



Article Quinoxaline-Based Dual Donor, Dual Acceptor Organic Dyes for Dye-Sensitized Solar Cells

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Featured Application: This report focuses on methods for understanding the rational design of near-infrared (NIR)-absorbing organic dyes for dye-sensitized solar cell applications.

Abstract: A novel metal-free quinoxaline-based molecular framework with a dual donor and dual acceptor (DD- π -AA) motif has been introduced. Four sensitizers (**AP6**, **AP8**, **AP9**, and **AP12**) have been synthesized and fully characterized via UV–Vis absorption, cyclic voltammetry, density functional theory (DFT) calculations, time-correlated single photon counting (TCSPC), and in dye-sensitized solar cell (DSC) devices. Structural modifications to both the donor and acceptor/anchor regions were evaluated via structure–property relationships without altering the quinoxaline π -bridge. Through careful dye design, a broadly absorbing near-infrared (NIR) sensitizer extending electricity production to 800 nm is realized in DSC devices. Ground- and excited-state oxidation potentials were measured to show energetically favorable charge transfer events. Importantly, the dye structure was found to have a strong influence on dye energetics in different environments with structural elements allowing for either similar or dramatically different solution versus film measurements. The DSC device electrolyte was also found to have a significant influence on dye energetics as well. Electron transfer events were probed for each dye with DSC device measurements and with TCSPC studies. The results are correlated to the dye structures.

Keywords: photovoltaics; dye-sensitized solar cells; organic dyes; chromophore; molecular engineering; dye energetics; fluorescence spectroscopy; density functional theory

1. Introduction

Dye-sensitized solar cells (DSCs) remain a promising and intensely studied area of research after two decades of exploration [1–15]. In typical n-type DSC devices, dye molecules are first photoexcited followed by the transfer of electrons to the conduction band (CB) of TiO₂. The electrons then traverse an external circuit before travelling back to the oxidized dye via a redox shuttle after collection at a counter electrode. The dye is one of the most important components of DSC devices for determining which photon energies are useable. Broad UV–Vis–near-infrared (NIR) absorption properties are crucial for realizing the highest efficiency DSC devices possible [16]. A DSC device employing organic dyes surpassing 14% power conversion efficiency (PCE) has been reported owing to well-positioned energy levels, high extinction coefficients, and strong binding properties [17]. However, in order to further improve DSC device performances, dyes with NIR absorption (>750 nm) are required. In this work, structure–property relationships of quinoxaline-based dual donor and dual acceptor (DD- π -AA) dyes are explored with absorptions extending to 800 nm.

Donor- π bridge-acceptor (D- π -A) and D-A'- π -A (where A' is an auxiliary acceptor) dye constructs have become increasingly popular in DSC research [4,5,9,18,19]. Fueled by PCEs in excess of 13%, this direction remains heavily pursued [17,20,21]. Additionally, tightly bound anchors are crucial in achieving higher efficiencies, because they allow co-sensitization and co-deposition of insulators to facilitate panchromatic absorption and to protect against the transfer of electrons from the TiO₂ CB to the oxidized redox shuttle (recombination), respectively. As a key example, **ADEKA-1**-based devices have used these strategies to set the current record for DSC device efficiency at 14.3% [17].

