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# Rapid Synthesis of D-A′-π-A Dyes through a One-Pot Three-Component Suzuki–Miyaura Coupling and an Evaluation of their Photovoltaic Properties for Use in Dye-Sensitized Solar Cells**

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**Abstract:** Twenty-four D-A′–π-A dyes were rapidly synthesized through a one-pot three-component Suzuki–Miyaura coupling reaction, which was assisted by microwave irradiation. We measured the absorption spectra, electrochemical properties, and solar-cell performance of all the synthesized dyes. The **D5πA4** dye contained our originally designed rigid and nonplanar donor and exerted the highest efficiency at 5.4%. The short-circuit current ($J_{sc}$) was the most important parameter for the conversion efficiency ($\eta$) in the case of the organic D-A′-π-A dyes. Optimal ranges for the D-A′-π-A dyes were observed for high values of $J_{sc}/\lambda_{max}$ at $\lambda = 560$–620 nm, an optical-absorption edge of $\lambda = 690$–790 nm, and $E_{HOMO}$ and $E_{LUMO}$ values of $<1.14$ and $-0.56$ to $-0.76$ V, respectively.

## Introduction

Dye-sensitized solar cells (DSSCs) have garnered considerable attention due to characteristics such as a high power-conversion efficiency (PCE), simple fabrication procedures, and a low production cost.[1] As sensitizers, dye molecules play a crucial role in DSSCs.[2] The most common, readily available high-performing dyes are the ruthenium-centered polypyridyls.[2] Metal-free, organic dyes comprise a very important class of compound owing to their large molar absorptivity, design flexibility, and lower potential production costs relative to the ruthenium–polypyridyl dyes.[3] However, one of the main drawbacks of organic dyes is a poor light response in the red to near-infrared (NIR) region ($\lambda > 600$ nm).[3a,c] NIR dyes should have narrow HOMO–LUMO gaps to enable sufficient photoabsorption in the NIR region. On the other hand, high HOMO and low LUMO values of the NIR dyes decrease the driving force of electron transfer at the $TiO_2$/dye or dye/electrolyte interfaces. Therefore, fine tuning of the HOMO and LUMO values is generally important for the development of high performance NIR dyes. It is important to create templates of the NIR organic dyes, and the HOMO and LUMO values can be readily tuned by rapid structural modification.[4] In addition, NIR organic dyes with sufficient chemical stability are highly desired, and although many organic NIR dyes such as cyanines[5] and squaraines[6] have been reported, few can satisfy all the above criteria (NIR-absorption, ready structural modification, and sufficient chemical stability).

We have developed a sequential/one-pot palladium-catalyzed cross-coupling approach to the rapid synthesis of systematically modified π-conjugated molecules.[7] Based on the developed synthetic methodology, we constructed a library of UV/Vis-absorbing organic donor–π-acceptor (D–π-A) dyes for DSSCs, evaluated their properties, and elucidated the structure–function relationships.[7a,d,e] Recently, Zhu and co-workers reported organic D-A′-π-A dyes.[8] The electron-withdrawing benzothiadiazole, benzotriazole, and quinoxaline structures were used for the A′ moiety, and the absorption of the dyes was redshifted. However, the PCE edges of these dyes usually are as high as $\lambda = 700$ nm.[8b,9]

Herein, we wish to report novel D-A′-π-A dyes with a strong electron-withdrawing triazoloquinoxaline structure used for the A′ moiety to enable power conversion in the NIR region. The HOMO–LUMO level could be readily tuned by rapid struc-

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[**] A = Acceptor, D = donor.

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tural modification based on a microwave-assisted one-pot three-component coupling approach. The **D3πA4**, **D5πA2**, and **D5πA4** dyes exerted good PCE in the UV–NIR regions ($\lambda <$ 900 nm). In addition, we disclose the optimal HOMO and LUMO values of the NIR organic dyes that enable both sufficient NIR absorption and smooth electron transfer at the interfaces in DSSCs.

## Results and Discussion

We selected the highly electron-withdrawing triazoloquinoxaline[10] structure as the A′ moiety. The triazoloquinoxaline structure is reportedly an acceptor unit in low-bandgap D–A polymers.[10] The use of the triazoloquinoxaline accepter allowed us to introduce side chains to improve the solubility of the dyes. We planned to couple donor block **I** with the aromatic scaffold of **II** because the C–Br bond of the first coupling product would be less reactive relative to the corresponding C–Br bond of the aromatic scaffold **II**. Therefore, an undesirable overreaction that afforded a D-A′-D compound would be suppressed (Figure 1).[7b–d] A one-pot Suzuki–Miyaura (SM) coupling[11] with **III** would afford the desired coupling product **IV**. The subsequent removal of the *tert*-butyl group in block A would afford the desired compound **V**. The NIR dyes and their synthetic intermediates are usually highly planar molecules; therefore, the isolation of the dyes from undesired planar products tended to become tedious. The one-pot procedure facilitates the laborious purification step. In addition, tuning of the HOMO–LUMO values is particularly important in the development of NIR dyes for DSSCs, which are usually influenced by the donor and acceptor structures. Therefore, this approach provides an opportunity to tune the HOMO–LUMO values by rapidly altering the donor and acceptor structures. Moreover, the designed dyes contained neither di- nor trisubstituted unstable acyclic alkenes, which are frequently found in conventional NIR dyes, such as cyanines and squaraines. Thus, we anticipated that the designed dyes would retain sufficient chemical stability.

