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Unravel the Impact of Anchoring Groups on the Photovoltaic Performances of Diketopyrrolopyrrole Sensitizers for Dye-Sensitized Solar Cells

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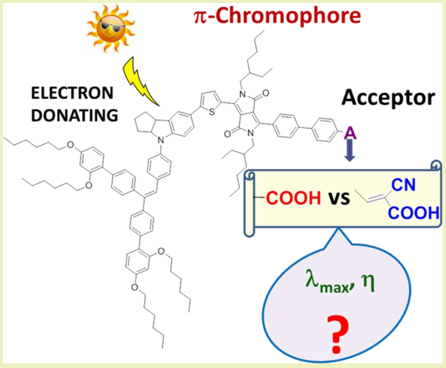
Supporting Information

ABSTRACT: Two D-π-A dyes, one with a strong electron withdrawing cyanoacrylic acid **DPP 20** and one with a weak acceptor carboxylic acid **DPP 21** have been synthesized and characterized for their application in dye-sensitized solar cells. This allows us to understand the role of electron withdrawing strength of the acceptor anchoring groups on the optoelectronic properties of chromophoric π spacer molecules, e.g., the diketopyrrolopyrrole (DPP) moiety. The low energy absorption maxima of DPP 20 is red-shifted by only 7 nm compared to DPP 21, implying a minimal role for the strong acceptor in the light harvesting properties of colored π spacer molecules. Because of this small red shift, J_{SC} of DPP 20 is marginally higher than that of DPP 21. However, because of the higher fill factor of DPP 21, the overall power conversion efficiency (PCE = 7.65%) is higher than that of DPP20 (7.34%). The data reveal that a weak acceptor is adequate to achieve good light harvesting as well as provide good photovoltaic efficiencies for colored π spacer sensitizers.



KEYWORDS: *Anchoring group, Cyanoacrylic acid, Diketopyrrolopyrrole, Dye-sensitized solar cells, TiO$_2$*

INTRODUCTION

Dye sensitized solar cells (DSSCs) have been considered a promising generation of photovoltaic since their inception, due to their low cost fabrication and efficient energy conversion.[1,2] The power conversion efficiency of DSSCs is greatly influenced by the visible light harvesting ability of the sensitizers. Sensitizers mainly focused on metal complexes (ruthenium, zinc porphyrin) and metal free organic dyes.[3−12] Limited sources and the high cost of the efficient ruthenium-based sensitizers drove research attention toward metal free organic sensitizers.[10−12] Numerous efforts on organic dyes emphasized that a donor fragment with a π spacer coupled to a strong electron accepting anchoring group (D-π-A) is a promising structural arrangement for better solar energy conversion.[10−12] In this type of arrangement, the light harvesting property is mainly influenced by the choice of donor and acceptor fragments. Donor groups, such as triphenylamine, indoline, carbazole, etc., and acceptor parts, such as cyanoacrylic acid, rhodanine acetic acid, etc., are widely utilized to enhance the sensitizer absorption in the longer wavelength region.[13−19] Benzene, thiophene, cyclopentadithiophene, thienothiophene, etc. have been successfully utilized as the π spacer; however, their role in light harvesting efficiency is minimal.[20−23]

Generally, the presence of a strong electron withdrawing (EW) group near the anchoring part, such as cyanoacrylic acid, is needed to pull the electron density from the donor fragment, narrowing the band gap through the mixing of donor−acceptor orbitals, which imparts absorption in the longer wavelength region and is thought to facilitate electron injection into TiO$_2$, as observed for several D-π-A molecules.[24−26] The cyanoacrylic acid present at the anchoring group undergoes cis−trans isomerization at the double bond upon UV-irradiation and results in enhancing the recombination process.[27] Removing the cyanoacrylic acid will increase the planarity of the complete dye and might help in reducing the recombination. In general, for the D-π-A dyes, the π bridge serves primarily to extend π-conjugation, while efficiently relaying electron density from the donor to the acceptor. However, light harvesting in the red and

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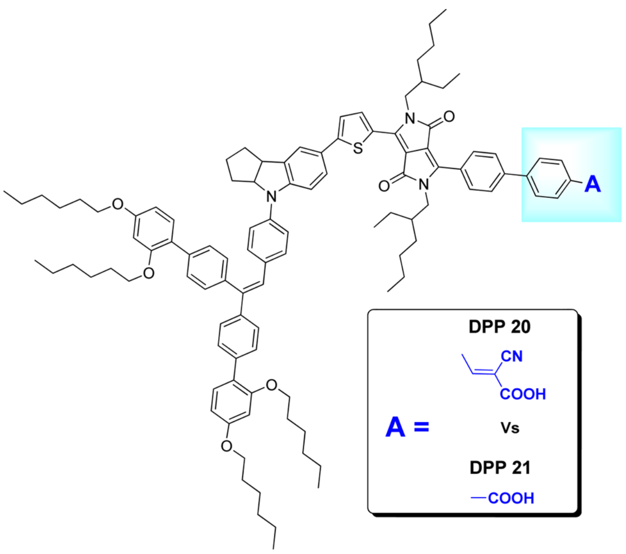
near IR region is still a major challenge among the D-π-A sensitizers without the cyanoacrylic acid functional group. In this context, introducing inherently colored molecules as π spacer will aid in spreading the spectral response of the dye molecule toward the red and near IR region. Recently, the organic pigment diketopyrrolopyrrole (DPP) is widely utilized for developing photovoltaic materials due to their remarkable photochemical, mechanical, and thermal stability.[28−30] Owing to their high color and strong electron withdrawing nature, DPP has been successfully employed as π spacer in dye sensitized solar cells in recent years.[31−35] The twist in the symmetric arrangement of DPP (thiophene-DPP-thiophene) to the asymmetric arrangement (thiophene-DPP-phenyl) enhances the incident photon-to-electron conversion efficiency (IPCE), and the overall solar energy conversion efficiency increased to 7.7% from 2.13% of symmetric DPP based sensitizers.[36,37] By employing bulky 2,4-bishexyloxybiphenyl indoline based donors on DPP core enhances the V_{OC} and the efficiency above 10% with cobalt based redox couple.[38,39] Although introducing the DPP core as π chromophore enhances the red light absorption region, all the DPP based dyes reported so far have a strong electron withdrawing (EW) cyanoacrylic acid anchoring group.[31−39] Switching the strong EW acceptor to a mild acceptor like carboxylic acid for π chromophore (D-πC-A) based sensitizers will provide prolific information about the significance of EW groups near the anchoring part in tuning the absorption, electrochemical, and power conversion efficiencies. On the basis of this, we have synthesized indoline based DPP π chromophore sensitizers (D-πDPP-A), **DPP 20** with a strong EW acceptor such as cyanoacrylic acid (**CA**) and **DPP 21** with a mild acceptor like carboxylic acid (**CH**) as depicted in Scheme 1. In this report, we have analyzed the effect of the different strength of the acceptor part on light harvesting, electrochemical, and solar energy conversion efficiencies.