The silanol anchoring group is regarded as both one of the strongest anchoring groups, with efficient electron transfers to TiO₂, and as a very challenging functional group to synthesize and employ in devices [22]. In this regard, sensitizers with panchromatic absorption and strong binding through multiple carboxylic acid anchors, such as with the DD-π-AA design, are highly attractive [23]. Quinoxaline-based dyes employing the DD- π -AA molecular framework have demonstrated broad absorptions and TiO₂ dissociation rates up to 180 times slower than dyes employing a traditional D- π -A structure [24]. Thienopyrazine (TPz)-based DD- π -AA dye, **AP3**, has shown a PCE of 5.5% (>10% under low light when co-sensitized) with panchromatic absorption [25,26]. Energetically, the PCE of devices made with AP3 could be increased by destabilizing the low-energy excited-state to facilitate faster electron injection into the TiO_2 CB by forgoing the need for excessive lithium iodide (LiI), which is known to lower DSC device photovoltages [25]. We reasoned that the use of a benzene in place of the thiophene group of TPz could broaden the dye optical energy gap enough to raise the dye excited-state energy without fully sacrificing panchromatic absorption properties [27–29]. Dyes AP6, **AP8**, **AP9**, and **AP12** were selected as target dyes, which vary at the donor and acceptor regions. **AP6** and **AP8** have been previously reported to have strong binding to TiO_2 and only differ at the dual carboxylic acid anchors, with **AP6** having a phenyl space between the anchors and the quinoxaline group (Figure 1) [24]. Both AP6 and AP8 had yet to be evaluated in DSC devices prior to this study, and both dyes require photons higher in energy than are present in the NIR region. Dye designs strategies for overcoming this limited absorption focus on extending conjugation, planarization of the π -conjugated system, and the increasing of the electron-donating/accepting group strengths. AP9 directly compares to AP8 with the addition of a thiophene spacer between the triphenyl amine (TPA) donors and the quinoxaline π -bridge. The added thiophene groups are selected to increase conjugation and to minimize the dihedral angle between the quinoxaline and donor region for efficient electron transfer from donor to acceptor upon photoexcitation. AP12 compares to AP6 with the same number of π -electrons in the conjugated dye system, but **AP12** differs in the planarization of the spacer groups between the carboxylic acids and at the quinoxaline π -bridge with the introduction of two nitrogen atoms in place of two C-H groups to reduce sterics at the TiO₂ surface. The planarization and introduction of two electron-accepting nitrogen groups is expected to broaden the absorption of **AP6**.



Figure 1. Target structures of AP6, AP8, AP9, and AP12.

2. Materials and Methods

Known Synthetic Intermediates

Diethyl 5,8-dibromo-4*a*,8*a*-dihydroquinoxaline-2,3-dicarboxylate (1) [24], 4-(hexyloxy)-*N*-(4-(hexyloxy)phenyl)-*N*-(4-(5-(tributylstannyl)thiophen-2-yl)phenyl)aniline (2) [30], 4,7-dibromobenzo [*c*][1,2,5]thiadiazole (4) [31], 4-(hexyloxy)-*N*-(4-(hexyloxy)phenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (5) [32], and diethyl 5,6-dioxo-5,6-dihydro-1,10-phenanthroline-2,9-dicarboxylate (8) [33] were synthesized according to literature procedures (Scheme 1).



Scheme 1. Synthetic route to target dyes AP9 and AP12.

3. Result and Discussion

3.1. AP9 and AP12 Synthesis Discussion

AP6 and **AP8** were synthesized according to the literature [24]. **AP9** was synthesized beginning with a Stille coupling of diester intermediate **1** with TPA-thiophene tin reagent **2** to give the diester precursor to **AP9** in 46% yield (Scheme 1, Figures S2 and S3). Basic hydrolysis of **3** with LiOH afforded **AP9** in high yield in two steps from known materials (Figure S4). The synthesis of **AP12** began with a Suzuki coupling of a TPA-boronic ester derivative (**5**) with dibromobenzothiadiazole **4** to give a *bis*TPA substituted benzothiadiazole derivative **6** in good yield (Figures S5 and S6). A sodium borohydride reduction of **6** yielded *bis*TPA-substituted phenyl diamine **7** in excellent yield (Figure S7). Upon condensation of **7** with known dione diester intermediate **8**, the diester precursor to **AP12** was synthesized (Figures S8 and S9). This diester intermediate **9** underwent basic hydrolysis to give the desired **AP12** dye (Figure S10).

