Near Infrared Unsymmetrical Squaraine Core Based Sensitizers for Co-Sensitized High Photocurrent Dye-Sensitized Solar Cells

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SUMMARY

Increased conversion of near-infrared (NIR) photons to electricity is needed to improve dye-sensitized solar cells (DSC). Here we report two squaraine dyes (**RR13** and **RR14**) with unsymmetrical cores as NIR dyes in DSCs. Both dyes feature a conjugated indolizine donor with an indoline donor on the opposite side of the squaraine core. The dyes are studied via absorption spectroscopy, computational interrogation, and electrochemical analysis. The use of the strongly donating indolizine donor results in NIR photon-to-current conversion extending beyond 800 nm on TiO_2 in DSC devices. The DSC devices were characterized by current-voltage curves, incident photon-to-current conversion efficiency measurements, and electrical impedance spectroscopy. After co-sensitized DSC device optimizations, the NIR absorbing squaraine dyes complemented with commercial organic dyes (**D35** and **Y123**) gave a high photocurrent output of ~21 mA/cm^2 with a PCE of 9.4%.

INTRODUCTION

Dye-sensitized solar cells (DCSs) are a practical, cost-effective alternative photovoltaic technology.[1-4] A working DSC contains a sensitizer for light absorption, a wide band-gap semiconductor to accept electrons from the photoexcited dye (usually TiO_2), and a redox shuttle (RS) to transfer electrons to the oxidized dye from a counter-electrode connected by an external circuit to the photoanode. Metal-free sensitizers are attractive due to facile spectral tunability, high molar absorptivities, and unparalleled performance in diffuse lighting environments which is desirable for applications such as building integrated photovoltaics, tandem and multijunction devices, and self-powered Internet of Things (IoT) devices operating on indoor lighting.[5-9] Organic photosensitizers have been shown to use photons < 750 nm with high power conversion efficiencies (PCEs); however, sensitizers utilizing photons >750 nm efficiently are rare in the literature.[10, 11] This represents an urgent challenge with respect to DSC development.

Squaraine-based sensitizers are well known in the literature to absorb low energy photons (<1.65 eV) with high molar absorptivities, which is attractive for a broad array of applications such as chemical sensing, carbon dioxide and water reduction via photocatalysis, photodetection, secure communications, bioimaging and phototherapy, and solar-to-electricity generation.[12-18] A key challenge in the DSC field is to design sensitizers with deeper NIR absorption that efficiently generate electricity in this spectral region.[10, 11] One approach to this challenge is to synthesize unsymmetrical squaraine sensitizers with strong electron donor functionality.[19, 20] Indeed, this strategy has led to some of the deepest NIR (and shortwave infrared (SWIR), >1000 nm) photon-to-current materials known in the DSC literature.[19, 20] The challenge remains to design dyes which not only allow for access to the NIR/SWIR spectral regions but also have high quantum yields for electricity production from these photons.[21-25] We reasoned that an unsymmetrical squaraine core dye with a strong indolizine donor and a indoline donor with an anchoring group could shift the absorption spectrum further into the NIR region than symmetric indoline-indoline core based squaraines. Indolizine heterocycles are fully conjugated strong donor groups with proaromatic characteristics that can enable deep NIR/SWIR absorption.[26-28] Additionally, this approach will allow for the design of sensitizers which are readily accessible with concise sizes and synthetic routes which is counter to current field trends in designing NIR chromophores.[10] Herein, we report the facile preparation and application of two unsymmetrical squaraine dyes **RR13** and **RR14** in DSC devices with exceptional photocurrent outputs for squaraine-based devices (Figure 1). **RR13** features a simple, compact indolizine donor for minimal dye footprint on the TiO_2 surface. **RR14** has additional aryl ether groups to both tune optical properties, reduce aggregation, and provide surface insulating groups to protect electrons in TiO_2 from the electrolyte.[29]

RESULTS

Synthesis and optical properties of unsymmetrical squaraine core dyes

The synthesis of **RR13** occurs in 1 step via the condensation of known indolizine (**1**)[30] and carboxylated indolinium (**2**)[31] with squaric acid (**3**) to give the desired product in 47% yield (Scheme 1). **RR14** was prepared similarly to **RR13** with known indolizine (**4**)[29] in place of indolizine (**1**) to give the desired product in 38% yield. Interestingly, **RR14** is observed to be susceptible to retro-condensation reactions presumably due to exposure to the trace DCl in $CDCl_3$ when collecting a ^1H NMR spectrum with an obvious color change from the green unsymmetrical squaraine to the blue symmetric bis-indoline squaraine (Figure S25).