■ RESULTS AND DISCUSSION

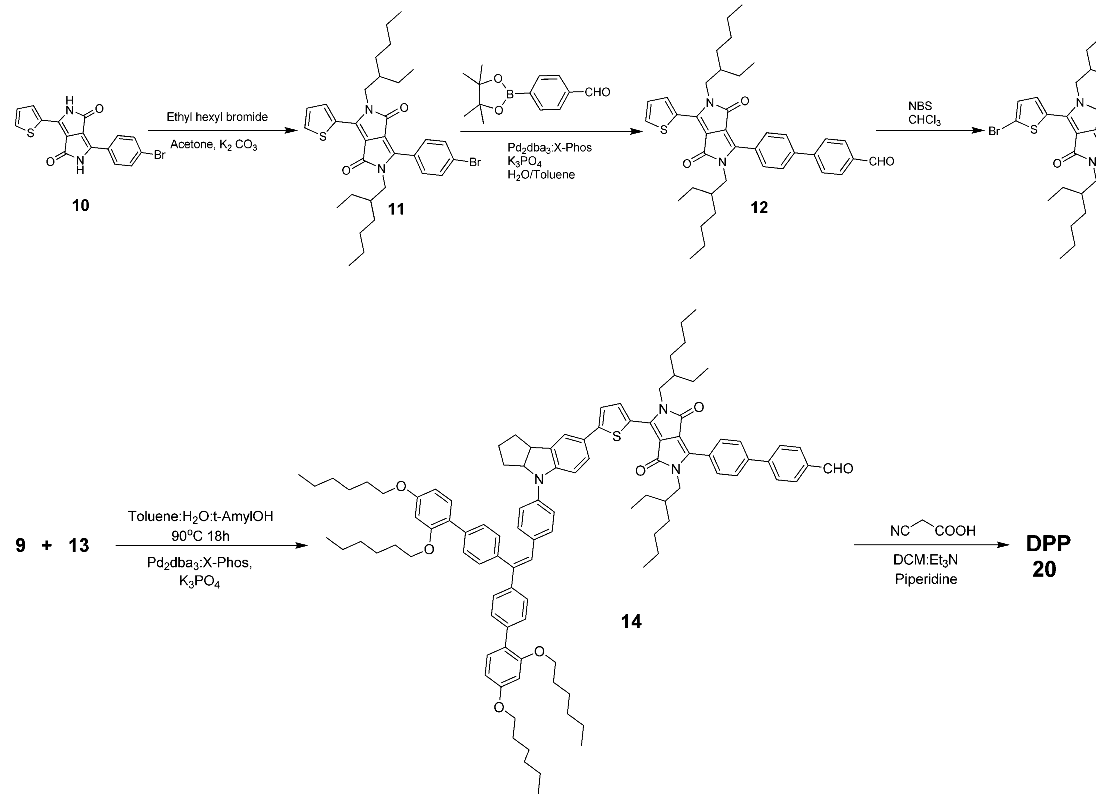
Synthesis and Characterization of DPP Based D-π-A Sensitizers. The synthetic route employed for the synthesis of **DPP 20** and **DPP 21** is shown in Schemes 2 and 3. Bulky indoline-based donor compound **9** and the π chromophore **10** were synthesized in an analogous method as reported earlier and the synthetic scheme is shown in section S2.[40,41] The DPP based π chromophore **10** is utilized as a common starting core for coupling with the acceptor part for both the dyes. Alkylation of chromophore **10** with ethylhexyl bromide yielded the alkylated π chromophore **11**. The alkylation helps in better solubility of the π chromophore **10**. Suzuki coupling of **11** with 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzaldehyde yield the π chromophore acceptor compound **12**. Bromination of **12** using NBS results in the bromo substituted π acceptor part **13**, which is further assembled with the donor group **9** via Suzuki coupling. Finally the obtained aldehyde terminated dye **14** undergoes Knoevenagel condensation with cyanoacetic acid to form the target **DPP 20** with the cyanoacrylic acid anchoring group. For synthesizing the carboxylic acid counterpart, first we tried to oxidize the aldehyde in **14** to carboxylic acid; however, the oxidation reactions mainly destruct the DPP core and then we achieved the target **DPP 21** in a different route as described in Scheme 3. We first synthesized the tertiary butyl ester of 4-bromo benzoic acid **15**. This bromo compound **15** is converted into its boronic ester **16** for assembling with the alkylated π chromophore **11** via Suzuki coupling to produce the π chromophore acceptor part **17**. To couple this π chromophore acceptor part **17** with the donor part, it is converted to its bromo compound **18** using NBS. Indoline donor moiety **9** undergoes Suzuki coupling with **18** and the resulting tertiary butyl ester protected carboxylic acid terminated dye **19** undergoes hydrolysis in the presence of few drops of TFA to yield **DPP21** with carboxylate anchoring dye. All the key intermediates and two final dyes were characterized by NMR and mass techniques. Results of ^{1}H NMR, ^{13}C NMR, and mass spectra are correlated very well with the final dyes. The signal at 1.32 ppm in the proton NMR spectrum of **2** is assignable to the methyl protons of the boronyl ester. The ^{1}H NMR spectrum of **9** also has a signal at 1.30 that corresponds to the formed boronyl ester from its bromo counterpart. The aldehyde signal appears at 10.09 and 191.64 ppm for **14** in the ^{1}H NMR and ^{13}C NMR spectrum, respectively. These signals disappeared in the NMR spectrum of **DPP20** confirming the coupling of aldehyde with cyanoacrylic acid. The tertiary butyl proton signal of **15**, **16**, **17**, **18**, and **19** appears around 1.6 ppm. The disappearance of this signal in the final dye **DPP21** confirms the deprotection of carboxylic acid.

