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Modulating dye $E_{(S+/S^*)}$ with efficient heterocyclic nitrogen containing acceptors for DSCs[†]

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Acceptor motifs based on nitrogen containing heterocycles have been synthesized for use in dye-sensitized solar cells (DSCs). Through the selective addition of nitrogen atoms and increased conjugation of the nitrogen containing heterocycles the excited-state oxidation potential, $E_{(S + /S^*)}$, may be conveniently tuned with minimal effect on the ground-state oxidation potential, $E_{(S + /S)}$, of the dye.

Dye sensitized solar cells (DSCs) have undergone continuous improvement since their introduction in 1991,¹ which is culminating with DSCs being a strong contributor toward the solar energy conversion market.² DSCs currently exhibit solar-to-electric power conversion efficiencies (PCEs) ranging from 9–12%.^{2,3} Among DSCs, metal-free organic sensitizers are attractive because they do not require the use of expensive metals and demonstrate strong extinction coefficients.⁴ Donor- π -acceptor (D- π -A) dyes are proving to be a good, strategic dye design scaffolding for metal-free dyes and this class of dyes is at the forefront of organic sensitizers displaying PCEs reproducibly near⁵ and greater than 10%.⁶

Currently, cyanoacrylate is commonly employed as the acceptor and anchor for D- π -A dyes presumably due to an increase in spectral response through intramolecular charge transfer (ICT) and good electron injection properties.⁷ We envisioned a new class of carboxylate anchored heterocyclic nitrogen containing acceptors which may increase spectral response through both ICT and lengthening π -conjugation while maintaining good charge injection.⁸ In this manuscript we examine the effect of the number of nitrogen atoms in heterocyclic aryl acceptors with one or two fused rings for metal-free dyes.

The selected DSC target dyes keep the donor and π -bridge regions consistent throughout the series examined and are based on a triarylamine donor and the good π -bridge, di-*n*-hexyl substituted cyclopentyldithiophene (CPDT).^{4,5c,9} A range of electron deficient heterocyclic nitrogen containing acceptor (pyridine, quinoline, pyrazine, and quinoxaline) based dyes were synthesized (Scheme 1). The synthetic route to dyes **JD2**, **JD4**, **JD7**, and **JD8** begins with Stille coupling of the brominated triphenylamine



Scheme 1 Heterocyclic nitrogen containing acceptor based D- π -A dyes for DSCs.

1 (TPA)¹⁰ and stannylated CPDT **2**¹¹ fragments (Scheme S1, ESI†). The TPA-CPDT molecule, **3**, was stannylated and Stille coupled to the desired brominated heterocyclic nitrogen containing acceptor ester. The final D- π -A dyes were synthesized after THF/LiOH hydrolysis to generate the carboxylic acid anchor. **JD8** was synthesized in a similar manner; however, a brominated quinoxaline benzyl alcohol was coupled in place of the corresponding ester (Scheme S2, ESI†). The alcohol was then subsequently oxidized to the desired **JD8** dye.

The optical and electrochemical properties of the completed D- π -A dyes were examined to ensure good device compatibility with TiO₂ semiconductor and I⁻/I₃⁻ redox couple. In order to estimate the excited-state oxidation potential ($E_{(S + /S^*)}$) according to the equation $E_{(S + /S^*)} = E_{(S + /S)} - E_g^{opt}$, both the ground-state oxidation potential $E_{(S + /S)}$ and the $E_{(S + /S^*)} - E_{(S + /S)}$ gap (E_g^{opt}) were measured. E_g^{opt} was determined from the absorption spectrum at λ_{onset} in CH₂Cl₂ (Fig. S1, ESI†).¹² The E_g^{opt} values are shrinking in heterocyclic nitrogen containing series from JD2 through JD8. Pyridine dye, JD2, with the largest E_g^{opt} (2.27 eV) has a λ_{max} of 461 nm (Table 1, Fig. S1, ESI†).