NMRs taken in $CDCl_3$ show a mixture consisting of ~50% **RR14** and ~25% each of the symmetrized bisindoline-squaraine despite the **RR14** sample appearing pure by chromatography before preparing the NMR sample. ^1H NMR spectra collected in $CDCl_3$ stored over K_2CO_3 show only **RR14** over a 24 hour period (Figures S23 – S24).

Absorption spectra were obtained in dichloromethane to examine the effect of replacing an indoline with an indolizine donor (Figure 2, Table 1). Both **RR13** and **RR14** exhibit narrow absorption bands characteristic of squaraine based sensitizers between 600 nm and 780 nm with absorption maxima (λ_{max}) at 689 nm and 712 nm, respectively. **RR14** gave the most red-shifted spectrum with an onset of absorption (λ_{onset}) found via the 0nset program[32] at 744 nm due to the inclusion of the aryl ether donor groups in conjugation with the indolizine-squaraine π system. **RR13** and **RR14** have high molar absorptivities (ε = 166,000 $M^{-1}cm^{-1}$ and 212,000 $M^{-1}cm^{-1}$, respectively) at λ_{max} which is characteristic of squaraine sensitizers (Table 1).[21, 25, 33-35] Relative to symmetric squaraine core benchmark dye **SQ1**, both **RR13** and **RR14** have red shifted λ_{max} values (by 53 nm and 76 nm, respectively) and larger ε values under identical conditions. These results show that the incorporation of indolizine on an unsymmetrical squaraine core has the desired shift in absorption spectrum λ_{max} values toward deeper NIR absorption. Absorption measurements of **RR13** and **RR14** on a TiO_2 surface revealed a broad absorption which could be due to aggregation or strong absorption of the film not allowing for light transmission (Figures 2 and S5).[19, 22, 25] Upon addition of chenodeoxycholic acid (CDCA) as a deaggregating agent during TiO_2 sensitization, the curve shape and breadth on TiO_2 more resembles that of solution measurements, and the absorptivity is lower which allows for light transmission during the measurements on the films studied here. Notably, when 10 mM CDCA is added to the **RR13** solution (0.1 mM dye), the full-width at half-maximum (FWHM) is 230 nm which is significantly more than the solution measurement at 33 nm. Additionally, in solution the shoulder at 650 nm is in a 1:3 ratio with the maximum absorbance peak while on film the shoulder increases in height to nearly 1:1 ratio with the maximum absorbance peak. This increase in the high energy absorption feature is indicative of aggregation such as occurs with H-aggregates. Addition of more CDCA to the sensitization solution results in a lowering of the shoulder absorption to give a 1:1.2 ratio with the absorption maxima. This shift in the shoulder to maximum absorbance peak ratio with different CDCA loadings again suggests aggregation may be problematic for these dyes. Similar effects are observed for **RR14** via solution and film measurements.

