Solar Cells

Elucidating the Structure–Property Relationships of Donor– π -Acceptor Dyes for Dye-Sensitized Solar Cells (DSSCs) through Rapid Library Synthesis by a One-Pot Procedure

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Abstract: The creation of organic dyes with excellent high power conversion efficiency (PCE) is important for the further improvement of dye-sensitized solar cells. We wish to describe the rapid synthesis of a 112-membered donor- π -acceptor dye library by a one-pot procedure, evaluation of PCEs, and elucidation of structure–property relationships. No obvious correlations between ε , and the η were observed, whereas the HOMO and LUMO levels of the dyes were critical for η . The dyes with a more positive E_{HOMO} , and with an $E_{\rm LUMO} < -0.80$ V, exerted higher PCEs. The proper driving forces were crucial for a high $J_{\rm scr}$ and it was the most important parameter for a high η . The above criteria of $E_{\rm HOMO}$ and $E_{\rm LUMO}$ should be useful for creating high PCE dyes; nevertheless, that was not sufficient for identifying the best combination of donor, π , and acceptor blocks. Combinatorial synthesis and evaluation was important for identifying the best dye.

Introduction

Dye-sensitized solar cells (DSSCs) have garnered considerable attention due to a high-power conversion efficiency (PCE), simple fabrication procedures, and a low production cost.^[1] The dye molecules as sensitizers play a crucial role in DSSCs.^[1b,2] The most common high-performing dyes are the ruthenium-centered polypyridyls. Metal-free, organic donor- π -acceptor (D- π -A) dyes comprise a very important class of compounds owing to their large molar absorptivity, design flexibility, and potential reduction in production costs compared with

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the polypyridyl Ru dyes^[3] The creation of high-performance organic dyes with an excellent PCE would be important for further improvement of the cell performance of DSSCs. One possibility for the design of high-performance dyes is the use of theoretical calculations. Recent dramatic progress in this field has made it possible to estimate the properties of dyes, such as the absorption spectra and the electron distribution of D- π -A dyes.^[4] However, the PCE is influenced by many factors including intermolecular interactions and the arrangement of dyes on TiO₂. It remains difficult to rationally estimate these important properties of dyes.^[3c,d] Another method of estimation is the use of dye structure-property information, which is drawn from extensive past reports. However, the extraction of precise structure-property information has not been a simple process, because the procedure for the preparation and evaluation of cells varies depending on the research group.^[1d] The combinatorial approach has been a powerful approach for elu-



Figure 1. One-pot approach for the synthesis of D- π -A dyes based on the Suzuki–Miyaura coupling reaction.

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Scheme 1. Synthesis of D- π -A dye 5 based on the one-pot approach. dba = dibenzylideneacetone; Xantphos = 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene; dppf = 1,1'-bis(diphenylphosphino)ferrocene; DPEphos = bis(2-diphenylphosphinophenyl)ether; Pin = pinacol.

cidation of the structure–property relationship.^[5] Herein, we report the rapid combinatorial synthesis of a 112-membered D- π -A dye library by a one-pot procedure, the evaluation of PCEs, and an elucidation of the structure–property relationship.



Figure 2. Building blocks for D- π -A dye library synthesis.

Results and Discussion

The construction of a large combinatorial library should meet the following criteria: 1) the multiple components should be sequentially coupled without extra steps, such as protection and deprotection; 2) the number of workup and purification steps should be minimized; 3) each of the coupling steps should produce a good yield and be compatible with a variety of functional groups and 4) readily available, nontoxic and environmentally benign substrates and reagents should be employed with no generation of toxic compounds. From this point of view, Suzuki-Miyaura (SM) coupling is attractive.^[6] Although many practical syntheses of D-π-A dyes based on SM coupling have been reported, they are not always suitable for the combinatorial approach.^[7] This is because they usually contain extra steps, such as halogenation, formylation, workup, and purification. We planned to develop a highly efficient, one-pot SM coupling procedure with no extra steps, as shown in Figure 1. In the onepot reaction, the remaining sub-

 Table 1. Yields in A) the one-pot SM coupling reaction and B) removal of the tBu group or the Knoevenagel condensation reaction.

