyl chains on the diphenylamine donor and the dioctyloxy substituents on the *meso*-phenyls which are superior at blocking recombination of TiO₂ electrons with the electrolyte and also preventing aggregation than the *tert*-butyl groups of VC-70.^{6,11} The $I-V$ curves are shown in Figure 2.

Electron density and electron lifetimes in these devices were probed using charge extraction and transient photovoltage measurements, respectively (Figure 3). Before light soaking, YD2-*o*-C8 and VC-70 devices show similar charge densities, but electron lifetimes in the YD2-*o*-C8 device are considerably longer than those of the VC-70 device at the same electron density. This explains the 100 mV higher V_{oc} for the reference YD2-*o*-C8 device. Upon light soaking for 90 min, the charge extraction data show an increase in charge density for the VC-70 device suggesting a downward shift in the TiO₂ conduction band. Electron density in the YD2-*o*-C8 device remains unchanged. Transient photovoltage data also show no effect

Table 1. Absorption, Emission, and Electrochemical Properties of YD2-*o*-C8 and VC-70

dye	λ_{abs} (nm) ^a	λ_{em} (nm) ^a	E_{ox} (V vs Fc/Fc+) ^b	E_{0-0} (eV) ^c	E_{HOMO} (eV) ^d	E_{LUMO} (eV) ^e
YD2- <i>o</i> -C8	448(21.04), 583(1.17), 642(3.01)	667	0.165	1.90	−5.05	−3.15
VC-70	445(41.46), 557(1.83), 630(4.46)	653	0.235	1.94	−5.12	−3.18

^aMeasured in THF. In parentheses molar extinction coefficient (ϵ) at λ_{abs} ($10^3 \text{ M}^{-1} \text{ cm}^{-1}$). ^bMeasured in 0.1 M tetrabutylammonium hexafluorophosphate in THF at scan rates of 50 mV s^{-1} (YD2-*o*-C8) and 100 mV s^{-1} (VC-70). The working electrode consisted of a platinum wire and the counter electrode a platinum mesh. The reference electrode was the silver calomel electrode (saturated KCl). All solutions were degassed with argon for 5 min prior to measurement. ^c E_{0-0} (energy for the electronic transition to and from the lowest vibrational states of a molecule) was determined from the intersection of absorption and emission spectra in dilute solutions. ^d E_{HOMO} was calculated using $E_{\text{HOMO}} \text{ (vs vacuum)} = -4.88 - E_{\text{ox}} \text{ (vs Fc/Fc+)}$. ^e E_{LUMO} was calculated using $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{0-0}$.

Table 2. Device Properties of YD2-*o*-C8 and VC-70 DSC Devices

dye	V_{oc} (V)	J_{sc} (mA/cm ²)	FF ^d (%)	η (%) ^c
YD2- <i>o</i> -C8 (0 min) ^a	0.774	13.48	73	7.60
YD2- <i>o</i> -C8 (90 min) ^b	0.774	12.83	75	7.43
VC-70 (0 min) ^a	0.674	12.20	67	5.59
VC-70 (90 min) ^b	0.699	14.47	72	7.31

^aRecorded after 0 min illumination. ^bRecorded after 90 min continuous illumination. ^cEfficiencies recorded with mask. ^dFill factor.

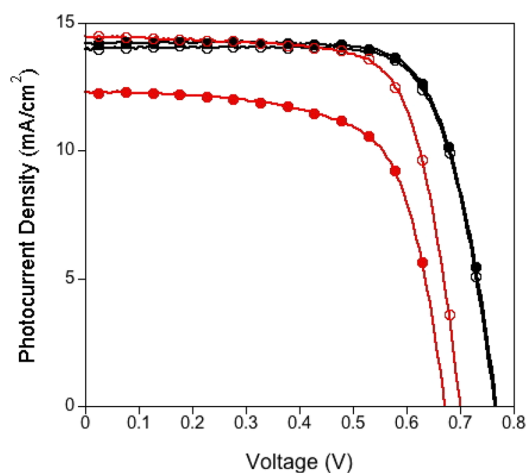


Figure 2. I – V curves recorded under AM 1.5G illumination for YD2-*o*-C8 (black) and VC-70 (red) DSC devices before (solid circles) and after (open circles) light soaking.