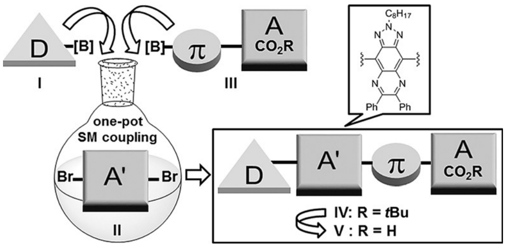
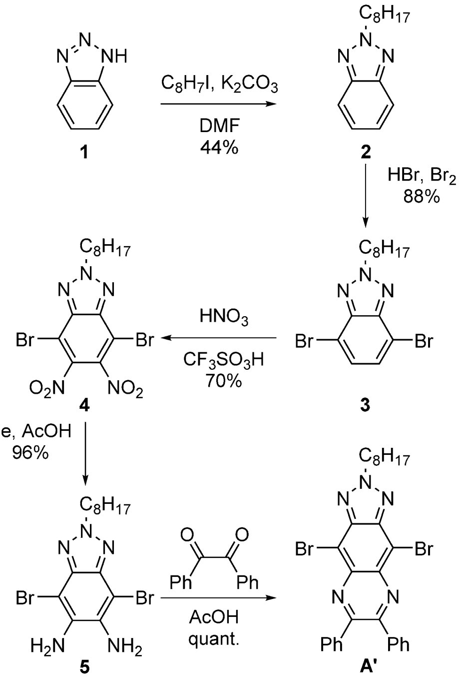


**Figure 1.** One-pot approach to the synthesis of D-A′-π-A dyes based on the Suzuki–Miyaura (SM) coupling. B = (dihydroxy)boryl or (pinacolato)boryl.

The triazoloquinoxaline block **A**′ was synthesized in accordance with a modified procedure.[10] The alkylation of 1,2,3-benzotriazole (**1**) and the following dibromination afforded **3** (Scheme 1). A slightly modified nitration procedure[10c,d,12] afforded the desired dinitro product **4** in a good yield. The reduction of dinitro aryl **4** and the subsequent quinoxaline ring formation afforded the desired dibromo triazoloquinoxaline **A**′ in an excellent yield.

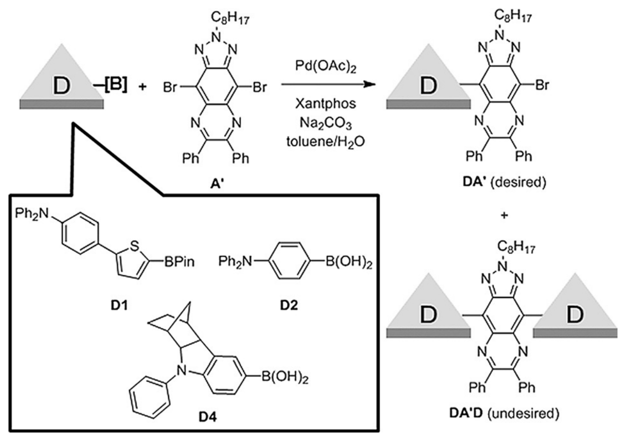


**Scheme 1.** Synthesis of the triazoloquinoxaline block **A**′. Ac = acetyl, Ph = phenyl.

The key SM coupling of triazoloquinoxaline block **A**′[13] with the simple donor building block **D1**[14] was examined by using a combination of Pd catalysts ($Pd(OAc)_2$,[15] $[Pd(PPh_3)_4]$,[16] and $[Pd_2(dba)_3]$,[17] phosphine ligands ($PPh_3$, $PCy_3{\cdot}BF_4$, 2-(di-*tert*-butylphosphino)biphenyl (JohnPhos),[18] XPhos,[19] $[(tBu_3P)H]BF$,[20] and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos)),[21] bases (NaOH and $Na_2CO_3$), and solvents ($THF/H_2O$, toluene/EtOH/$H_2O$, and toluene/$H_2O$). As a result, the combination of $Pd(OAc)_2$, Xantphos, and $Na_2CO_3$ in toluene/$H_2O$ at 60 °C for 8 hours afforded the best result (Table 1, entry 1). The microwave-irradiation conditions shortened the reaction time from 8 to 3 hours, and slightly improved the yield of the desired product (Table 1, entry 2). The SM coupling of **A**′ with **D2**[14] and **D4**, which contained our originally developed fused-ring structure,[7d] was examined under microwave-irradiation conditions (Table 1, entries 3 and 4). The use of **D2** afforded better results.