Scheme 1. Structure of DPP Based D-π-A Sensitizers



Optical Properties. Absorption measurements were carried out to understand the consequence in light harvesting properties of the DPP based dyes when their acceptor part is changed from strong EW CA to mild acceptor CH anchoring group. Figure 1a (left) displays the absorption spectra of **DPP 20** and **DPP 21** in dichloromethane solvent. Both the dyes exhibit broad absorption in the 450−700 nm regions with absorption maxima at 590 nm for CA acceptor and 583 nm for CH acceptor. The slight red shift of 7 nm is ascribed to the strong EW nature of CA compared with the CH group. Further, the absorption behavior of these two dyes on 3 μm TiO_2 film was measured and shown in Figure 1b. When compared with their solution state behavior, both the dyes show red-shifted absorption behavior on binding with TiO_2 indicating the formation of *J*-aggregation on the surface of the TiO_2 as envisaged in the literature.[42] The difference in absorption between the two dyes on binding with TiO_2 is around 15 nm. Generally, when the CA anchoring part is changed to the CH anchoring group in the case of the D-π-A dyes utilizing simple aromatic molecules as the π spacer, the

Scheme 2. Synthetic Route Employed for Cyanoacrylic Acid Anchoring DPP Dye (DPP 20)



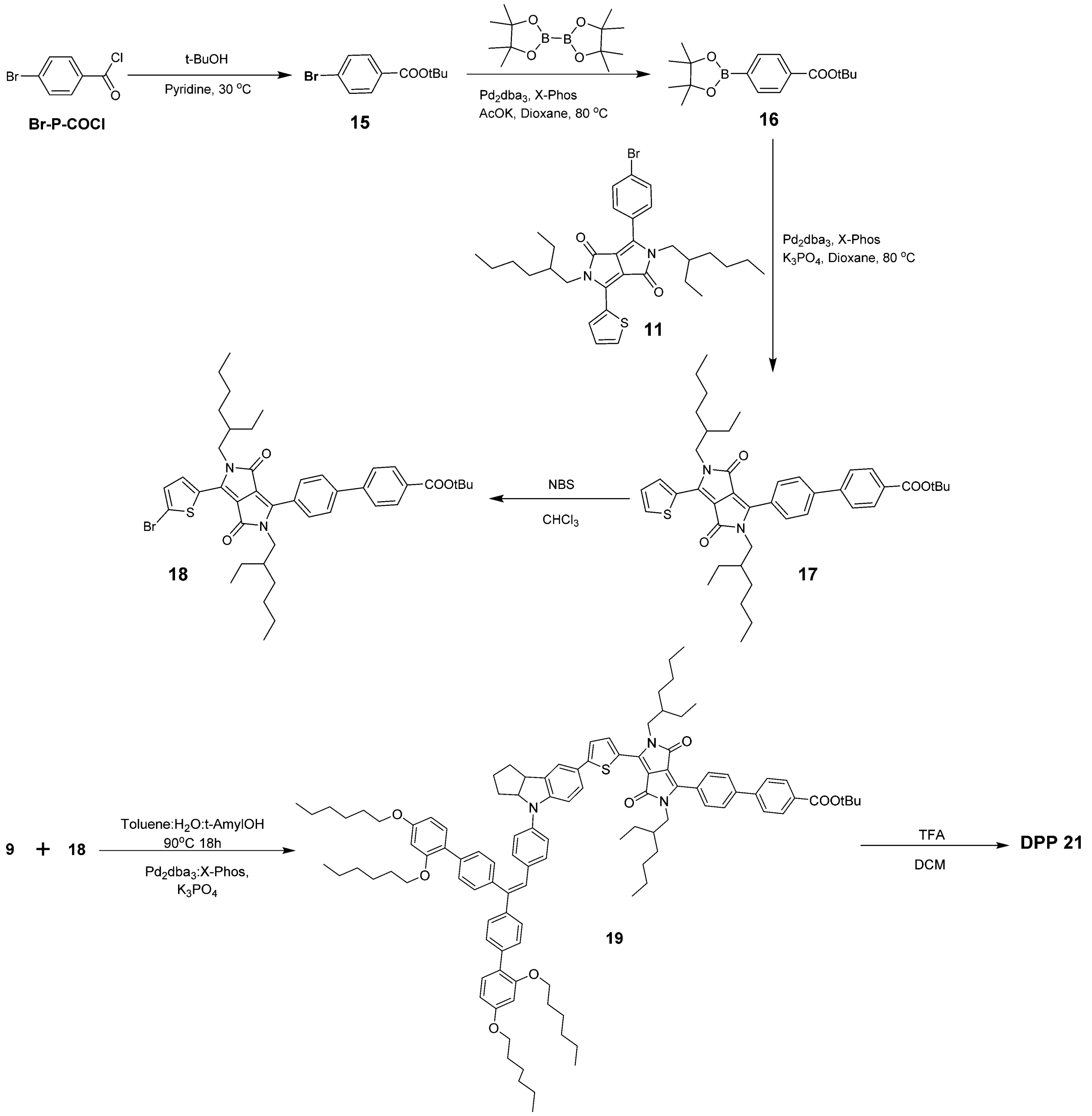
difference in absorption was observed around 50 nm.[26,43−45] However, only a small red shift is observed in case of D-π-DPP-A dyes utilizing the diketopyrrolopyrrole (DPP) as the π-chromophore linker. The observed results reveal that the strength of the EW anchoring moiety (CA) has minimal effect on the absorption behavior of D-πDPP-A dyes. The molar extinction coefficient of these dyes was found to be 2.87×10^4 and 2.48×10^4 M^{-1} cm^{-1} for **DPP 20** and **DPP 21**, respectively. The similar light harvesting efficiency for the two dyes indicates that their absorption behavior mainly relies on the donor π chromophore part despite their variation in their acceptor groups. Figure 1a (right) also depicts the emission spectrum of both dyes and the emission maximum is found to be 663 nm for **DPP 20** and 665 nm for **DPP 21** specifying that there is no significant difference in the excited state behavior of the two dyes.