Density functional theory calculations

Density functional theory (DFT) computational studies were undertaken to obtain the molecular orbital positions using the BPW91[36-38] functional and 6-311G(*d*,*p*)[39] basis set with Gaussian09 (Tables S13-S15).[40] Spatial orbital positions are critical to allow for efficient electron injection from the dye to the TiO_2 conduction band (CB) after photoexcitation and to allow for prolonged interfacial charge separation after electron injection. Ideally, the highest occupied molecular orbital (HOMO) should be far from the TiO_2 surface to inhibit back electron transfer after electron injection. Also, the lowest unoccupied molecular orbital (LUMO) should be positioned near to the TiO_2 surface to allow for electron injection after excitation of an electron from a HOMO to the LUMO orbital. **RR13** and **RR14** have delocalized HOMOs across the indolizine-squaraine core-indoline groups (Figure 3). The added aryl ether group at the 7-position of the **RR14** indolizine results in an extension of the HOMO onto the aryl ether moiety which is correlated to the observed red-shift of its absorption spectrum. The LUMO is delocalized across the entire dye with a slightly larger contribution on the carboxylic acid acceptor group. The presence of the LUMO near the anchoring point to TiO_2 is desirable for efficient electron injection. Overall, there are only minor shifts in the region of the molecule where the HOMO and LUMO are located, which indicates the HOMO to LUMO transition is of $\pi \rightarrow \pi^*$ character. This observation correlates to the observed absorption spectrum showing a high energy shoulder feature that is assigned as vibronic in nature as is commonly observed for $\pi \rightarrow \pi^*$ transitions such as with cyanines.[41]

Time dependent (TD)-DFT was employed to evaluate the agreement between experimental absorption values and the predicted vertical transitions. TD-DFT is also employed to observe which orbitals are involved in the lowest energy strong transition. The predicted vertical transition values agree closely with the experimentally obtained λ_{max} values to within 0.2 eV (Table 2). An intense (oscillator strength >1.1) vertical transition at 2.00 eV is predicted for **RR13** which is primarily HOMO to LUMO in character (88%). Similarly, **RR14** has a predicted λ_{max} of 1.88 eV with a higher oscillator strength (>1.4) and the transition being primarily HOMO to LUMO (89%). The higher oscillator strength of **RR14** is correlated to the observed higher ε value in solution measurements (Table 1, Figure 2).

Electrochemical properties

The thermodynamics of electron injection (ΔG_{inj}) into the TiO_2 CB and dye regeneration (ΔG_{reg}) with I^-/I_3^- were determined by electrochemical characterization.

Cyclic voltammetry measurements were performed in dichloromethane solutions using 0.1 M Bu_4NPF_6 as electrolyte and ferrocene as internal standard (Figure S2). The ground state oxidation potential ($E_{(S+/S)}$) was measured at 0.83 V vs. normal hydrogen electrode (NHE) as the half-wave potential for the reversible oxidation of **RR13** (Figures S2, Table 1). As expected, the more strongly donated **RR14** is easier to oxidize with an $E_{(S+/S)}$ of 0.74 V. Notably, immobilization of the sensitizers on TiO_2 does not affect the reversibility of the oxidation wave (Figure S3). These values suggest that dye regeneration is reasonable with the I^-/I_3^- redox system with driving forces of regeneration (ΔG_{reg}) of 480 mV and 390 mV when the I^-/I_3^- oxidation potential is taken at 0.35 V via the equation $\Delta G_{reg} = E_{(S+/S)} - 0.35$ V. We note that the use of 0.35 V is a gross approximation commonly used in the DSC literature[4, 42-45] and that the I^-/I_3^- system is quite complex.[46, 47] The excited state oxidation potential ($E_{(S+/S*)}$) is important for characterizing the energetic driving force of electron injection (ΔG_{inj}) into TiO_2 from the photoexcited dye and is calculated using the equation $E_{(S+/S*)} = E_{(S+/S)} - E_g^{opt}$. The E_g^{opt} values for **RR13** and **RR14** were determined from the absorption curve onset energy to be 1.73 eV and 1.67 eV, respectively. Both dyes give similar $E_{(S+/S*)}$ values at –0.90 V (**RR13)** and –0.93 V (**RR14**) corresponding to ΔG_{inj} at ≥ 400 mV when the TiO_2 conduction band is taken at –0.5 V via the equation $\Delta G_{inj} = -0.5 \text{ V} - E_{(S+/S*)}$ (Figure S4, Table 1).[4, 44, 48-50]