3.2. UV–Vis Absorption Properties

After synthesis, the dyes were first evaluated by UV–Vis absorption spectroscopy to analyze the effects each structural modification had on the dye optical energy gaps (Figure 2, Table 1). All four dyes showed a single, broad charge transfer absorption band as the lowest energy transition in solution. Absorption maxima values were observed in the following order AP6 < AP8 < AP9 \approx AP12 in dichloromethane (479, 531, 590, and 588 nm, respectively). While the absorption maxima of AP9 and AP12 were similar in energy, the absorption onset values varied significantly due to a broader absorption from AP9 in solution. Because DSC devices typically produce electricity until a dye onset, these values are more representative of the energies relevant to DSC devices. The dye λ_{onset} values were estimated from both solution measurements in dichloromethane (DCM) and on TiO₂ films. The comparison with TiO_2 films is critical for dual anchor dyes, because the carboxylic acid is part of the charge transfer system, and the carboxylic acid conformation relative to the dye π -system can be dramatically affected by surface binding orientations [26]. AP6 showed an absorption onset of 560 nm in DCM and only a slight red-shift on TiO₂ to 585 nm. The removal of the π -spacer phenyl groups between the quinoxaline and the carboxylic acids red-shifted the solution onset by 80 nm to give an onset of 640 nm for AP8 in DCM. This red-shift was rationalized by the phenyl groups having significant steric influence on the dye conformation, which prohibited the carboxylic acids of AP6 from being completely planar with the dye π -system as is needed for maximal influence on the charge transfer band. The carboxylic acid groups of AP8 can access a completely planar orientation leading to a red-shift in absorption despite **AP8** having fewer π -electrons. Interestingly, **AP8** showed a 70 nm λ_{onset} blue-shift on TiO₂. We attributed this to a significantly different film conformation being accessed relative to that observed in the DCM solution, which was potentially due to both anchors binding the TiO₂ surface leading to a dye conformation with a reduced π -system overlap between the carboxylic acids and the quinoxaline group. This highlights the need for careful assessment of the dyes on TiO_2 films rather than just from the solution when estimating dye energetics, as the change in the dye optical energy gap was 240 mV for the case of **AP8**. This was a substantial change, especially at longer wavelengths as there is little room in this spectral region for non-ideal energetics.



Figure 2. (a) Molar absorptivities of AP6, AP8, AP9, and AP12 in DCM and (b) normalized absorption on TiO₂.

Absorbance Data ^[a]					Electrochemical Data					
Dye	λ _{max} (nm)	λ _{onset} DCM (nm)	λ _{onsetTiO2} (nm)	IPCE _{onset} (nm)	ϵ (M ⁻¹ cm ⁻¹)	E _(S+/S) DCM	Eg ^{opt} (eV) ^[b]	<i>E</i> (S+/S*) DCM ^[c]	$E_{(S+/S^*)}$ TiO ₂ ^[c]	<i>E</i> (S+/S*) IPCE ^[c]
AP6	479	560	585	590	12,000	0.88	2.21	-1.33	-1.24	-1.22
AP8	531	640	570	675	8,000	0.90	1.94	-1.04	-1.28	-0.94
AP9	590	770	660	680	5,500	0.88	1.61	-0.73	-1.00	-0.94
AP12	588	720	720	800	5,600	0.89	1.72	-0.83	-0.83	-0.66

Table 1. Optical and electrochemical data of AP6, AP8, AP9, and AP12.

^[a] Onset values are taken as the x-intercept of a downward tangent line on the absorption curves on the low-energy side; ^[b] Calculated from the equation $E_{g^{opt}} = 1240/\lambda_{onset}$; ^[c] Calculated from the equation $E_{(S+/S^*)} = E_{(S+/S)} - E_{g^{opt}}$.