Electrochemical Properties. Cyclic voltammetry (CV) measurement is employed to estimate the first oxidation potential (E_{ox}) of the DPP dyes which corresponds to the HOMO levels and their corresponding cyclic voltammogram are displayed in Figure 2. **DPP 21** (1.1 V) having the CH anchoring group oxidizes at slightly higher potential than **DPP 20** (0.97 V) with the CA anchoring group. This small potential difference between these two dyes suggests that the strength of anchoring groups have minimal effect in the electronic oxidation behavior of D-πDPP-A based dyes. The observed potential levels are more positive than the iodide/triiodide redox electrolyte pledging the efficient dye regeneration.[46] LUMO levels of the dyes were calculated from the (i) E_{0-0} energy derived from the intersection of the absorption and emission spectra and (ii) HOMO level of the dyes. The obtained LUMO levels (−0.98 V for **DPP 20** and −0.86 V for **DPP 21**) are more negative than the conduction band of TiO_2 allowing efficient electron injection from the excited state dyes to the TiO_2.[46] The photophysical data of the two dyes were shown in Table 1.

Photovoltaic Properties. The photovoltaic performance of the two dyes **DPP 20**, **DPP 21** was evaluated by employing them in the DSSCs using iodide/triiodide (I^-/I_3^-) based redox mediator in acetonitrile. The photocurrent density−voltage (J−V) characteristics of these devices under simulated one sun illumination (AM1.5G, 100 mW/cm^2) are displayed in Figure 3 and the corresponding photovoltaic data were summarized in Table 2. On analyzing the photovoltaic parameters separately, one could notice that the short circuit current density (J_{SC}) obtained in the case of **DPP 21** are slightly lower than that of **DPP 20**. This is due to the fact that **DPP 20** possesses a 10 nm red-shift in the absorption spectrum compared to that of **DPP 21**. Because of this red shift, the dye sensitized solar cells made with the **DPP 20** resulted in higher J_{SC} of 15.3 mA/cm^2 as opposed to 14.9 mA/cm^2 obtained in the case of **DPP 21**. The open-circuit potential (V_{OC}) of the devices made with both the dyes are similar and exhibited around 690 mV for both the **DPP 20** and **DPP 21**. Interestingly, the fill factor of the devices made with the sensitizer **DPP 21** are higher compared to the **DPP 20** as well as the other DPP dyes reported previously.[12] Overall, the solar cells sensitized with **DPP 21** dye, led to a power conversion efficiencies (PCE) of **7.65%**, whereas, DSSCs employing the sensitizer **DPP 20**, exhibited PCE of **7.34%** even though a higher J_{SC} was observed in the latter due to the 20 nm red shift. Despite the higher photocurrents obtained in the case of **DPP 20**, the loss in the fill factor resulted in the lower power conversion efficiency compared to that of the **DPP 21**.

Slightly higher efficiencies of 8% was achieved at low sun, i.e., at 0.5 and 0.1 sun intensities in the case of **DPP 20**, whereas, in

Scheme 3. Synthetic Route Employed for Carboxylic Acid Anchoring DPP Dye (DPP 21)



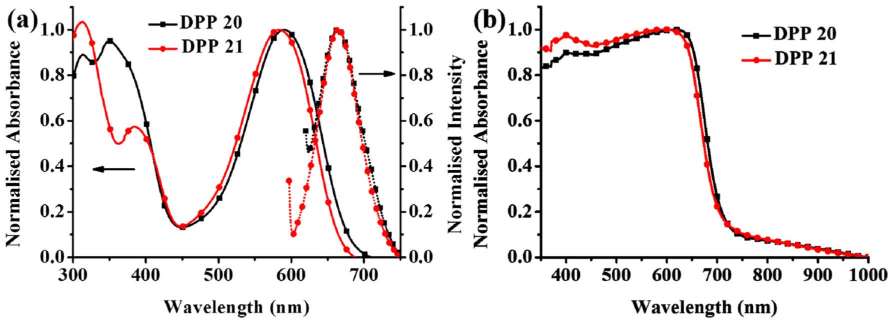


Figure 1. (a) Normalized UV−vis absorption and emission spectra of **DPP 20** and **DPP 21** in dichloromethane. (b) Normalized UV−vis absorption spectra of **DPP 20** and **DPP 21** adsorbed on the TiO_2 film.

the case of **DPP 21**, similar efficiencies were obtained at all the sun intensities. The lower efficiency at the full sun is mainly due to the loss of the fill factor at the full sun compared to that of the low sun intensities. The loss in the fill factor in the case of

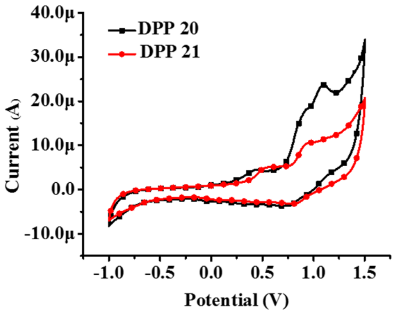


Figure 2. Cyclic voltammogram of **DPP 20** and **DPP 21** in dichloromethane.

Table 1. Photophysical and Electrochemical Properties of Sensitizers DPP 20 and DPP21

sensitizers	absorption λ_{max}[a] (nm)	emission λ_{max}[a] (nm)	HOMO[b] (V vs NHE)	band gap[c] (eV)	LUMO[d] (V vs NHE)
DPP20	590	663	0.97	1.95	−0.98
DPP21	583	665	1.10	1.96	−0.86

[a] Absorption or emission maximum in dichloromethane solution. [b] The HOMO was taken from the first redox potential in the CV plot. [c] The band gap (E_{0-0}) was estimated from the intersection of the normalized absorption and emission spectra. [d] The LUMO was calculated with the expression of LUMO = HOMO − band gap.