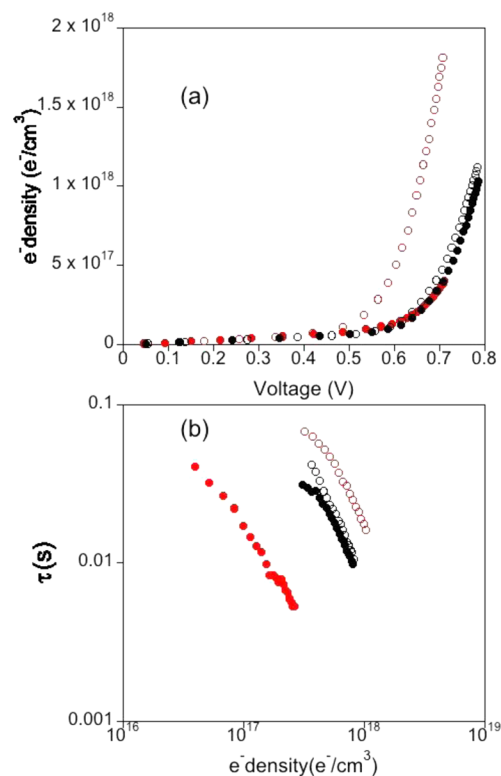


Figure 3. (a) Electron density as a function of cell voltage and (b) device electron lifetime τ as a function of charge density for YD2-*o*-C8 (black) and VC-70 (red) devices measured before (solid circles) and after (open circles) light soaking.

on electron lifetimes in the YD2-*o*-C8 device, whereas electron lifetimes become much longer for the VC-70 device and even longer than for the YD2-*o*-C8 device in fact. This helps explain the 25 mV increase in V_{oc} for the VC-70 device upon light soaking, though the V_{oc} of the YD2-*o*-C8 device is still considerably larger (75 mV).

Transient absorption spectroscopy was used to probe charge recombination and regeneration by the I_3^-/I^- redox couple in transparent DSC devices (Figure 4). The data recorded in the absence of red/ox active electrolyte (black decays) show similar long-lived decays for both devices assigned to the dye cation formed following photoexcitation and charge separation. These kinetics are similar to those which we have observed previously in DSCs containing similar porphyrin dyes.¹⁸ In the presence of the redox couple the kinetics become biphasic with the loss of the cation signal due to regeneration by I^- and the appearance of a long-lived signal assigned to TiO_2 injected electrons and/or $\text{I}_2^{\bullet-}$ (red decays). The $t_{50\%}$ (time taken for 50% of signal to disappear) for the regeneration reaction is estimated as 40 and 3 μs for YD2-*o*-C8 and VC-70, respectively. This difference

may be explained by the difference in ground state oxidation (E_{ox}) potential for these dyes, with the more positive potential of VC-70 of 70 mV providing greater driving force for the regeneration reaction as we have observed previously.¹³

Returning to the effect of light soaking on device efficiency, similar observations were observed in two other studies involving DSCs employing porphyrin sensitizers.^{19,20} In both cases notable increases in device V_{oc} and J_{sc} were observed following light soaking. Furthermore, though increases in device electron lifetime were observed, no change in device electron density was recorded in either study, and improvements in device performance were therefore attributed to increased charge injection and reduced charge recombination rather than a shift in the TiO_2 conduction band. Griffith et al.²⁰ explained the effect of light soaking as a result of a cation exchange at the TiO_2 surface between Li^+ (from LiI) and DMPI^+ (from 1,2-dimethyl-3-propylimidazolium) ions present in the electrolyte. It was noted that the light soaking effect was greater in devices where lower TiO_2 dye loadings were used, suggesting that the presence of large exposed spaces on the film