Table 1 Optical and electrochemical data

Dye	$\lambda_{\max}{}^a/nm$	$E_{\rm g}^{{ m opt}b}/{ m eV}$	$E_{(S+/S)}^{c}/V$	$E_{(S+/S^*)}^d/V$
JD2	461	2.27	0.81	-1.46
JD4	507	2.11	0.82	-1.29
JD7	508	2.05	0.82	-1.23
JD8	579	1.79	0.79	-1.00
C218 ^e	550	1.95	0.89	-1.06

^{*a*} Measured in CH₂Cl₂. ^{*b*} Calculated from UV-vis spectrum at λ_{onset} . ^{*c*} Measured in a 0.1 M Bu₄NPF₆ in CH₂Cl₂ solution with glassy carbon working electrode, Pt reference electrode, and Pt counter electrode with ferrocene as an internal standard. Values are reported *versus* NHE. ^{*d*} Calculated from $E_{(S+/S^*)} = E_{(S+/S)} - E_g^{opt}$. ^{*e*} C218 was synthesized through a modified synthetic route compared to the original report (see ESI).

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Both the quinoline acceptor (**JD4**) and pyrazine acceptor (**JD7**) are stronger electron withdrawing groups than pyridine which results in bathochromic shifts at a λ_{max} of 46 nm and 47 nm, respectively. The quinoxaline acceptor (**JD8**) is the most red shifted with a λ_{max} of 579 nm and strong absorbance into the near-infrared (NIR) with a value of 710 nm at 5% the λ_{max} height. All of the dyes reported have significant absorbance (>20% λ_{max} peak height) from 400 nm to the λ_{max} value of the dye. The absorption onset at low energy for **JD4**, **JD7** and **JD8** is at wavelengths greater than 600 nm. The heterocyclic nitrogen containing acceptors display a strong effect on E_g^{opt} ranging from 2.27 eV to 1.79 eV.

Cyclic voltammetry was performed in CH₂Cl₂ with ferrocene as an internal standard (Table 1). The oxidation potentials, $E_{(S \pm S)}$, of all the dyes synthesized were measured to be within 30 mV and are reported versus normal hydrogen electrode (NHE). The close $E_{(S + S)}$ values indicate that $E_{(S + S)}$ is only slightly affected based on the heterocyclic nitrogen containing structure.¹³ No reversible reduction potentials were observed during cyclic voltammetry experiments (Table S1, ESI⁺). The $E_{(S+/S^*)}$ values were calculated from the measured values for $E_{(S+/S)}$ and E_{g}^{opt} . A large effect is seen for the range of $E_{(S+/S^*)}$ values when compared to $E_{(S+/S)}$ (460 mV vs. 30 mV). The heterocyclic acceptors modulate $E_{(S + /S^*)}$ with little effect on $E_{(S+S)}$ presumably due to the added electron density through increased conjugation introduced with each of the heterocycles. The increase in π -conjugation negates any stabilization to $E_{(S+/S)}$ which is commonly observed with the addition of an electron acceptor. Effectively, these heterocyclic nitrogen containing acceptors provide a simple, efficient way to tune the $E_{(S + /S^*)}$ of D- π -A dyes with marginal influence on $E_{(S + /S)}$.

Due to the donor and π -bridge regions remaining the same with only the acceptor groups changing for dyes **JD2**, **JD4**, **JD7**, **JD8** and **C128**, $E_{(S+/S^*)}$ values are used to determine acceptor strength (Table 1). $E_{(S+/S^*)}$ becomes progressively less negative as the electron withdrawing strength of the acceptor group is increased.¹⁴ The cyanoacrylate electron withdrawing group of **C218** is less withdrawn than the quinoxaline acceptor and the series progresses as follows for increasing electron withdrawing strength: **JD2** < **JD4** < **JD7** < **C218** < **JD8**.