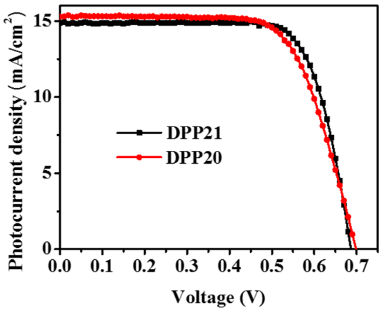


Figure 3. *J*−*V* data obtained with the DPP 20 and DPP 21 dyes using the Iodide/triiodide redox mediator.

Table 2. Photovoltaic Performance of DSSCs of DPP Based Sensitizers Using Iodide/Triiodide Redox Mediator[a]

sensitizers	DPP 20			DPP 21		
parameters	1 sun	0.5 sun	0.1 sun	1 sun	0.5 sun	0.1 sun
V_{OC} (mV)	698	684	648	687	669	622
J_{SC} (mA/cm^2)	15.28	7.97	1.61	14.86	7.55	1.52
FF	0.688	0.726	0.769	0.75	0.755	0.783
η (%)	**7.34**	7.91	8.02	**7.65**	7.63	7.40

[a] TiO_2 film with thickness of 8 µm scattering layer and 5 µm transparent layer. The electrolyte composition 1.0 M DMII (1,3-dimethylimidazolium iodide), 0.03 M iodine, 0.025 M NaI, 0.5 TBP, 0.1 M guanidinium thiocyanide, and acetonitrile solvent.

DPP 20 could be attributed to the strong aggregation of the dyes on the TiO_2 surface. This is also evident from the devices made with lower amount of deaggregating agent (chenodeoxycholic acid concentration of 5 mM) resulted in poor fill factors and hence poor power conversion efficiencies as shown in the Figure S5. In the case of **DPP 21** chenodeoxycholic acid (CDCA) concentration of 5 mM is found to be optimum whereas in the case of **DPP 20**, 10 mM concentration is necessary to get higher fill factors. Increasing the concentration of CDCA further in the case of **DPP 20** resulted in lower efficiencies mainly due to lower dye loading. The observed aggregation behavior of DPP 20 is due to the photoisomerization behavior of cyanoacrylic acid anchoring dyes that will affect the uniform adsorption of the dyes on the surface of TiO_2 and enhances the aggregation behavior. While in the case of **DPP 21**, the presence of only the carboxylic acid anchoring group helps in uniform surface adsorption and minimizes the aggregation behavior. At the low sun intensities, higher fill factors and hence higher power conversion efficiencies were obtained in the case of **DPP 20** compared to that of the **DPP 21**. The open circuit voltage at various sun intensities is a bit higher in the case of **DPP 20** compared to **DPP 21**. To identify the reason for the slightly higher open circuit potential, dye loading measurements were carried out by desorbing the dye from the TiO_2 films and it was found out that the dye loading is slightly higher in the case of **DPP 20** compared to **DPP 21**. In the case of **DPP 20** dye loading of approximately 1.74×10^{-7} mol/cm^2 is observed whereas in the case of **DPP 21** dye loading of 0.98×10^{-7} mol/cm^2 is observed. The higher open circuit voltage in the case of **DPP 20** could be attributed to the higher dye loading observed. The complete *J*−*V* details for **DPP 20** and **DPP 21** are given in Table 2.

The photocurrent action spectra of the dyes **DPP 21** and **DPP 20** are measured with their corresponding photovoltaic devices and the plot of incident photon-to-current conversion efficiency as a function of wavelength is displayed in Figure 4.

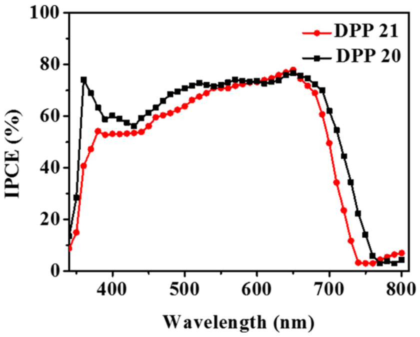


Figure 4. IPCE of **DPP 20** and **DPP 21** dyes using the iodide/triiodide redox mediator on 8 + 5 µm TiO_2 films.

The IPCE spectra of these devices made with these two dyes closely follows the shape of the absorptivity of the sensitized TiO_2 layer. The devices made with the **DPP 20** exhibit an IPCE onset at around 760 nm and the **DPP 21** has the onset around 740 nm. The mismatch of the IPCE spectra with absorption spectrum can be due to the electron transfer from the excited aggregates to the TiO_2 as well as from the monomers which have different quantum yields.[47,48] The IPCE spectral profile of both the dyes shows the maximum of 85% at around ∼680 nm. Both the dyes exhibit high IPCE value across the whole visible wavelength range maintaining a value of 70% from 450 to 720 nm.

Transient photovoltage and photocurrent decay measurements were carried out to examine if there is any difference in the collection efficiency along the *I*−*V* bias by varying the strength of the acceptor groups. Figure 5a shows the lifetime of the electrons in the TiO_2 film within the device as a function of the voltage bias for the two dyes using iodide/triiodide redox

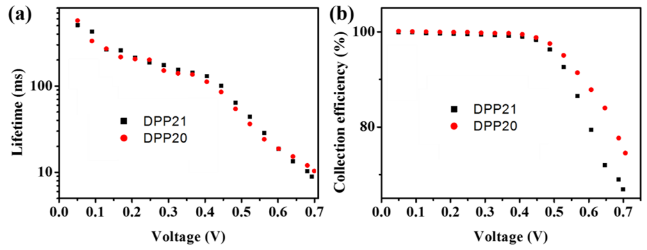


Figure 5. (a) Lifetime of electrons in the conduction band of TiO_2 in various voltages. (b) Electron collection efficiency in various voltages.

mediator. The electron lifetime in both the cases is similar along the *I*−*V* bias. Figure S6 shows the transport rate of the electrons for the two dyes using iodide/triiodide redox couple. The collection efficiency is determined by the ratio of the transport rate to the transport rate + recombination rate. The plot of collection efficiency as a function of voltage bias is shown in Figure 5b. The collection efficiency is almost similar along the *I*−*V* bias for both the dyes. The observed similar electron lifetime and collection efficiency for both the **DPP 20** and **DPP 21** further supports the minimal role of strength of the acceptor groups on the photovoltaic properties.