A one-pot SM coupling was examined (Table 2). The **D** block, **A**′ block, $Na_2CO_3$, $Pd(OAc)_2$, and Xantphos were placed in an argon atmosphere. Toluene and $H_2O$ were added, and the mixture was degassed with argon. The reaction tube was equipped with a rubber cap and placed in the microwave-synthesis system that operated at 60 °C and 200 W for 3 hours. After cooling to room temperature, the **πA** block, $Na_2CO_3$, $[Pd_2(dba)_3]$, $[(tBu_3P)H]BF$, toluene, and $H_2O$ were added in succession, and the mixture was degassed with argon.[7d] The resultant mixture was stirred at room temperature for 3–

**Table 1.** The SM coupling reaction between donor blocks **D1** and **D2** with the triazoloquinoxaline block **A′**.



| Entry | D | Heating conditions | DA′[a] [%] | DA′D[a] [%] |
|---|---|---|---|---|
| 1 | **D1** | conventional, 60 °C, 8 h | 25 | trace |
| 2 | **D1** | MW = 200 W, 60 °C, 3 h | 31 | 16 |
| 3 | **D2** | MW = 200 W, 60 °C, 3 h | 49 | 7 |
| 4 | **D4** | MW = 200 W, 60 °C, 3 h | 39 | 1 |

[a] Yield of the isolated products. BPin = (pinacolato)boryl, MW = microwave, Xantphos = 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene.

19 hours (as monitored by TLC analysis). A standard workup procedure afforded the desired coupling products.

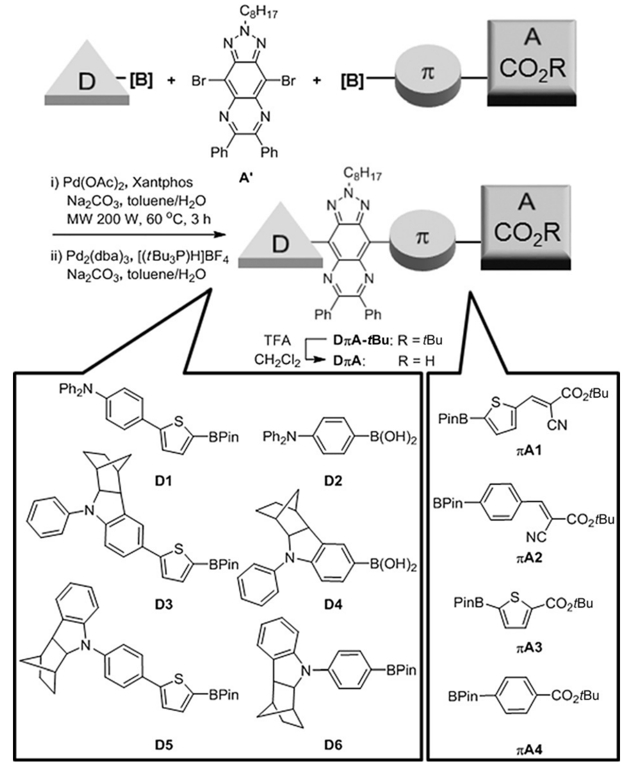
Treatment of the coupling products with TFA followed by simple removal of the volatile TFA afforded the desired carboxylic acids in good purity. The obtained carboxylic acids were used to measure the absorption spectra and the electrochemical and photovoltaic properties without further purification.

All the synthesized dyes were soluble in DMF, $CH_2Cl_2$, and $CHCl_3$, but were not soluble in MeOH, MeCN, or acetone. As expected, the synthesized dyes were sufficiently stable under a fluorescent lamp in air (>1 month) as solids or in solution (i.e., $CH_2Cl_2$).

The absorption spectra and electrochemical properties of the 24 dyes were measured (see Figure S1 in the Supporting Information and Table 3). As expected, the absorption wavelengths of the D-A′-π-A dyes containing the strong electron-withdrawing triazoloquinoxaline structure were redshifted ($\Delta\lambda \approx 200$ nm) relative to our previously synthesized D–π-A dyes **1** and **2** (Figure 2).[7d]

As the donors influenced the $E_{\text{HOMO}}$ values of the dyes, the $E_{\text{HOMO}}$ value became more positive on the order of **D3** < **D5** < **D6** ≈ **D4** ≤ **D1** ≤ **D2** (Figure 3a). On the other hand, the acceptors influenced the $E_{\text{LUMO}}$ value of the dyes; therefore, the $E_{\text{LUMO}}$ value became more negative on the order of **πA1** < **πA3** ≤ **πA2** ≤ **πA4** (Figure 3d). The HOMO values of all the synthesized dyes met the minimum requirement for a dye sensitizer in DSSCs, and HOMO level had a more positive value than the iodine/iodide redox potential (+0.4 V vs. the normal hydrogen electrode (NHE)). On the other hand, the $E_{\text{LUMO}}$ value of 7 dyes (i.e., **D1πA1**, **D1πA2**, **D1πA3**, **D2πA1**, **D3πA1**, **D4πA1**, and **D5πA1**) was more positive than the conduction-band edge of $TiO_2$ (−0.5 V vs. NHE).

**Table 2.** One-pot SM coupling reaction assisted by microwave irradiation.



| Entry | D | πA | DπA–tBu [%][a] |
|---|---|---|---|
| 1 | **D1** | **πA1** | 26 |
| 2 | **D1** | **πA2** | 38 |
| 3 | **D1** | **πA3** | 35 |
| 4 | **D1** | **πA4** | 34 |
| 5 | **D2** | **πA1** | 49 |
| 6 | **D2** | **πA2** | 46 |
| 7 | **D2** | **πA3** | 48 |
| 8 | **D2** | **πA4** | 50 |
| 9 | **D3** | **πA1** | 33 |
| 10 | **D3** | **πA2** | 35 |
| 11 | **D3** | **πA3** | 30 |
| 12 | **D3** | **πA4** | 32 |
| 13 | **D4** | **πA1** | 39 |
| 14 | **D4** | **πA2** | 42 |
| 15 | **D4** | **πA3** | 46 |
| 16 | **D4** | **πA4** | 46 |
| 17 | **D5** | **πA1** | 24 |
| 18 | **D5** | **πA2** | 34 |
| 19 | **D5** | **πA3** | 33 |
| 20 | **D5** | **πA4** | 30 |
| 21 | **D6** | **πA1** | 15 |
| 22 | **D6** | **πA2** | 28 |
| 23 | **D6** | **πA3** | 36 |
| 24 | **D6** | **πA4** | 32 |

[a] Yield of the isolated products. dba = Dibenzylideneacetone, TFA = trifluoroacetic acid, Xphos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl.