Photovoltaic performance of squaraine sensitizers in NIR-DSCs

DSC devices were prepared with both of the dyes with TiO_2 (10 µm active layer thickness) and I^-/I_3^-. The photovoltaic properties of the devices were measured by generating current density-voltage (*J-V*) curves under AM 1.5G simulated solar illumination. Device PCEs were calculated according to the equation $\eta = J_{SC}*V_{OC}*FF/I_0$, where J_{SC} is the short circuit current density, V_{OC} is the open-circuit voltage, *FF* is the fill factor, and I_0 is the incident photon flux illuminated on the cells set to 1 sun (100 mW/cm^2) unless otherwise noted. DSC devices from both **RR13** and **RR14** have low overall PCE values of 0.86% and 2.14% due primarily to low photocurrent values (<6 mA/cm^2, Table S3). Incident photon-to-current conversion efficiency (IPCE) measurements reveal IPCE peak values of <30% throughout the visible and NIR region spectral regions (Figure S10). A low IPCE response in the higher energy visible region is noted which agrees with the absorption spectrum. The low photocurrent and peak IPCE values are primarily attributed to detrimental aggregation at the TiO_2 surface since added CDCA improved device parameters for both dyes (Table S3). Importantly, as light harvesting efficiency (LHE) goes down with added CDCA that reduces **RR13** dye loading by almost 5x (Table S1; Figure S8), the IPCE intensity goes up by 4x in the NIR region (Figure S10). Similar trends are observed for **RR14**. This is an indication that aggregation is reducing IPCE efficiency which is commonly attributed to dye-dye energy transfer resulting in annihilation, aggregate states without appropriate energetics or spatial positioning for injection, or electron transfer reactions rather than dye-TiO_2 electron injection.[21, 51-53] Notably, both dyes have exceptional IPCE onset values at or beyond 800 nm (Figure S10). The insulating alkyl aryl ethers on the **RR14** donor led to lower CDCA loadings being required for optimized DSC device performance (Figure S10). Nonetheless, both dyes require significant CDCA loadings at up to 1:200 dye:CDCA in the case of **RR13** for optimal performances.

Squaraines dyes often have characteristically narrow absorption bands which makes efficient panchromatic electricity generation challenging when implemented within DSC devices as single dyes due to typically low-to-moderate IPCE values (<50%) in the visible region. Recent molecular design strategies have focused on the engineering of higher energy transitions by linearly extending π-conjugation of the chromophore.[19, 22-24, 54] Alternatively, co-sensitization with a visible light absorbing dye having a complementary spectrum can lead to higher performing DSC devices.[45, 55, 56] An added advantage to the co-sensitization strategy is the potential use of the co-sensitizing dye as a deaggregating agent. Aggregation is often a significant concern for squaraine sensitizers due to the planarized, zwitterionic nature of the chromophores. An optically inactive co-adsorbent CDCA is traditionally employed as a deaggregating agent. However, CDCA consumes TiO_2 binding sites with an optically inactive material in the visible spectral region which could be better used by a visible light absorbing dye (see Table S1 for dye loading results).[57]

A series of co-sensitization studies were performed with well-known, visible light absorbing commercial dyes **D35** and **Y123** to probe the possible dual role of these dyes as deaggregating agents and visible light-to-electricity producing chromophores in DSC devices with **RR13** and **RR14** (see Figure S1 for **D35** and **Y123** structures).[58, 59] The cocktail sensitizing method where both dyes are simultaneously present in the sensitizing solution led to better DSC device performances in all cases compared to sequentially dipping the electrodes in single dye solutions (Figures S11 – S14, Tables S4 – S7).[60, 61] Optimal dye ratios consisted of 1:3 NIR squaraine dye:visible light absorbing dye, which is a drastic improvement over the required CDCA loadings for optimal PCE values. **RR13** operates more synergistically with the **D35** co-sensitizer than the **Y123** co-sensitizer leading to a 5.3% PCE DSC device (compared to 1.9% with CDCA). The **RR13**/**D35** DSC devices more than double the photocurrent output when compared to the **RR13**/CDCA device with the IPCE improving in both the visible range where **D35** absorbs and in the NIR region where **RR13** absorbs (Figure S11, Tables S3-S4). **RR14** devices performed better with the **Y123** co-sensitizer leading to a J_{SC} value of 14 mA/cm^2. The PCE of the **RR14/Y123** DSC device is more than double the PCE of the **RR14/**CDCA device (6.5% versus 2.9%, respectively) (Figure S12, Tables S3 & S5). The **RR14**-based DSC devices gave higher photovoltages than the **RR13**-based DSC devices due to superior surface insulation, rather than a shift in the TiO_2 capacitance, reaching a maximum V_{OC} of 708 mV with minimal voltage losses within the cell (Figure S22, Tables S3 – S5). Though device performances are comparable for **RR14** with both co-sensitizers, **Y123** is the best candidate due to better spectral matching as evidenced in the IPCE spectra (Figures S12 & S18). Interestingly, the co-sensitizers provide the dual function of light absorbers and strong deaggregating agents since additional CDCA loading provides no advantage with the co-sensitized systems (Figure S16).