AP9 showed a dramatic shift in the absorption curve onset in solution to 770 nm when compared with **AP8**, where the only difference in the two dyes was a thiophene spacer between the quinoxaline and TPA groups. This could be due to both extending the conjugation of the dye π -system and to reducing the steric interactions between the quinoxaline π -bridge and donor region by the introduction of a 5-member ring at the quinoxaline bridge. The anchor group spacing is identical to that of AP8, and a significant shift in the absorption onset would again be expected on TiO_2 . Indeed, a 110 nm blue-shift was observed for AP9 on TiO2. AP12 compares most directly to AP6, and AP12 had a solution absorption onset of 720 nm. This was a 160-nm red-shift in the absorption onset relative to **AP6**, where **AP12** differed by only the linking of the phenyl π -spacers between the quinoxaline and carboxylic acid to force planarity of this group and the addition of two nitrogen atoms to reduce sterics at the TiO₂ surface. Both changes likely influenced the absorption onset. Because the anchor spacing of **AP12** is similar to **AP6**, which did not show a significant shift of absorption onset on TiO₂ relative to in solution, no significant change was expected for AP12 on the TiO_2 films. As predicted, the onset for **AP12** on TiO_2 was very similar to that in solution. Additionally, it is particularly noteworthy that all of these dyes suffered from poor molar absorptivities ranging from 12,000 to 5500 M⁻¹ cm⁻¹. AP8, AP9, and **AP12** all had molar absorptivities $\leq 8000 \text{ M}^{-1} \text{ cm}^{-1}$. Low molar absorptivities can be problematic in DSC devices.

3.3. Electrochemical Properties

For dyes to function efficiently in DSC devices, the dye energy levels should be thermodynamically well positioned relative to the TiO₂ CB for efficient electron injection and the redox shuttle for efficient dye regeneration. Thus, electrochemical measurements were carried out in dichloromethane solutions and on TiO₂ electrodes to evaluate the suitability of these dyes to work in DSC devices based on TiO₂ and I^-/I_3^- . The ground-state oxidation potentials ($E_{(S+/S)}$) of the dye should be lower in energy than

the redox shuttle (0.35 V vs. normal hydrogen electrode (NHE)). All of the dyes had similar $E_{(S+/S)}$ values within 20 mV ranging from 0.88 to 0.90 V both in DCM and on TiO₂ (Table 1, Figure 3 and Figure S1). Thus, all the dyes can undergo thermodynamically favorable electron transfers from I⁻ to regenerate the neutral dye after electron injection into TiO₂. This suggests that despite the dye conformation change when the solution and film absorption spectrum were compared, no significant effect was seen for any of the dyes via the $E_{(S+/S)}$ value measurements. Therefore, all of the energetic changes with regard to the narrowing or widening of the optical energy gap on film relative to solution is due to changes in the excited-state oxidation potentials ($E_{(S+/S^*)}$). This observation is somewhat intuitive, because the $E_{(S+/S^*)}$ values are primarily controlled by the dye acceptor groups anchored to the TiO₂ surface.



Figure 3. Energy level diagram for **AP6**, **AP8**, **AP9**, and **AP12** in DCM (solid bars) and on TiO_2 (dashed bars). The S+/S values change by <0.02 V on TiO_2 when compared with the solution values shown in the figure.