In order to efficiently inject electrons into the TiO₂ conduction band, the excited-state oxidation potential of the sensitizer should be more negative than -0.50 V *versus* normal hydrogen electrode (NHE). The dyes reported herein are all thermodynamically suitable for good electron injection with $E_{(S+/S^*)}$ ranging from -1.46 V to -1.00 V (Table 1). For efficient dye regeneration $E_{(S+/S)}$ should be more positive than +0.35 V based on the potential of I^-/I_3^- . With $E_{(S+/S)}$ ranging from 0.79 to 0.82 eV all dyes are capable of being regenerated from the I^-/I_3^- redox couple. Therefore the heterocyclic nitrogen containing dyes studied are all suitable for TiO₂/iodine based DSCs.

A range of electron withdrawing strengths from efficient acceptors for D- π -A dyes are desirable for tuning $E_{(S^+/S^*)}$ according to the demands from the rest of the dye. The heterocyclic nitrogen containing acceptors offer a range of electron withdrawing strengths; however, for widespread use they must demonstrate efficient incident photon-to-current conversion efficiencies (IPCEs) over the absorbance range of the dye. Liquid electrolyte based photovoltaic devices were



Fig. 1 IPCE spectrum of JD2, JD4, JD7 and JD8.

prepared with each dye and TiO₂ semiconductor as described in the ESI.[†] IPCEs for the series are shown in Fig. 1 with optimized electrolyte additives for each device. Of the four dyes, JD7 was found to be the most efficient over its absorption window with an IPCE near 90% from 440-550 nm. The remaining dyes required the addition of chenodeoxycholic acid (CDCA) for optimal IPCEs performance. The loss in IPCEs without CDCA is due to dye aggregation which is known to be disrupted by CDCA (Fig. S2, ESI[†]). Dyes JD2, JD4 and JD8 also exhibit lower dye loadings leading to less TiO2 surface coverage when compared to JD7 which favors diminished IPCEs (Table S2, ESI[†]). A strikingly pronounced effect on the IPCE was observed with JD2. This dye shows a strong IPCE maximum (85%) when the dye is co-adsorbed with CDCA; however, without CDCA a weak IPCE spectrum was obtained with a maximum of <50% (Fig. S2, ESI⁺). Similar behaviors were noted for the IPCE spectrum of dyes JD4 and JD8. These two dyes generally suffer from lower dye loading possibly due to the increased steric hindrance near the carboxylate anchor.

The photovoltaic parameters of the DSCs prepared with the dyes **JD2**, **JD4**, **JD7** and **JD8** under standard AM 1.5 illumination, 100 mW cm⁻², are summarized in Table 2. The best power conversion efficiency (PCE) of 6.55% was obtained with dye **JD7** as derived from the equation $\eta = J_{sc}V_{oc}FF/I(sun)$. An optimal **JD7**-based cell shows a short-circuit photocurrent density (J_{sc}) of 11.5 mA cm⁻², an open-circuit voltage (V_{oc}) of 743 mV, and a 0.76 *FF* resulting in a η of 6.55% without any co-adsorbent in the dye solution (Fig. 2). A 40 mV loss

Table 2 Photovoltaic parameters measured under AM 1.5. CDCA is chenodeoxycholic acid. JD2 optimal electrolyte 1.0 M DMII (1,3-dimethylimidazolium iodide), 0.03 M iodine, 0.025 M LiI, 0.5 TBP, 0.1 M guanidinium thiocyanide, acetonitrile solvent. JD4 same as JD2 except 0.6 M DMII and 0.05 M LiI. JD7 same as JD4 except no LiI was added. JD8 same as JD2 except 0.05 M LiI added