The DSC device performances were further optimized by increasing the active photoanode thickness to 12.5 μm. The **RR13**/**D35** DSC device reaches a maximum J_{SC} value of 16 mA/cm^2 with a PCE of 6.5% with the thicker electrodes (Figure S17, Table S9). Under these conditions, the **RR14/Y123** DSC device gave the highest PCE observed in these studies at 9.4% with an exceptional J_{SC} of 21 mA/cm^2 (Figure 4, Tables 3 & S10). The IPCE shows a nearly panchromatic response from 400 nm to 825 nm with a maximum of near 85% in the visible region which is limited by the percent transmittance of the FTO used (Figures 4 & S7). The IPCE spectrum is similarly shaped with a similar percent conversion efficiency to the LHE spectrum indicating that there is little loss of energy from the absorbed photons (Figure S8). Improved electricity production in the NIR region relative to the non-cosensitized device is observed with a peak IPCE value of ~60% (LHE at 70% in this region) with an integrated photocurrent of 20.4 mA/cm^2 (Figure S19). This is one of the highest PCE squaraine-based devices known in the DSC literature to the best of our knowledge and may be one of the first squaraine-based DSC devices to reach >9.0% PCE. DSC devices with photocurrent outputs in excess of 20 mA/cm^2 are scarce for all organic DSC devices, especially without requiring significant lithium loadings to modulate the TiO_2 CB (Figure S15, Table S8).[62] Only 0.05 M LiI was used in these studies. Notably, minimal V_{OC} losses were observed in both co-sensitized systems not exceeding 250 mV with the I^-/I_3^- redox system assuming a maximum V_{OC} of ~900 mV is possible.

Electrochemical impedance spectroscopy and small modulated photovoltage transient spectroscopy

In order to investigate recombination kinetics for the series, electrical impedance spectroscopy (EIS) measurements were performed in the dark (see Figure S20 for the fitted circuit).[63] The modified Nyquist plot model shows the resistance of electron transfer at the various interfaces within the DSC with the smaller semicircle at low resistance showing electron transfer resistance at the counter electrode-RS interface (R_{CE}) and the larger semicircle representative of electron transfer resistance at the TiO_2-dye-RS interface (R_{rec}). Co-sensitized DSC devices show **RR14/Y123**-based devices having a desirably larger R_{rec} than **RR13/D35**-based devices (144 Ω versus 86 Ω at V_{OC}, respectively; Table 4). This trend is observed for single dye devices with and without CDCA (Figure S20, Table S11). These observations highlight the need for a high degree of surface protection via the insulating groups on **RR14**.[64] Both devices have characteristically low R_{CE} values for Pt and the I^-/I_3^- redox system. Charge collection efficiencies (η_{cc}) were calculated according to the equation $\eta_{cc} = 1/(1 + (R_{CE}/R_{rec}))$. A η_{cc} value of 98% is observed for the **RR14/Y123** devices. The η_{cc} value for the **RR13**/**D35** device is diminished to 92% (Table 4), which is correlated to the lack of surface protecting insulating groups on the **RR13** indolizine motif.