The $E_{(S+/S^*)}$ values were estimated via the equation $E_{(S+/S^*)} = E_{(S+/S)} - E_g^{opt}$ for the **AP** dyes both on TiO₂ and in solution. Because the dye structural modifications had little effect on the $E_{(S+/S)}$ values, and the dye E_g^{opt} values were found to vary broadly via UV–Vis spectroscopy in solution, a broad range of $E_{(S+/S^*)}$ values are observed for this series ranging from -0.73 to -1.33 V vs. NHE. All of these values indicate a thermodynamically favorable electron transfer to the TiO₂ CB from a photoexcited dye. AP9 with thiophene spacers extending conjugation between the quinoxaline and TPA groups was found to have the lowest energy $E_{(S+/S^*)}$ value of -0.73 V in DCM. The removal of the thiophene groups gave dye **AP8** an $E_{(S+/S^*)}$ value of -1.04 V. **AP12** with the planarized acceptor region gave the second lowest energy $E_{(S+/S^*)}$ value of -0.83 V, which was significantly lower than that of the non-planarized AP6 (-1.33 V). Because film energetic values are more relevant to DSC devices, each of the dyes were energetically analyzed on TiO₂ films. On the TiO₂ films, the $E_{(S+/S^*)}$ values for AP8 and **AP9** both upshifted significantly by \geq 240 mV. This was likely due to the spacing of the dual anchors resulting in a dramatically different conformation on TiO₂ than in solution. Based on the energetic changes, a significant twist angle was introduced between the carboxylic acid and quinoxaline groups for these dyes on film relative to in solution. After this change in AP9 energetics on TiO₂ compared with the solution measurements, AP12 had the lowest energy excited-state on films, as no change was observed when solution and TiO_2 excited-states were compared. The modest-to-no change in excited-states for AP6 and AP12 on films compared with solution suggests a similar conformation in both environments indicating solution measurements were a reasonable approximation of energy levels for this dual anchor spacing in DSC devices. This observation has also been reported for thienopyrazine-based dual anchor DSC dyes with similar carboxylic acid anchor spacings, where the phenyl spacer-based systems showed similar solution and film energetics, while the dyes with no phenyl spacer showed significantly altered energetics on the TiO_2 films [26]. In all cases, the dye thermodynamics on film indicated that a facile electron transfer event to TiO_2 is possible.

3.4. Computational Analysis

In addition to thermodynamically favorable energy levels, molecular orbital positions are critical for facile, productive electron transfers in DSC devices. Ideally, the highest occupied molecular orbital (HOMO) of the dye should be located away from the TiO₂ surface to avoid back electron transfers after electron injection, and the lowest unoccupied molecular orbital (LUMO) of the dye should be localized closer to the TiO₂ surface for efficient electron injection to TiO₂ after photoinduced intramolecular charge transfer (ICT). Density functional theory (DFT) calculations at the B3LYP/6-311G(*d*,*p*) level were carried out in Gaussian09 to visualize the frontier orbital distribution of the target structures [34]. The HOMO was found to be distributed across both donors on each dye with some presence on the quinoxaline benzene ring. This HOMO location is well positioned to be far from the TiO₂ surface, as desired. The LUMO was localized on the quinoxaline bridge and carboxylic acid anchors at the TiO₂ surface (Figure 4). The LUMO is ideally positioned for electron transfer to TiO₂. Significant HOMO–LUMO overlap was observed at the quinoxaline (primarily at the benzene ring), which shows the role of this group as a π -bridge. Thus, efficient ICT from donor to acceptor in the DD- π -AA molecular framework is possible, which is critical to absorbing lower energy light with reasonable molar absorptivities.



Figure 4. Frontier molecular orbital distributions of AP6, AP8, AP9, and AP12.