Photovoltaic properties were evaluated for the solar cells that were prepared by using the 24 synthesized dyes and D149[22] (Table 4). Four dyes (i.e., **D3πA4**, **D4πA2**, **D5πA2**, and **D5πA4**) exerted good PCEs (≥4.5%). To our delight, the **D5πA4** dye, which contained our originally developed rigid and nonplanar **D5** unit, exerted the highest PCE at 5.4%.

**Table 3.** Photophysical and electrochemical properties of the 24 dyes.

| Entry | Dye | $\lambda_{max}$ [nm][a] | $\varepsilon$ [$L\,mol^{-1}\,cm^{-1}$][b] | Opt. edge [nm][c] | $E_{HOMO}$ [V][d] (vs. NHE) | $E_{LUMO}$ [V][e] (vs. NHE) |
|---|---|---|---|---|---|---|
| 1 | **D1πA1** | 664 | 19600 | 843 | 1.10 | −0.37 |
| 2 | **D1πA2** | 592 | 14600 | 756 | 1.35 | −0.29 |
| 3 | **D1πA3** | 629 | 23800 | 785 | 1.12 | −0.46 |
| 4 | **D1πA4** | 578 | 25200 | 729 | 1.14 | −0.56 |
| 5 | **D2πA1** | 595 | 35100 | 746 | 1.27 | −0.39 |
| 6 | **D2πA2** | 520 | 12400 | 658 | 1.28 | −0.60 |
| 7 | **D2πA3** | 558 | 14900 | 687 | 1.24 | −0.57 |
| 8 | **D2πA4** | 511 | 13500 | 627 | 1.24 | −0.74 |
| 9 | **D3πA1** | 714 | 22200 | 887 | 0.91 | −0.49 |
| 10 | **D3πA2** | 630 | 27300 | 811 | 0.93 | −0.60 |
| 11 | **D3πA3** | 669 | 21900 | 852 | 0.92 | −0.54 |
| 12 | **D3πA4** | 617 | 25200 | 788 | 0.93 | −0.65 |
| 13 | **D4πA1** | 644 | 19600 | 805 | 1.07 | −0.47 |
| 14 | **D4πA2** | 564 | 12600 | 695 | 1.02 | −0.76 |
| 15 | **D4πA3** | 602 | 18200 | 741 | 1.06 | −0.62 |
| 16 | **D4πA4** | 552 | 13200 | 681 | 1.09 | −0.73 |
| 17 | **D5πA1** | 685 | 42800 | 873 | 1.00 | −0.42 |
| 18 | **D5πA2** | 604 | 38400 | 772 | 1.01 | −0.59 |
| 19 | **D5πA3** | 641 | 31100 | 830 | 0.99 | −0.51 |
| 20 | **D5πA4** | 589 | 14100 | 765 | 1.02 | −0.61 |
| 21 | **D6πA1** | 617 | 23100 | 759 | 1.05 | −0.58 |
| 22 | **D6πA2** | 546 | 18100 | 665 | 1.05 | −0.82 |
| 23 | **D6πA3** | 575 | 20500 | 721 | 1.04 | −0.68 |
| 24 | **D6πA4** | 529 | 17500 | 657 | 1.05 | −0.84 |

[a] Absorption maxima in $CH_2Cl_2$. [b] Molar absorption coefficients in $CH_2Cl_2$. [c] Optical-transmittance edge was defined by extrapolating the leading edge of the optical-transmission spectra of the dyes on $TiO_2$ (see the Supporting Information) to the baseline. [d] The $E_{HOMO}$ value was determined by means of cyclic voltammetry. [e] The $E_{HOMO}-E_{LUMO}$ gap was determined from the optical-transmittance edge; that is, the $E_{HOMO}-E_{LUMO}$ gap [eV] was calculated by using $\lambda = 1240$ [nm]/optical edge [nm] and the $E_{LUMO}$ value was calculated by summation of the HOMO potential and the $E_{HOMO}-E_{LUMO}$ gap.