Electron lifetimes in the TiO_2 semiconductor (τ_{TiO2}) were measured via Bode plots in the dark at V_{OC} bias and described by the equation $\tau_{TiO2} = 1/(2\pi f)$, where f is the peak frequency value in the low frequency region of the plot (Figures 5 and S20). The **RR14/Y123** system shows a higher τ_{TiO2} value when compared to **RR13**/**D35** and standalone **Y123** devices (63 ms versus 32 ms and 40 ms, respectively; Tables 4 and S11). Additionally, small modulated photovoltage transient (SMPVT) measurements were undertaken to probe the electron lifetime in TiO_2 under steady-state illumination via measurement of the fitted lifetimes of the rise and decay in V_{OC} induced by small changes in light intensity (Figure S21).[65, 66] **RR14/Y123** devices show nearly an order of magnitude longer electron lifetime in TiO_2 when compared to **RR13/D35** at that same V_{OC} value. Maximum electron lifetimes as high as 0.1 s are observed for the **RR14**/**Y123**-based DSC devices. The longer lifetime of **RR14**-based cells is observed when compared to **RR13**-based cells both with and without CDCA as well (Figure S21). Thus, the EIS and SMPVT measurements under two separate conditions (dark and light environments) both suggest the surface insulating groups on the **RR14** dye are critical to long lived electrons in TiO_2 which is correlated to the higher photovoltage observed with the **RR14**-based DSC devices that leads to significantly higher power conversion efficiencies than **RR13**-based DSC devices.

DISCUSSION

Two unsymmetrical indolizine-indoline-based squaraine sensitizers, **RR13** and **RR14**, were synthesized and characterized in solution and in DSC devices. The sensitizers exhibited strong NIR absorption extending to 800 nm on a TiO_2 surface. Electrochemical and optical analysis reveals both sensitizers are well suited for use in DSC devices energetically. Computational studies show good orbital distribution on the dyes for electron injection into TiO_2. On TiO_2, aggregation-induced absorption was correlated to diminished DSC device performances for both dyes via CDCA deaggregation studies showing high CDCA loadings (>50:1 CDCA:dye) having optimal performances. To address both the minimal light absorption in the visible region of the dyes and the aggregated squaraine dyes on the surface, co-sensitizers working in the visible region of the spectrum were added to the DSC devices in place of CDCA. This strategy reduces the need to design a single chromophore for panchromatic collection of solar energy and improves the current output by removal of CDCA. The highest performing device was based on co-sensitized dyes **RR14/Y123** resulting in a PCE value of 9.4% with a J_{SC} value of 21 mA/cm^2. To the best of our knowledge, this is the highest performing squaraine-based device in the DSC literature. Minimal photovoltage loss is present in these DSC devices due to excellent surface insulation of electrons in TiO_2 from the electrolyte by the alkyl groups on the dye as confirmed by EIS and SMPVT measurements. Given the very low lithium loadings (0.05 M Li+) and high photocurrent density with NIR light use, the **RR14/Y123** dye system is a good candidate for use in sequential series multijunction (SSM) DSC systems as the long wavelength utilizing material. Future studies are focusing on identifying energetically well-paired redox shuttles for NIR DSCs, SSM-DSCs, and low light DSC applications.

EXPERIMENTAL PROCEDURES

Resource Availability

Lead Contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Jared H. Delcamp (delcamp@olemiss.edu).

Materials Availability

The dyes synthesized for these studies may be available from the Lead contact upon request as supplies are available.

Data and Code Availability

All data generated for this study are included in this article or the supporting information. This study did not generate code.

General procedures

All commercially obtained reagents were used as received. Full descriptions of the synthesis and characterization, computational methods, instrumentation, and device fabrication can be found in the Supplemental Experimental Procedures (Notes S1-Note S3).

Supplemental Experimental Procedures

Supplemental experimental procedures can be found online at http://doi.org/XXXX

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AUTHOR CONTRIBUTIONS

R.R. synthesized and characterized the dyes and performed preliminary device studies for the series. J.W. performed DFT calculations, additional dye characterization, device fabrication/characterization, and wrote the original manuscript draft. J.H.D. conceived the project, oversaw the research, and wrote the final draft of the manuscript.