CONCLUSIONS

In conclusion, two dyes **DPP 20** and **DPP 21** based on strong electron withdrawing cyanoacrylic acid and mild acceptor carboxylic acid have been successfully synthesized and characterized. Compared to the previously reported other D-π-A dyes, the dye **DPP 21** shows only a small blue shift in the absorption even though the strong electron withdrawing cyanoacrylic acid is substituted with the carboxylic acid. Interestingly, **DPP 21** with the carboxylic acid anchoring group shows slightly higher power conversion efficiency compared to that of the **DPP 20** with the cyanoacrylic acid anchoring group. Despite the red shift and the higher J_{SC} obtained with the **DPP 20**, the loss in the fill factor resulted in slightly lower power conversion efficiency compared to that of the **DPP 21**. Transient photovoltage and photocurrent decay measurements reveals that both the dyes have similar electron lifetime and collection efficiency. All these observed parameters suggest the minimal role of strength of the acceptor groups in achieving decent photovoltaic efficiencies with D-πC-A based dyes as also indicated in the case of porphyrin based dyes.[49] We envisage that the observed results will pave the way to design new type of sensitizers with π chromophore based spacers which are electron deficient in nature for enhancing light absorption and better energy conversion efficiencies. Further studies on electron deficient chromophores like Indigo, Isoindigo to replace the typical cyanoacrylic acid group are in progress in our laboratory.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00332.

Synthetic details of indoline based donor fragment, IV, and transient plots (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) O'Regan, B.; Gratzel, M. A Low-Cost, High-Efficiency Solar Cell Based on Dye-Sensitized Colloidal TiO2 Films. *Nature* **1991**, *353*, 737−740.

(2) Grätzel, M. Photoelectrochemical Cells. *Nature* **2001**, *414*, 338−344.

(3) Grätzel, M. Conversion of Sunlight to Electric Power by Nanocrystalline Dye-Sensitized Solar Cells. *J. Photochem. Photobiol., A* **2004**, *164*, 3−14.

(4) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Mueller, E.; Liska, P.; Vlachopoulos, N.; Graetzel, M. Conversion of Light to Electricity by Cis-X2bis(2,2′-Bipyridyl-4,4′-dicarboxylate)-ruthenium(II) Charge-Transfer Sensitizers (X = Cl-, Br-, I-, CN-, and SCN-) on Nanocrystalline Titanium Dioxide Electrodes. *J. Am. Chem. Soc.* **1993**, *115*, 6382−6390.

(5) Nazeeruddin, M. K.; Splivallo, R.; Liska, P.; Comte, P.; Gratzel, M. A Swift Dye Uptake Procedure for Dye Sensitized Solar Cells. *Chem. Commun.* **2003**, 1456−1457.

(6) Wang, P.; Zakeeruddin, S. M.; Exnar, I.; Gratzel, M. High Efficiency Dye-Sensitized Nanocrystalline Solar Cells Based on Ionic Liquid Polymer Gel Electrolyte. *Chem. Commun.* **2002**, 2972−2973.

(7) Wang, P.; Zakeeruddin, S. M.; Moser, J. E.; Nazeeruddin, M. K.; Sekiguchi, T.; Gratzel, M. A Stable Quasi-Solid-State Dye-Sensitized Solar Cell with an Amphiphilic Ruthenium Sensitizer and Polymer Gel Electrolyte. *Nat. Mater.* **2003**, *2*, 402−407.

(8) Yella, A.; Lee, H.-W.; Tsao, H. N.; Yi, C.; Chandiran, A. K.; Nazeeruddin, M. K.; Diau, E. W.-G.; Yeh, C.-Y.; Zakeeruddin, S. M.; Grätzel, M. Porphyrin-Sensitized Solar Cells with Cobalt (II/III)−Based Redox Electrolyte Exceed 12% Efficiency. *Science* **2011**, *334*, 629−634.

(9) Mathew, S.; Yella, A.; Gao, P.; Humphry-Baker, R.; Curchod, B. F. E.; Ashari-Astani, N.; Tavernelli, I.; Rothlisberger, U.; Nazeeruddin,

M. K.; Grätzel, M. Dye-Sensitized Solar Cells with 13% Efficiency Achieved through the Molecular Engineering of Porphyrin Sensitizers. *Nat. Chem.* **2014**, *6*, 242−247.

(10) Chen, R.; Yang, X.; Tian, H.; Sun, L. Tetrahydroquinoline Dyes with Different Spacers for Organic Dye-Sensitized Solar Cells. *J. Photochem. Photobiol., A* **2007**, *189*, 295−300.

(11) Chen, R.; Yang, X.; Tian, H.; Wang, X.; Hagfeldt, A.; Sun, L. Effect of Tetrahydroquinoline Dyes Structure on the Performance of Organic Dye-Sensitized Solar Cells. *Chem. Mater.* **2007**, *19*, 4007−4015.

(12) Hao, Y.; Yang, X.; Cong, J.; Tian, H.; Hagfeldt, A.; Sun, L. Efficient near Infrared D-[small Pi]-A Sensitizers with Lateral Anchoring Group for Dye-Sensitized Solar Cells. *Chem. Commun.* **2009**, 4031−4033.

(13) Ahmad, S.; Guillén, E.; Kavan, L.; Grätzel, M.; Nazeeruddin, M. K. Metal Free Sensitizer and Catalyst for Dye Sensitized Solar Cells. *Energy Environ. Sci.* **2013**, *6*, 3439.

(14) Bai, Y.; Zhang, J.; Zhou, D.; Wang, Y.; Zhang, M.; Wang, P. Engineering Organic Sensitizers for Iodine-Free Dye-Sensitized Solar Cells: Red-Shifted Current Response Concomitant with Attenuated Charge Recombination. *J. Am. Chem. Soc.* **2011**, *133*, 11442−11445.