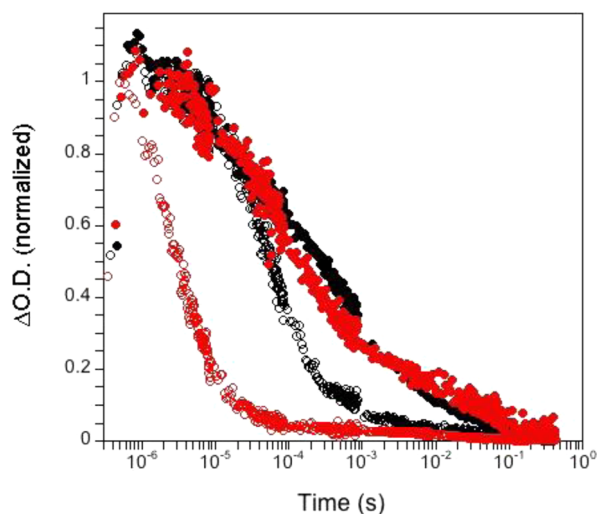


Figure 4. Transient absorption kinetics of YD2-*o*-C8 (black) and VC-70 (red) for 1 cm² area devices comprising transparent TiO₂ films in the presence of a blank electrolyte and an I₃[−]/I[−] red/ox electrolyte. Open symbols correspond to the samples with I₃[−]/I[−] electrolyte. Kinetics were recorded at 800 nm (YD2-*o*-C8) and 850 nm (VC-70) following excitation at 470 nm (Δ O.D. refers to change in optical density of the sample).

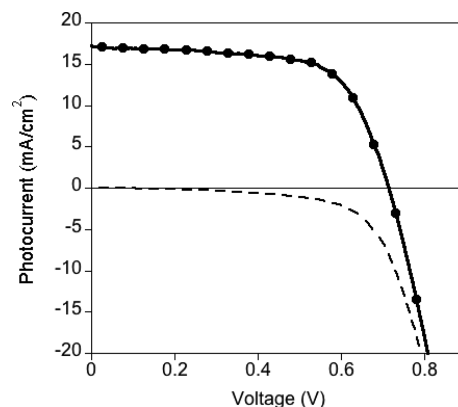


Figure 5. *I*–*V* curves recorded under AM 1.5G illumination and in the dark for a DSC device cosensitized with D205 and VC-70.

increases in both V_{oc} and J_{sc} observed. Charge extraction and transient photovoltage data indicate that the increase in J_{sc} is due to a downward shift of the TiO₂ conduction band, while the increase in V_{oc} is due to an increase in device electron lifetime, which may be related to the migration of ions in the electrolyte to the TiO₂ surface due to bad dye packing of VC-70 on the TiO₂ film. Finally, when VC-70 is cosensitized with the indoline dye D205 having complementary absorbance, device efficiency was improved further to 8.10%.

■ ASSOCIATED CONTENT

● Supporting Information

Additional experimental details, Figures S1–S4, and device fabrication and optimization conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

L.P., C.V.K., and J.N.C. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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could lead to a greater degree of cation exchange. A similar scenario may also explain the light soaking effect we observe in our study with ineffective packing on the surface of the TiO₂ caused by the bulky indoline group not being coplanar with the porphyrin ring in VC-70 facilitating cation exchange to some extent. We note that our electrolyte is identical to that used in the two studies mentioned except that 0.5 M 1-butyl-3-methylimidazolium iodide (BMII) was used instead of 0.6 M 1,2-dimethyl-3-propylimidazolium (DMPII). This could be a reason why we observe a shift in the TiO₂ conduction, though we are still unsure why. We note we also observed a shift in the TiO₂ conduction band following light soaking for devices containing an organic dye with the same electrolyte in a previous study.¹³

Finally, in an effort to improve device efficiency, VC-70 was cosensitized with the indoline dye D205²¹²¹ which has a complementary absorption band centered at 525 nm. Sensitizing conditions for optimized devices were found to be 3 h in D205 solution followed by a further 3 h in VC-70 solution (see Experimental Section). With this dual dye system the best device gave a J_{sc} of 17.18 mA cm^{−2}, a V_{oc} of 0.71 V, and a fill factor of 66% resulting in an overall cell efficiency of 8.10%, which is higher than the corresponding device based on VC-70 alone (7.31%). Again, light soaking of 90 min was used to optimize efficiency in cosensitized devices. The *I*–*V* curve for the D205/VC-70 cosensitized DSC device is shown in Figure 5.

■ CONCLUSIONS

A novel D- π -A porphyrin sensitizer, VC-70, in which an indoline unit is employed as the donor group was synthesized, and its photophysical and electrochemical properties were fully characterized. In DSC devices an efficiency of 7.31% compared extremely favorably with devices based on the reference porphyrin YD2-*o*-C8 (7.60%). The efficiency of VC-70 devices was found to depend upon exposure to illumination (light soaking) with maximum efficiencies observed after 90 min with

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