DECLARATION OF INTERESTS

J.H.D. is an inventor on a patent application filed by the University of Mississippi related to the dyes in this work.

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FIGURE TITLES AND LEGENDS

Figure 1. Top: A plot of photocurrent values observed with NIR absorbing squaraines in DSC devices (symmetric core dyes have black bars and unsymmetrical core dyes have red bars). *Indicates the DSC device is co-sensitized. See Table S12 for a full list of dye references. Bottom: Example squaraine dyes where the structures have squaraine cores in blue with functional groups in black for either anchoring (**SQ1**) or π-extending and anchoring (**JD10**) dyes. **RR13** and **RR14** have unsymmetrical squaraine cores in blue.

Scheme 1. Synthetic route to **RR13** and **RR14.**

Figure 2. Absorption spectra of **RR13** and **RR14** in dichloromethane (top) and normalized spectra of **RR13** on TiO_2 (5 μm, 16 hour sensitization time) (bottom). See Figures S5-S6 for additional optical data.

Figure 3: Frontier molecular orbital pictures for **RR13** and **RR14**.

Figure 4: *J*–*V* (left) and IPCE (right) curves for optimized devices with CDCA and co-sensitizer.

Figure 5: EIS data for optimized co-sensitized devices. Bode plot (left) and Nyquist plot (right). See Supplemental Experimental Procedures for additional EIS data (Figure S20 and Table S11).

TABLES, TABLE TITLES, AND LEGENDS

Table 1. Optical and electrochemical properties of **RR13** and **RR14**.

dye	λ_{max} (nm)	ε ($M^{-1}cm^{-1}$)	λ_{onset} (nm)	$E_{(S+/S)}$ (V)	$E_{(S+/S^*)}$ (V)	E_g^{opt} (eV)
RR13	689	166,000	718	0.83	–0.90	1.73
RR14	712	212,000	744	0.74	–0.93	1.67

Table 2. Electronic transitions predicted by TD-DFT computation using the BPW91 functional and 6-311G(*d,p*) basis set.

dye	state	orbitals	contribution	vertical transition (eV | nm)	oscillator strength
RR13	$S_0 \rightarrow S_2$	$H \rightarrow L$	88%	2.00 | 621	1.103
RR14	$S_0 \rightarrow S_3$	$H \rightarrow L$	89%	1.88 | 660	1.455

Note: The $S_0 \rightarrow S_1$ transition for both dyes and the $S_0 \rightarrow S_2$ transition for **RR14** are very low oscillator strengths (<0.03) and are therefore not reported in the table. See Supplemental Experimental Procedures for additional orbital contributions to these states and for additional transitions (Figure S9 and Table S2).

Table 3: Optimized DSC device data.

Dye	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
RR13	467 ± 10	4.0 ± 0	69.8 ± 3.3	1.40 ± 0.10
RR13/CDCA	527 ± 5	7.6 ± 0.1	74.5 ± 0.1	3.22 ± 0.06
RR13/D35	612 ± 5	15.7 ± 0	63.3 ± 1.6	6.52 ± 0.21
RR14	523 ± 0	5.8 ± 0.1	68.4 ± 0.7	2.31 ± 0.04
RR14/CDCA	548 ± 5	9.0 ± 0.5	67.6 ± 1.0	3.68 ± 0.11
RR14/Y123	662 ± 5	20.9 ± 0.7	61.4 ± 0.9	9.44 ± 0.24

Table 4: EIS data summary for the optimized co-sensitized devices where R_S is the series resistance, C_μ represents the chemical capacitance for charge accumulation at the photoanode, and C_{CE} is the capacitance at the electrolyte-counter electrode interface.

Dye	R_s (Ω)	R_{rec} (Ω)	C_μ (mF)	R_{CE} (Ω)	C_{CE} (mF)	η_{cc} (%)	τ_{TiO2} (ms)
RR13/D35	14	86	7.5×10^{-4}	7	4.8×10^{-6}	92	32
RR14/Y123	17	144	1.2×10^{-3}	3	2.6×10^{-5}	98	63