(15) Tsao, H. N.; Yi, C.; Moehl, T.; Yum, J.-H.; Zakeeruddin, S. M.; Nazeeruddin, M. K.; Grätzel, M. Cyclopentadithiophene Bridged Donor-Acceptor Dyes Achieve High Power Conversion Efficiencies in Dye-Sensitized Solar Cells Based on the Tris-Cobalt Bipyridine Redox Couple. *ChemSusChem* **2011**, *4*, 591−594.

(16) Xu, L.; Liu, C.; Qin, Z.; Jiang, R.; Li, Y. Core Expansion of Perylenetetracarboxdiimide Dyes with Anthraquinone Units for Electron-Accepting Materials. *Eur. J. Org. Chem.* **2013**, *2013*, 300−306.

(17) Mao, J.; He, N.; Ning, Z.; Zhang, Q.; Guo, F.; Chen, L.; Wu, W.; Hua, J.; Tian, H. Stable Dyes Containing Double Acceptors without COOH as Anchors for Highly Efficient Dye-Sensitized Solar Cells. *Angew. Chem., Int. Ed.* **2012**, *51*, 9873−9876.

(18) Ganesan, P.; Chandiran, A.; Gao, P.; Rajalingam, R.; Grätzel, M.; Nazeeruddin, M. K. Molecular Engineering of 2-Quinolinone Based Anchoring Groups for Dye-Sensitized Solar Cells. *J. Phys. Chem. C* **2014**, *118*, 16896−16903.

(19) Yen, Y.-S.; Chou, H.-H.; Chen, Y.-C.; Hsu, C.-Y.; Lin, J. T. Recent Developments in Molecule-Based Organic Materials for Dye-Sensitized Solar Cells. *J. Mater. Chem.* **2012**, *22*, 8734−8747.

(20) Lin, L.-Y.; Tsai, C.-H.; Wong, K.-T.; Huang, T.-W.; Wu, C.-C.; Chou, S.-H.; Lin, F.; Chen, S.-H.; Tsai, A.-I. Efficient Organic DSSC Sensitizers Bearing an Electron-Deficient Pyrimidine as an Effective [small Pi]-Spacer. *J. Mater. Chem.* **2011**, *21*, 5950−5958.

(21) Chen, B.-S.; Chen, D.-Y.; Chen, C.-L.; Hsu, C.-W.; Hsu, H.-C.; Wu, K.-L.; Liu, S.-H.; Chou, P.-T.; Chi, Y. Donor-Acceptor Dyes with Fluorine Substituted Phenylene Spacer for Dye-Sensitized Solar Cells. *J. Mater. Chem.* **2011**, *21*, 1937−1945.

(22) Zhang, G.; Bala, H.; Cheng, Y.; Shi, D.; Lv, X.; Yu, Q.; Wang, P. High Efficiency and Stable Dye-Sensitized Solar Cells with an Organic Chromophore Featuring a Binary [small Pi]-Conjugated Spacer. *Chem. Commun.* **2009**, 2198−2200.

(23) Marszalek, M.; Nagane, S.; Ichake, A.; Humphry-Baker, R.; Paul, V.; Zakeeruddin, S. M.; Gratzel, M. Structural Variations of D-[small Pi]-A Dyes Influence on the Photovoltaic Performance of Dye-Sensitized Solar Cells. *RSC Adv.* **2013**, *3*, 7921−7927.

(24) Wiberg, J.; Marinado, T.; Hagberg, D. P.; Sun, L.; Hagfeldt, A.; Albinsson, B. Effect of Anchoring Group on Electron Injection and Recombination Dynamics in Organic Dye-Sensitized Solar Cells. *J. Phys. Chem. C* **2009**, *113*, 3881−3886.

(25) Ganesan, P.; Rajadurai, V. S.; Sivanadanam, J.; Ponnambalam, V.; Rajalingam, R. Effect of Electron Withdrawing Anchoring Groups on the Optoelectronic Properties of Pyrene Sensitizers and Their Interaction with TiO2: A Combined Experimental and Theoretical Approach. *J. Photochem. Photobiol., A* **2013**, *271*, 31−44.

(26) Srinivas, K.; Yesudas, K.; Bhanuprakash, K.; Giribabu, L. A Combined Experimental and Computational Investigation of Anthracene Based Sensitizers for DSSC: Comparison of Cyanoacrylic and Malonic Acid Electron Withdrawing Groups Binding onto the TiO2 Anatase (101) Surface. *J. Phys. Chem. C* **2009**, *113*, 20117−20126.

(27) Zietz, B.; Gabrielsson, E.; Johansson, V.; El-Zohry, A. M.; Sun, L.; Kloo, L. Photoisomerization of the Cyanoacrylic Acid Acceptor Group - a Potential Problem for Organic Dyes in Solar Cells. *Phys. Chem. Chem. Phys.* **2014**, *16*, 2251−2255.

(28) Hao, Z.; Iqbal, A. Some Aspects of Organic Pigments. *Chem. Soc. Rev.* **1997**, *26*, 203−213.

(29) Beaujuge, P. M.; Fréchet, J. M. J. Molecular Design and Ordering Effects in Π-Functional Materials for Transistor and Solar Cell Applications. *J. Am. Chem. Soc.* **2011**, *133*, 20009−20029.

(30) Qu, S.; Tian, H. Diketopyrrolopyrrole (DPP)-Based Materials for Organic Photovoltaics. *Chem. Commun.* **2012**, *48*, 3039−3051.

(31) Kanimozhi, C.; Balraju, P.; Sharma, G. D.; Patil, S. Diketopyrrolopyrrole-Based Donor−Acceptor Copolymers as Organic Sensitizers for Dye Sensitized Solar Cells. *J. Phys. Chem. C* **2010**, *114*, 3287−3291.

(32) Qu, S.; Wu, W.; Hua, J.; Kong, C.; Long, Y.; Tian, H. New Diketopyrrolopyrrole (DPP) Dyes for Efficient Dye-Sensitized Solar Cells. *J. Phys. Chem. C* **2010**, *114*, 1343−1349.