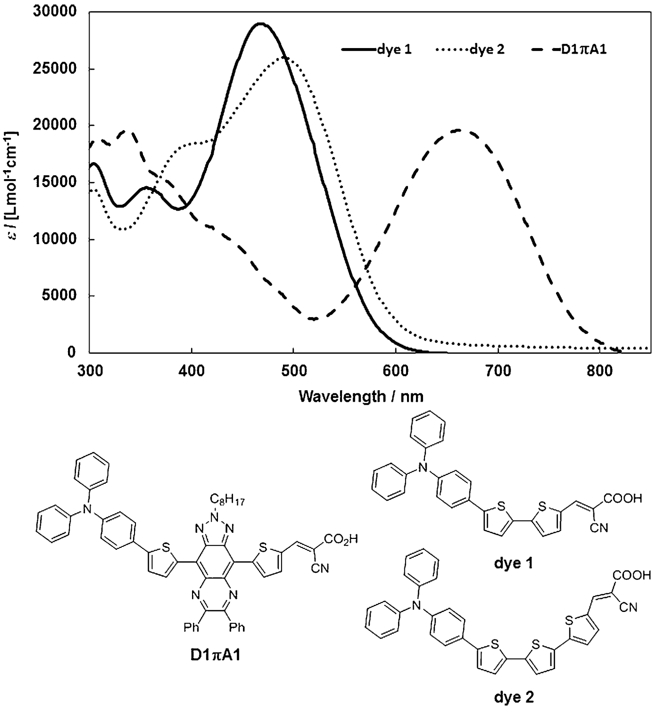


**Figure 2.** Comparison of absorption spectra of **D1 A1** with our previously reported dyes **1** and **2** without the triazoloquinoxaline structure in $CH_2Cl_2$.

We previously reported that the short-circuit current ($J_{sc}$) was the most important parameter for the conversion efficiency ($\eta$) in the case of UV/Vis-absorbing D–π-A dyes.[7d] Similarly, the $J_{sc}$ value is strongly correlated with $\eta$ ($R^2 = 0.98$; Figure 4c) in the case of D-A′-π-A dyes, whereas no correlation was ob-

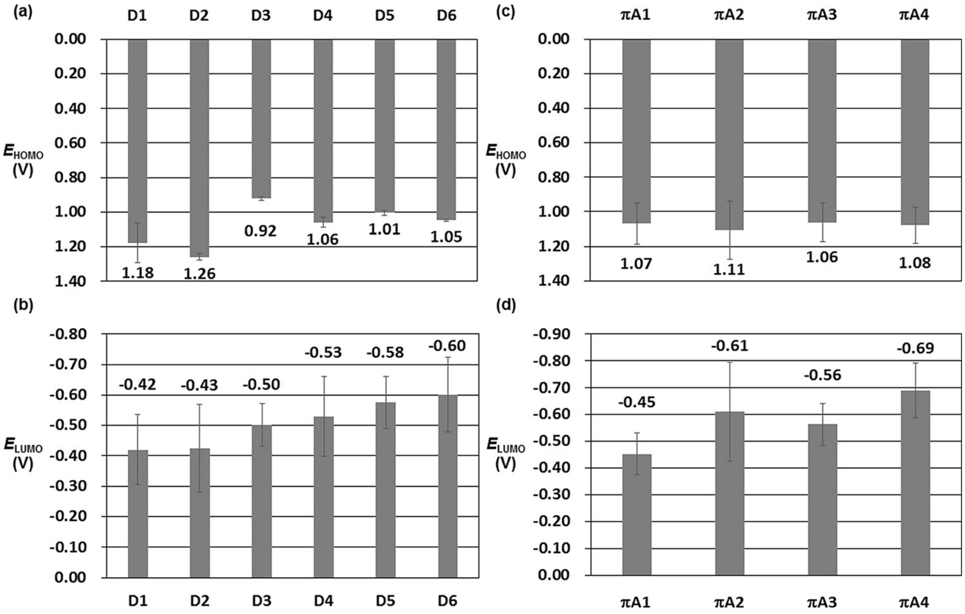


**Figure 3.** a) The average values for the $E_{HOMO}$ versus the NHE of dyes containing **D1** (4 dyes), **D2** (4 dyes), **D3** (4 dyes), **D4** (4 dyes), **D5** (4 dyes), and **D6** (4 dyes). b) The average values for the $E_{LUMO}$ versus the NHE of dyes containing **D1** (4 dyes), **D2** (4 dyes), **D3** (4 dyes), **D4** (4 dyes), **D5** (4 dyes), and **D6** (4 dyes). c) The average values for the $E_{HOMO}$ versus the NHE of dyes containing **πA1** (6 dyes), **πA2** (6 dyes), **πA3** (6 dyes), and **πA4** (6 dyes). d) The average values for the $E_{LUMO}$ versus the NHE of **πA1** (6 dyes), **πA2** (6 dyes), **πA3** (6 dyes), and **πA4** (6 dyes). The values are expressed as the mean ± standard deviation (SD).