Dye	Additive	$J_{\rm sc}/{ m mA~cm^{-2}}$	$V_{\rm oc}/{ m mV}$	FF	η (%)
JD2	None	5.62	665	0.71	2.63
JD2	CDCA	7.87	691	0.75	4.05
JD4	None	7.80	680	0.71	3.77
JD4	CDCA	7.74	693	0.75	4.02
JD7	None	11.5	743	0.76	6.55
JD7	CDCA	11.1	703	0.74	5.78
JD8	Lil	11.8	607	0.73	5.20
JD8	CDCA	9.89	696	0.77	5.25



Fig. 2 Current versus potential plot for dyes JD2, JD4, JD7 and JD8.

in $V_{\rm oc}$ is observed for devices with JD7 and CDCA. All the devices tested (with or without CDCA) give substantially lower voltage than JD7 which can in part be attributed to the difference in dye loading since higher loadings aid in blocking potential recombination sites with the electrolyte and semiconductor surface (see ESI[†]). Comparatively, JD2 has significantly less absorbance in the visible region which leads to a lower J_{sc} of 7.87 mA cm⁻² and an optimized PCE of 4.05% in the presence of CDCA (Table 2). JD2 is the most strongly affected dye with respect to the benefits of CDCA and displays an increase in both current and voltage when compared to solutions with no co-adsorbent. JD8 shows an increase in voltage with the addition of CDCA and a loss of current. JD8 suffers from a decreased driving force for injection, lower dye loading and aggregation (see ESI[†]). In all cases except devices with JD7, lack of CDCA addition to the dye solutions led to diminished photovoltaic performance. Dye aggregation likely causes intermolecular energy transfer and subsequently results in excited-state quenching of the dyes.

To further understand the role of CDCA as a co-adsorbent for these new acceptor based dyes, photovoltage decay transients were studied at various white light bias intensities (Fig. S3, ESI⁺). The charge recombination rates are plotted versus the open circuit potential $(V_{\rm oc})$ of the device adjusted by varying the white light bias. The recombination rate is known to increase exponentially with increasing white light bias due to a filling of intraband trap states in the TiO₂, which allows a faster detrapping of electrons to the conduction band and subsequent recombination with the electrolyte. A large decrease in the recombination rates for devices made with CDCA and JD2 (2-fold decrease) and JD8 (16-fold decrease) was measured. This increase in lifetime is clearly represented by the gain in V_{oc} for both JD2 (26 mV) and JD8 (89 mV) when CDCA is included in the electrolyte. No obvious change in the recombination rate was observed for JD4 with the addition of CDCA. Interestingly, in the case of JD7, addition of CDCA enhances charge recombination, which is also visible as the loss of the open circuit potential resulting in a lower PCE. Additionally, the higher charge recombination rate reduces the charge collection efficiency and consequently the J_{sc} and IPCE.

Several new nitrogen acceptor-based dyes have been synthesized and characterized for use in liquid electrolyte DSC devices. $E_{(S^+/S^*)}$ can be modulated by 460 mV through proper selection of a

heterocyclic nitrogen containing acceptor for metal-free D-π-A DSC dyes. The acceptors presented in this work offer a range of withdrawing strengths for maximizing color and injection efficiency based on $E_{(S + S^*)}$. These efficient acceptors include two heterocycles, pyridine and pyrazine, with less withdrawing strength than cyanoacrylate and one heterocycle, quinoxaline, with more withdrawing strength. The carboxylate anchored pyrazine acceptor used in JD7 and the pyridine acceptor used in dye JD2 demonstrate excellent charge separation and efficient charge injection. These acceptors will likely find future application for dye design involving π -bridge chromophores where $E_{(S^+/S^*)}$ is already too low for the addition of a strongly withdrawn cyanoacrylate. In this case, both pyridine and pyrazine acceptors would provide a dipole for photon induced charge separation and a better driving force for injection by generating a smaller shift with respect to the $E_{(S+S^*)}$ level than cyanoacrylate. Furthermore, dye JD7 is a promising dye for co-sensitized DSC devices due to a strong IPCE from 400-550 nm (near 90%) and no need for the addition of CDCA to diminish aggregation.

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