(33) Warnan, J.; Favereau, L.; Pellegrin, Y.; Blart, E.; Jacquemin, D.; Odobel, F. A Compact Diketopyrrolopyrrole Dye as Efficient Sensitizer in Titanium Dioxide Dye-Sensitized Solar Cells. *J. Photochem. Photobiol., A* **2011**, *226*, 9−15.

(34) Qu, S.; Qin, C.; Islam, A.; Wu, Y.; Zhu, W.; Hua, J.; Tian, H.; Han, L. A Novel D-A-[small Pi]-A Organic Sensitizer Containing a Diketopyrrolopyrrole Unit with a Branched Alkyl Chain for Highly Efficient and Stable Dye-Sensitized Solar Cells. *Chem. Commun.* **2012**, *48*, 6972−6974.

(35) Qu, S.; Wang, B.; Guo, F.; Li, J.; Wu, W.; Kong, C.; Long, Y.; Hua, J. New Diketo-Pyrrolo-Pyrrole (DPP) Sensitizer Containing a Furan Moiety for Efficient and Stable Dye-Sensitized Solar Cells. *Dyes Pigm.* **2012**, *92*, 1384−1393.

(36) Holcombe, T. W.; Yum, J.-H.; Yoon, J.; Gao, P.; Marszalek, M.; Censo, D. D.; Rakstys, K.; Nazeeruddin, M. K.; Graetzel, M. A Structural Study of DPP-Based Sensitizers for DSC Applications. *Chem. Commun.* **2012**, *48*, 10724−10726.

(37) Yum, J.-H.; Holcombe, T. W.; Kim, Y.; Yoon, J.; Rakstys, K.; Nazeeruddin, M. K.; Gratzel, M. Towards High-Performance DPP-Based Sensitizers for DSC Applications. *Chem. Commun.* **2012**, *48*, 10727−10729.

(38) Yang, J.; Ganesan, P.; Teuscher, J.; Moehl, T.; Kim, Y. J.; Yi, C.; Comte, P.; Pei, K.; Holcombe, T. W.; Nazeeruddin, M. K.; et al. Influence of the Donor Size in D-Π-A Organic Dyes for Dye-Sensitized Solar Cells. *J. Am. Chem. Soc.* **2014**, *136*, 5722−5730.

(39) Yum, J.-H.; Holcombe, T. W.; Kim, Y.; Rakstys, K.; Moehl, T.; Teuscher, J.; Delcamp, J. H.; Nazeeruddin, M. K.; Grätzel, M. Blue-Coloured Highly Efficient Dye-Sensitized Solar Cells by Implementing the Diketopyrrolopyrrole Chromophore. *Sci. Rep.* **2013**, *3*, 2446.

(40) Gao, P.; Kim, Y. J.; Yum, J.-H.; Holcombe, T. W.; Nazeeruddin, M. K.; Gratzel, M. Facile Synthesis of a Bulky BPTPA Donor Group Suitable for Cobalt Electrolyte Based Dye Sensitized Solar Cells. *J. Mater. Chem. A* **2013**, *1*, 5535−5544.

(41) Ganesan, P.; Chandiran, A. K.; Gao, P.; Rajalingam, R.; Grätzel, M.; Nazeeruddin, M. K. Double D-Π-A Dye Linked by 2,2′-Bipyridine Dicarboxylic Acid: Influence of Para- and Meta- Substituted Carboxyl Anchoring Group. *ChemPhysChem* **2015**, *16*, 1035.

(42) Wang, Z.-S.; Hara, K.; Dan-oh, Y.; Kasada, C.; Shinpo, A.; Suga, S.; Arakawa, H.; Sugihara, H. Photophysical and (Photo)-electrochemical Properties of a Coumarin Dye. *J. Phys. Chem. B* **2005**, *109*, 3907−3914.

(43) Chen, Y.-S.; Li, C.; Zeng, Z.-H.; Wang, W.-B.; Wang, X.-S.; Zhang, B.-W. Efficient Electron Injection due to a Special Adsorbing Group's Combination of Carboxyl and Hydroxyl: Dye-Sensitized Solar Cells Based on New Hemicyanine Dyes. *J. Mater. Chem.* **2005**, *15*, 1654−1661.

(44) Chen, K.-F.; Hsu, Y.-C.; Wu, Q.; Yeh, M.-C. P.; Sun, S.-S. Structurally Simple Dipolar Organic Dyes Featuring 1,3-Cyclo-

hexadiene Conjugated Unit for Dye-Sensitized Solar Cells. *Org. Lett.* **2009**, *11*, 377−380.

(45) Hara, K.; Sato, T.; Katoh, R.; Furube, A.; Ohga, Y.; Shinpo, A.; Suga, S.; Sayama, K.; Sugihara, H.; Arakawa, H. Molecular Design of Coumarin Dyes for Efficient Dye-Sensitized Solar Cells. *J. Phys. Chem. B* **2002**, *107*, 597−606.

(46) Gao, P.; Tsao, H. N.; Grätzel, M.; Nazeeruddin, M. K. Fine-Tuning the Electronic Structure of Organic Dyes for Dye-Sensitized Solar Cells. *Org. Lett.* **2012**, *14*, 4330−4333.

(47) Ehret, A.; Stuhl, L.; Spitler, M. T. Spectral Sensitization of TiO2 Nanocrystalline Electrodes with Aggregated Cyanine Dyes. *J. Phys. Chem. B* **2001**, *105*, 9960−9965.

(48) Sayama, K.; Tsukagoshi, S.; Hara, K.; Ohga, Y.; Shinpou, A.; Abe, Y.; Suga, S.; Arakawa, H. Photoelectrochemical Properties of J Aggregates of Benzothiazole Merocyanine Dyes on a Nanostructured TiO2 Film. *J. Phys. Chem. B* **2002**, *106*, 1363−1371.

(49) Ripolles-Sanchis, T.; Guo, B.-C.; Wu, H.-P.; Pan, T.-Y.; Lee, H.-W.; Raga, S. R.; Fabregat-Santiago, F.; Bisquert, J.; Yeh, C.-Y.; Diau, E. W.-G. Design and characterization of alkoxy-wrapped push−pull porphyrins for dye-sensitized solar cells. *Chem. Commun.* **2012**, *48*, 4368−4370.