**Table 4.** Photovoltaic properties of solar cells prepared by using the 24 dyes.

| Entry | Dye | $\eta$[a] [%] | FF[a] | $V_{oc}$[a] [V] | $J_{sc}$[a] [mA cm$^{-1}$] |
|---|---|---|---|---|---|
| 1 | **D149** | 6.1 | 0.69 | 0.71 | 12.3 |
| 2 | **D1πA1** | 1.4 | 0.66 | 0.52 | 4.0 |
| 3 | **D1πA2** | 2.6 | 0.59 | 0.61 | 7.1 |
| 4 | **D1πA3** | 2.6 | 0.62 | 0.58 | 7.3 |
| 5 | **D1πA4** | 4.4 | 0.68 | 0.61 | 10.5 |
| 6 | **D2πA1** | 4.2 | 0.71 | 0.59 | 10.1 |
| 7 | **D2πA2** | 2.2 | 0.52 | 0.64 | 6.5 |
| 8 | **D2πA3** | 3.4 | 0.72 | 0.60 | 7.9 |
| 9 | **D2πA4** | 3.3 | 0.68 | 0.64 | 7.6 |
| 10 | **D3πA1** | 0.3 | 0.54 | 0.44 | 1.2 |
| 11 | **D3πA2** | 2.7 | 0.69 | 0.57 | 6.8 |
| 12 | **D3πA3** | 1.2 | 0.68 | 0.53 | 3.4 |
| 13 | **D3πA4** | 4.8 | 0.62 | 0.61 | 12.5 |
| 14 | **D4πA1** | 2.8 | 0.69 | 0.55 | 7.5 |
| 15 | **D4πA2** | 4.8 | 0.67 | 0.61 | 11.5 |
| 16 | **D4πA3** | 4.4 | 0.70 | 0.61 | 10.4 |
| 17 | **D4πA4** | 4.1 | 0.67 | 0.63 | 9.7 |
| 18 | **D5πA1** | 0.7 | 0.69 | 0.48 | 2.1 |
| 19 | **D5πA2** | 4.5 | 0.66 | 0.56 | 11.6 |
| 20 | **D5πA3** | 3.2 | 0.67 | 0.55 | 8.6 |
| 21 | **D5πA4** | 5.4 | 0.64 | 0.63 | 13.3 |
| 22 | **D6πA1** | 3.1 | 0.70 | 0.56 | 7.9 |
| 23 | **D6πA2** | 2.0 | 0.71 | 0.63 | 4.4 |
| 24 | **D6πA3** | 4.1 | 0.66 | 0.61 | 10.2 |
| 25 | **D6πA4** | 3.9 | 0.66 | 0.64 | 9.2 |

[a] Average values from two or three independent experiments.

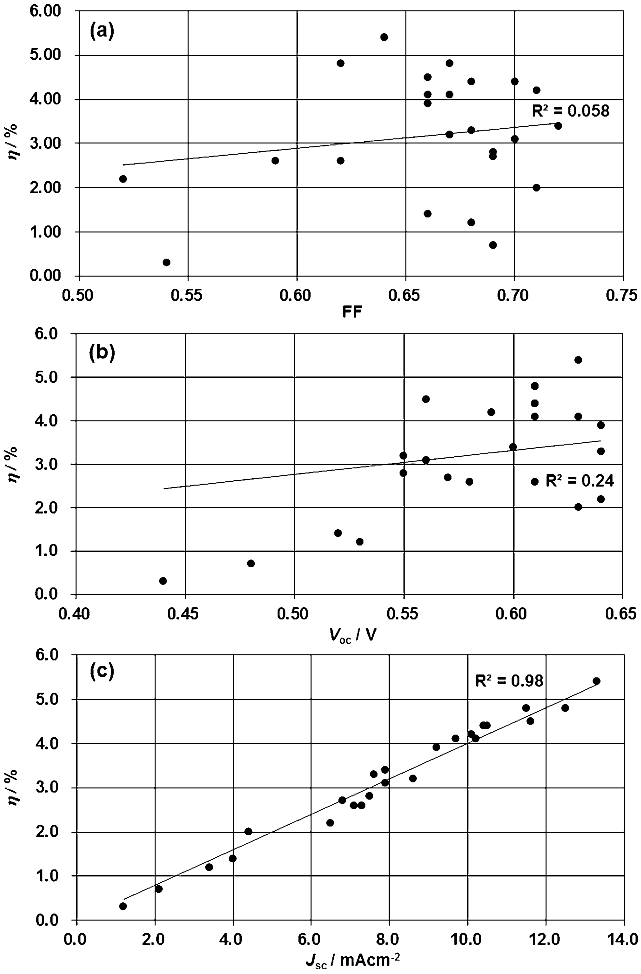


**Figure 4.** Correlation between a) FF and $\eta$, b) $V_{oc}$ and $\eta$, and c) $J_{sc}$ and $\eta$ of the 24 dyes studied herein.

served between the fill factor (FF) and $\eta$ ($R^2 = 0.058$; Figure 4 a) and only a weak correlation was observed between the open-circuit voltage ($V_{oc}$) and $\eta$ ($R^2 = 0.24$; Figure 4 b).

To determine the important factors for a high $J_{sc}$ value to be obtained, correlations between the $J_{sc}$ value and the absorption extinction coefficient ($\varepsilon$), absorption maximum ($\lambda_{max}$), optical-absorption edge, and the HOMO ($E_{HOMO}$) and LUMO ($E_{LUMO}$) energies were examined (Figure 5). In the case of UV/Vis-absorbing D–π-A dyes, no obvious correlations between $\varepsilon$ and $J_{sc}$, $\lambda_{max}$ and $J_{sc}$, and the optical-absorption edge and $J_{sc}$ were observed, whereas the $E_{HOMO}$ and $E_{LUMO}$ values were critical for high $J_{sc}$ values.[7d] The UV/Vis dyes with more positive $E_{HOMO}$ values and $E_{LUMO} < -0.80$ V exerted higher $J_{sc}$ values The UV/Vis dyes that met the above criteria enabled smooth electron transfer at the $TiO_2$/dye or dye/electrolyte interfaces because of a sufficient driving force; thus, they exerted higher $J_{sc}$ values.