3.5. Photovoltaic Analysis

Based on optical, electrochemical, and computational data, all of the dyes studied can perform well in I⁻/I₃⁻/TiO₂-based DSCs. The devices were analyzed under AM 1.5 G incident solar simulation with PCEs calculated according to the equation, PCE = $(J_{SC} \times V_{OC} \times FF)/I_0$, 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 light intensity equal to 1 sun in this study. The highest PCE of the series was measured for **AP6** at 3.7% with a J_{SC} value of 7.0 mA/cm² (Figure 5 and Table 2). **AP6** also had the highest observed Voc value of 694 mV, with the remaining dyes having very similar V_{OC} values of 591–615 mV, which also contributed to **AP6** showing the highest PCE of the series. **AP6**-based devices have the highest J_{SC} value for the series followed by **AP12** > **AP9** > **AP8**. Interestingly, the J_{SC} trend followed the same trend for absorption onsets on TiO₂, with the longest wavelength absorbing dyes producing the highest J_{SC} values except for **AP6**. **AP6** had the narrowest absorption of the series yet had the highest photocurrent in DSC devices. This was likely the result of a significantly higher molar absorptivity for **AP6** relative to the other dyes in the series. **AP6** also showed the highest peak incident photon-to-current conversion efficiency (IPCE) value of the dyes in this series at >70%. AP8, AP9, and AP12 reached a peak IPCE of ~40%, which was roughly half that of AP6. This observation correlates to the observed molar absorptivities for AP8, AP9, and AP12 being roughly half that of AP6. The J_{SC} values for AP8, AP9, and AP12 ranged from 3.8 to 6.1 mA/cm², which was significantly closer to the J_{SC} value of **AP6** due to the broader absorption of these dyes. It is noteworthy that the broadest IPCE spectrum was observed for AP12, which reached 800 nm. Very few organic dyes produce electricity from such a low-energy wavelength [35]. Importantly, through this double donor, double anchor design strategy, the IPCE breadth can be increased relative to a more traditional D-A- π -A dye design using the same TPA donor, quinoxaline auxiliary acceptor, thiophene π -bridge, and the stronger-accepting cyanoacrylic acid, and, for the case of **AP12**, the IPCE breadth exceeds that observed for even metal-based dyes such as N719 [36]. Given this improvement on DSC device electricity production wavelength range and the observed slow desorption from TiO₂ surfaces for DD- π -AA structures (similar to dual anchors popularized with heteroleptic-Ru dyes), this organic design is attractive [37,38]. Molecular engineering strategies to improve the molar absorptivity are important to improve the peak IPCE value, and the focus of future designs should be on maintaining or extending this exceptional IPCE breadth. Interestingly, both **AP8** and **AP12** showed a dramatic red-shift in the IPCE onset relative to the film absorption on TiO₂ of \geq 80 nm (Table 1). This change was likely due in part to the interaction of the dyes with the electrolyte, whereas if this were the result of a solid-state ordering on film (such as J-aggregates) this shift would have presented during the TiO₂ film absorption studies [39]. Accounting for these interactions energetically when rationally designing DSC dyes is not straightforward, but these interactions can have profound effects on dye energetics. Directly measuring how the electrolyte is affecting the dye energy levels is challenging; however, if the assumption that the dye $E_{(S+/S)}$ energy level remains unchanged, as it does when comparing solution and TiO_2 film measurements for these dyes, then the excited state energy levels are shifting dramatically upon the addition of the electrolyte. For example, in the case of AP12, a driving force for electron injection (ΔG_{ini}) into the TiO₂ CB of 330 mV is estimated from both solution and film measurements when the TiO₂ CB is taken as -0.50 V vs. NHE (Table 1). However, using the IPCE onset value to calculate the excited-state energy level of **AP12** gives a ΔG_{ini} value of only 160 mV. This lower ΔG_{inj} value could have a dramatic influence on electron injection efficiencies and may also contribute to lower peak IPCE values. Methods to both predict and control dye energetics within a full DSC cell environment are critical to move toward rational dye design and away from pseudo-empirical dye design protocols where the energetics within a DSC device only mirror that of the solution or film estimates on an unpredictable case-by-case basis. The inability to directly account for the dye-electrolyte energetic changes has rendered a very promising broad absorbing dye (AP12) as estimated energetically from the solution and film measurements, low performing in DSC devices (2.9% PCE).



Figure 5. (a) *J*–*V* curves for DSC devices with **AP6**, **AP8**, **AP9**, and **AP12**. (b) IPCE curves for **AP6**, **AP8**, **AP9**, and **AP12**-based DSC devices.

Dye	$J_{\rm SC}$ (mA/cm ²)	V _{OC} (mV)	FF	PCE (%)
AP6	7.0	694	0.76	3.7
AP8	3.8	615	0.71	1.7
AP9	5.4	591	0.72	2.3
AP12	6.1	599	0.74	2.8

 Table 2. Summary of photovoltaic parameters for AP dyes.