Interestingly, no obvious correlation was observed between the $\varepsilon$ and $J_{sc}$ values in the case of NIR-absorbing D-A′-π-A dyes, whereas the optimal ranges for the $\lambda_{max}$ values ($\lambda = 560$–620 nm), optical-absorption edge ($\lambda = 690$–790 nm), and the $E_{HOMO}$ and $E_{LUMO}$ values of the dyes (< 1.14 and −0.56 to −0.76 V, respectively) for high $J_{sc}$ values were observed (Figure 5 b–e, boxes). Generally, the $J_{sc}$ value is correlated with the sensitizer-absorptive capability and the electron-injection efficiency. The dyes that can absorb long-wavelength light (i.e., long $\lambda_{max}$, a long optical-absorption edge, and high $E_{HOMO}$, and low $E_{LUMO}$ values) would have a good absorptive capability. On the other hand, the electron-injection efficiency of the dyes when absorbing long-wavelength light tended to decrease due to their high $E_{HOMO}$ and low $E_{LUMO}$ values (insufficient driving force of electron transfer at the $TiO_2$/dye or dye/electrolyte interfaces). Thus, it is conceivable that the optimal ranges of the $\lambda_{max}$ value, optical-absorption edge, and $E_{HOMO}$, and $E_{LUMO}$ values for high $J_{sc}$ values were observed in the case of the D-A′-π-A dyes. In fact, the combinations of **D4**, **D5**, and **D6** and **πA2** and **πA4** that met the criteria of the $E_{HOMO}$ and $E_{LUMO}$ values (< 1.14 V and −0.56 to −0.76 V, respectively; Figure 3 a, d) exerted high PCEs. Three of the four best PCE dyes (i.e., **D4πA2**, **D5πA2**, and **D5πA4**) were found in these combinations. It should be noted that as far as we could ascertain, there have been no reports that describe the proper HOMO and LUMO values of NIR organic dyes that will enable both sufficient NIR absorption and smooth electron transfer at the interfaces in DSSCs.

The photocurrent–voltage curves and the incident photon-to-current conversion efficiency (IPCE) spectra of **D3πA4**, **D4πA2**, **D5πA2**, and **D5πA4** were compared with our previously reported best UV/Vis dye **3** ($\eta = 6.2$ %)[7d] and D149 as a reference (Figure 6). As expected, the IPCE edges of the high-performance dyes **D3πA4**, **D5πA2**, and **D5πA4** exceeded

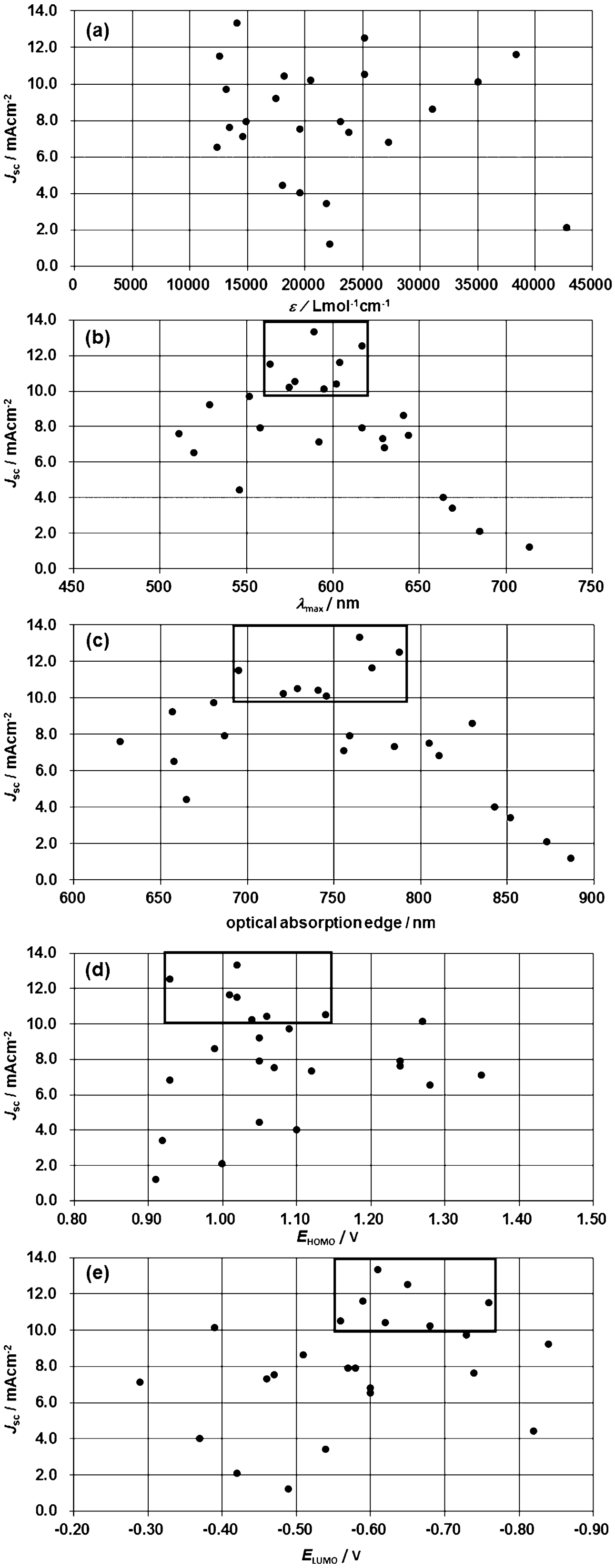
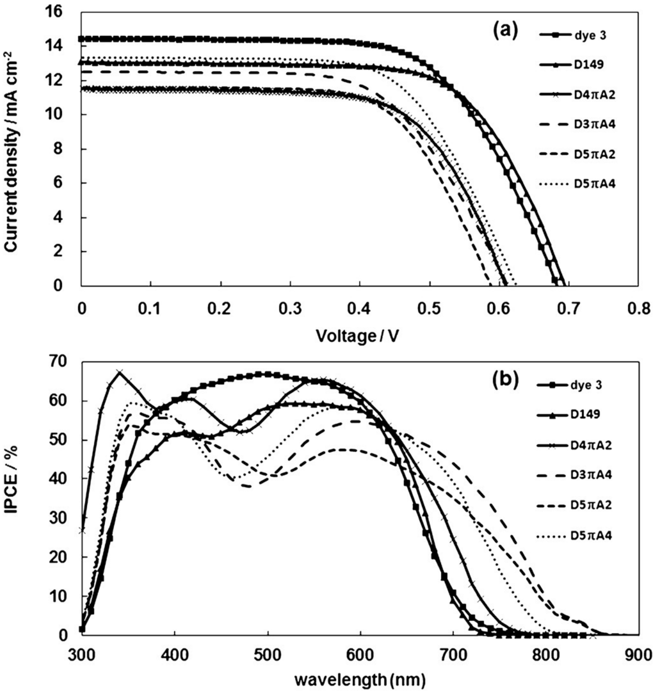
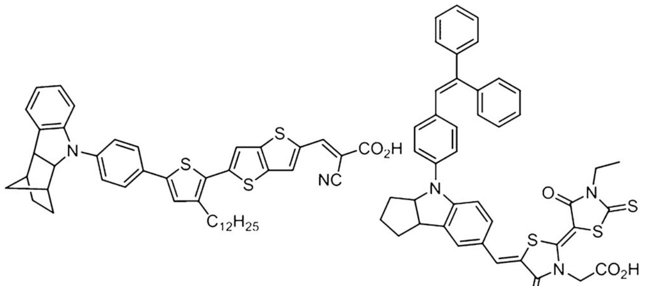


**Figure 5.** Correlations between a) ε and $J_{sc}$, b) $\lambda_{max}$ and $J_{sc}$, c) optical-absorption edge and $J_{sc}$, d) $E_{HOMO}$ and $J_{sc}$, and e) $E_{LUMO}$ and $J_{sc}$ of the 24 dyes studied herein.





dye 3 D149

**Figure 6.** Photocurrent–voltage curves obtained with DSSCs based on **3**, D149, **D4πA2**, **D3πA4**, **D5πA2**, and **D5πA4** under a) solar conditions with a standard air mass (AM) of 1.5 and b) incident photon-to-current conversion efficiency (IPCE) spectra for DSSCs based on **3**, D149, **D4πA2**, **D3πA4**, **D5πA2**, and **D5πA4**.

$\lambda = 800$ nm. Relative to **3** and D149, the IPCEs for dyes **D3πA4**, **D5πA2**, and **D5πA4** were lower in the region $\lambda = 400$–600 nm and higher in the region $\lambda = 650$–850 nm. Thus, dyes **D3πA4**, **D5πA2**, and **D5πA4** would be an attractive element in the dye cocktails used in high-performance DSSCs.

## Conclusion

We have achieved a rapid synthesis of 24 D-A′-π-A dyes by using a one-pot, three-component Suzuki–Miyaura coupling reaction assisted by microwave irradiation. The developed synthetic approach has allowed us to readily modify the dye structure. We measured the absorption spectra, electrochemical properties, and the cell performance of all the synthesized dyes. As expected, the absorption wavelength of the synthesized dyes was strongly redshifted ($\Delta\lambda \approx 200$ nm) relative to our previously synthesized D-π-A dyes due to the triazoloquinoxaline structure. The **D5πA4** dye contained our originally designed rigid nonplanar donor and exerted the highest efficiency at 5.4 %. The $J_{sc}$ value was the most important parameter for efficiency $\eta$ in the case of these organic D-A′-π-A yes. The optimal ranges for high $J_{sc}$ values of the D-A′-π-A dyes were observed at $\lambda_{max} = 560$–620 nm, an optical-absorption edge of $\lambda = 690$-790 nm, and $E_{HOMO}$ and $E_{LUMO}$ values of $<1.14$ and $-0.56$ $-0.76$ V, respectively. As far as we have been able to ascertain, there have been no reports that describe the proper HOMO and LUMO values of NIR organic dyes that enable both sufficient NIR absorption and smooth electron transfer at the interfaces in DSSCs. These results should be valuable in the design of high-performance D-A′-π-A dyes in the future. It should be noted that the IPCEs of the **D3πA4**, **D5πA2**, and **D5πA4** dyes are complementary to those of dye **3** and the D149 dye. Thus, these dyes would be an attractive element in the dye cocktails used for high-performance DSSCs.

## Experimental Section

The experimental details are given in the Supporting Information, including the synthetic, photophysical, and electrochemical procedures and the characterization of the synthesized compounds.

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**Keywords:** combinatorial chemistry · cross-coupling · dyes/pigments · solar cells · one-pot reactions

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