All devices were prepared with an I^-/I_3^- electrolyte comprised of 0.1 M guanidinium thiocyanate (GuNCS), 1.0 M 1,3-dimethylimidazolium iodide (DMII), 30 mM I_2 , 0.5 M 4-*tert*-butylpyridine (TBP), and 0.05 M lithium iodide (LiI) in acetonitrile/valeronitrile (85:15).

3.6. Time-Correlated Single Photon Counting (TCSPC) Studies

Electron injection efficiencies were estimated from time-correlated single photon counting (TCSPC) studies with **AP9** and **AP12** to compare with the reported values for **AP6** and **AP8** [24]. The experiments were conducted for each dye in DCM solution, on TiO₂, on TiO₂ with chenodeoxycholic acid (CDCA) as a deaggregating agent, and on TiO₂ with CDCA and LiI [26,40,41]. Due to the short excited-state lifetimes of the dyes in solution combined with instrument response function limitations (>150 ps timescale), injection efficiencies can only be reported as a lower limit and are likely faster than that reported. The equation $\eta_{\text{eff}} = 1 - (\tau_{\text{TiO}_2}/\tau_{\text{sol}})$ is used to estimate the photoinduced dye electron injection efficiency to the TiO₂ CB where the overall efficiency (η_{eff}) is calculated based on the fluorescence decay lifetime (τ) of the dye in different environments. The solution lifetimes of the dyes ranged from 0.34 to 0.79 ns in the following order: **AP12** > **AP9** > **AP6** > **AP8** (Figure 6 and Table 3).

Table 3. Fluorescence lifetime and charge injection efficiencies of AP6, AP8, AP9, and AP12 in different environments.

Dye	$ au_{ m sol}$ (ns) $^{ m a}$	$ au_{\mathrm{TiO}_2}$ (ns) ^b	η_{eff} (%) ^b	$ au_{\mathrm{TiO}_2}$ (ns) ^c	η _{eff} (%) ^c	$ au_{\mathrm{TiO}_2}$ (ns) ^d	η_{eff} (%) ^d
AP6	0.38	0.30	29	0.29	24	< 0.15	>61
AP8	0.34	0.29	27	0.27	21	< 0.15	>54
AP9	0.77	0.44	42	0.32	58	< 0.15	>80
AP12	0.79	0.55	30	0.25	68	< 0.15	>81

^a In dichloromethane (DCM); ^b On TiO₂; ^c On TiO₂ with chenodeoxycholic acid (CDCA); ^d On TiO₂ with CDCA and LiI.



Figure 6. Fluorescence lifetimes of (a) AP9 and (b) AP12 in different environments.

The lifetimes of the π -extended **AP9** and the fused ring **AP12** were significantly longer than that of derivatives **AP8** and **AP6**, respectively (~0.78 ns vs. ~0.36 ns). On TiO₂ with no additives, an emission can still be observed, but lifetimes were shorter than observed in solution ranging from 0.29–0.55 ns

with η_{eff} values of 27–42%. In this environment, **AP9** showed the highest injection efficiency, with **AP6** and **AP8** showing the lowest η_{eff} values of ~28%. The addition of the deaggregating agent CDCA to the dyeing solution resulted in significantly increased charge injection efficiencies for AP9 and AP12 from 42% to 58% and 30% to 68%, respectively. AP6 and AP8 remained relatively unchanged, which suggests these dyes have fewer dye-dye energy transfer pathways and excited-state deactivation pathways than AP9 and AP12. AP9 and AP12 inject best in isolation from other dye molecules when the CDCA insulator is added. The addition of LiI resulted in fluorescence lifetimes shorter than the response function of the instrument, leading to the highest injection efficiencies observable for each dye ranging from >54% (AP8) to >81% (AP12). Given that the dye excited-state lifetimes exceeded the response time of the instrument with the LiI additive, no further additives were evaluated. This does suggest that the low peak IPCE observed for AP12 was not due to electron injection into TiO_2 and was more likely a combination of results from a low molar absorptivity and possibly a relatively slow regeneration event, as has been previously observed for DD- π -AA dyes [26]. However, the >81% electron injection efficiency from the novel AP12 anchor/acceptor group with a very low driving force for electron transfer (160 mV) strongly suggests this group is valuable for the future design of NIR organic dyes for DSCs.

It is noteworthy that the excited-state lifetimes for the dyes evaluated in this series are short relative to typical D- π -A dye designs, which are often $\geq 1-2$ ns. This may be an inherent limitation to the DD- π -AA design, as short lifetimes have also been observed for a thienopyrazine-based DD- π -AA dye **AP3** (0.36 ns in DCM) [26]. However, **AP3** gave DSC devices with >10% PCE and >80% peak IPCE values in low light in the prior study. **AP6** also showed a reasonable peak IPCE of ~70% despite having one of the shortest excited-state lifetimes of the series. Thus, despite the short lifetimes, electron transfer to TiO₂ may still be facile.

4. Conclusions

Quinoxaline was successfully employed and studied as a π -bridge for four dyes using the dual donor, dual acceptor (DD- π -AA) construct. The effect of structural modifications was studied via UV–Vis absorption spectroscopy, electrochemical analysis, computational DFT analysis, TCSPC spectroscopy, and DSC device analysis. With this design, dyes could be rationally designed, which absorb light beyond 750 nm in solution. The evaluation of the dye energetics on film showed that the dye anchor spacing plays a critical role in the validity of using solution measurements to approximate dye–Ti O_2 film energetics. The anchor group spacing using two benzoic acid groups *ortho* substituted on a 6-member ring provides a reliable group arrangement for rational dye energy level translation from solution to TiO₂ films. Additionally, the IPCE spectrum onset shifts dramatically in some cases further exacerbating the challenge of trying to reliably predict dye energetics within a working DSC device regardless of if the estimates for dye energetics were made on film or in solution. AP12 has the widest IPCE response reaching beyond 800 nm. This is an exceptional IPCE onset for an organic dye and was presumably due in part to dye–electrolyte interaction as the dye–TiO₂ absorption onset was 80 nm blue-shifted compared with the IPCE onset. TCSPC studies revealed short excited-states for all of the dyes in this series, but with the addition of Li ions, dye-emission became unobservable, indicating that electron transfer from the dye to TiO₂ upon photoexcitation was facile. These results suggest that the primary drawback for this dye design is the poor molar absorptivities, such as 5,600 M^{-1} cm⁻¹ for AP12. Future dye designs will focus on bolstering the dye molar absorptivities while retaining good electron transfer kinetics with properly spaced dual anchor groups.

Supplementary Materials: The following are available online at http://www.mdpi.com/2076-3417/8/9/1421/s1. Synthetic Details for **AP9** and **AP12**; General Computational Information; General Photovoltaic Measurement Information; Device Fabrication Protocol; Time-Correlated Single Photon Counting General Information; Figure S1. Cyclic voltammetry plots of **AP** dyes in DCM solution and on TiO₂; Figure S2. ¹H NMR spectrum of compound **3** (CDCl₃, 500 MHz); Figure S3. ¹³C NMR spectrum of compound **3** (CDCl₃, 75 MHz); Figure S4. ¹H NMR spectrum of compound **AP9** (DMSO-*d6*, 500 MHz); Figure S5. ¹H NMR spectrum of compound **6** (CDCl₃, 500 MHz); Figure S6. ¹³C NMR spectrum of compound **6** (CDCl₃, 125 MHz); Figure S7. ¹H NMR spectrum of compound **7** (CDCl₃, 300 MHz); Figure S8. ¹H NMR spectrum of compound **9** (CDCl₃, 300 MHz); Figure S9. ¹³C NMR spectrum of compound **9** (CDCl₃, 75 MHz); Figure S10. ¹H NMR spectrum of compound **AP12** (DMSO-*d6*, 500 MHz, 80°C); and DFT cartesian coordinates for the **AP** series dyes.

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