Dye	Yield (A) [%] ^[a]	Yield (B) [%] ^[b]	Dye	Yield (A) [%] ^[a]	Yield (B) [%] ^[b]	Dye	Yield (A) [%] ^[a]	Yield (B) [%] ^[b]	Dye	Yield (A) [%] ^[a]	Yield (B) [%] ^[b]
D1π1A1	60	87	D2π1A1	52	82	D3π1A1	60	quant.	D4π1A1	64	82
D1π2A1	56	90	D2π2A1	40	88	D3π2A1	72	quant.	D4π2A1	51	9
D1π3A1	78	92	D2π3A1	65	quant.	D3π3A1	74	78	D4π3A1	50	quant.
D1π4A1	66	97	D2π4A1	62	quant.	D3π4A1	74	88	D4π4A1	52	79
D1π5A1	16	quant.	D2π5A1	16	65	D3π5A1	52	92	D4π5A1	40	87
D1π6A1	64	99	D2π6A1	51	78	D3π6A1	78	52	D4π6A1	48	93
D1π7A1	68	79	D2π7A1	32	90	D3π7A1	69	93	D4π7A1	55	74
D1π1A2	63	98	D2π1A2	4	87	D3π1A2	65	76	D4π1A2	58	58
D1π2A2	60	79	D2π2A2	34	83	D3π2A2	44	72	D4π2A2	56	90
D1π3A2	69	quant.	D2π3A2	36	quant.	D3π3A2	55	89	D4π3A2	48	quant.
D1π4A2	67	76	D2π4A2	42	96	D3π4A2	67	99	D4π4A2	45	98
D1π5A2	30	79	D2π5A2	17	quant.	D3π5A2	37	quant.	D4π5A2	58	79
D1π6A2	68	93	D2π6A2	38	quant.	D3π6A2	57	97	D4π6A2	61	86
D1π7A2	57	91	D2π7A2	40	82	D3π7A2	40	87	D4π7A2	58	88
D1π1A3	41	75	D2π1A3	41	98	D3π1A3	6	quant.	D4π1A3	57	96
D1π2A3	53	81	D2π2A3	35	84	D3π2A3	53	quant.	D4π2A3	29	quant.
D1π3A3	59	71	D2π3A3	41	quant.	D3π3A3	45	86	D4π3A3	43	97
D1π4A3	38	65	D2π4A3	35	89	D3π4A3	48	95	D4π4A3	42	99
D1π5A3	36	82	D2π5A3	26	76	D3π5A3	32	96	D4π5A3	40	quant.
D1π6A3	36	84	D2π6A3	26	quant.	D3π6A3	49	76	D4π6A3	51	82
D1π7A3	37	quant.	D2π7A3	41	99	D3π7A3	5	96	D4π7A3	46	93
$D1\pi 1A4'$	60	89	$D2\pi 1A4'$	59	87	D3π1A4′	64	79	$D4\pi 1A4'$	56	77
D1π2A4	20	89	D2π2A4′	27	64	D3π2A4′	44	70	$D4\pi 2A4'$	38	81
D1π3A4	_ ^[c]	65	D2π3A4′	60	72	D3π3A4′	72	77	$D4\pi 3A4'$	54	74
$D1\pi 4A4'$	49	77	D2π4A4′	45	77	D3π4A4′	64	85	$D4\pi 4A4'$	41	70
$D1\pi 5A4'$	18	74	$D2\pi 5A4'$	37	98	D3π5A4′	53	97	$D4\pi 5A4'$	34	91
$D1\pi 6A4'$	63	99	D2π6A4′	36	69	D3π6A4′	54	53	$D4\pi 6A4'$	66	62
D1π7A4′	52	88	D2π7A4′	33	52	D3π7A4′	20	70	D4π7A4′	17	64

[a] Isolated yields in the one-pot SM coupling reaction. [b] Isolated yields in acidic removal of tBu group in the case of A1-, A2-, A3-, or A4-containing dyes, or Knoevenagel condensation reaction in the case of A4'-containing dyes. [c] It was difficult to isolate the one-pot SM coupling product, D1 π 3A4, therefore only short-pad column chromatography was performed, and the obtained compound was used for the next reaction (removal of tBu group) without further purification.

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strates or reagents in the first step should not suffer the following step, but the Pd catalyst is somewhat susceptible to contaminants. Therefore, the number of the reported one-pot Pd coupling reactions is surprisingly limited.^[8] A π -block I retaining two bromo groups was selected as an aromatic scaffold due to its sufficient stability, reactivity, and ready availability. We first planned to couple donor block II with the aromatic scaffold I because the C–Br bond of the first coupling product would be less reactive compared with the corresponding C-Br bond of the aromatic scaffold I, and, therefore, an undesired overreaction affording a D- π -D compound would be suppressed. The coupling product IV with tert-butyl (tBu) ester would retain good solubility and could be easily purified. The following removal of the tBu group by using volatile acid and simple purification would afford the desired D- π -A dye V in good purity.

For the development of the one-pot procedure, a simple and typical D- π -A dye **5**^[7a, 9] was selected as a target



Scheme 2. Improved synthesis of D- π -A dye 9 with the acceptor A4.

a substantial amount of undesired protodeboronated compounds from 4 were generated. As expected, the removal of the tBu group by using TFA (trifluoroacetic acid) and a simple short pad column chromatography afforded the desired dye 5 in high purity.

Four donors, D1–D4, seven π -bridges, π 1– π 7, and four acceptors, A1-A4 were selected for the construction of the D- π -

Table 2. synthesiz	Absorp ed D-π	tion max -A dyes (I	ima (λ _{max}), optio D1 and D2).	cal edge,	and mo	olar absorp	otion co	oefficients	5 (ε), Ε _{ΗΟΜΟ} , Ε _{LUM}	₁₀ vs. NH	E of the
Dye	$\lambda_{\max}^{[a]}$ [nm]	Optical edge [nm]	$\varepsilon^{[b]}$ [Lmol ⁻¹ cm ⁻¹]	Е _{номо} ^[с] [V]	E _{LUMO} ^[c] [V]	Dye	λ _{max} ^[a] [nm]	Optical edge [nm]	$\varepsilon^{[b]}$ [Lmol ⁻¹ cm ⁻¹]	Е _{номо} ^[с] [V]	Е _{LUMO} ^[с] [V]
D1π1A1	467	580	29000	1.32	-0.81	D2π1A1	503	617	28600	1.28	-0.73
D1π2A1	493	637	26000	1.26	-0.68	D2π2A1	526	616	35 000	1.17	-0.84
D1π3A1	492	608	39000	1.34	-0.69	D2π3A1	500	628	24000	1.16	-0.81
D1π4A1	493	586	32700	1.33	-0.79	D2π4A1	489	618	31 000	1.15	-0.85
D1π5A1	509	622	32000	1.25	-0.74	D2π5A1	530	648	24000	1.12	-0.79
D1π6A1	503	614	34000	1.32	-0.70	D2π6A1	512	614	48700	1.15	-0.87
D1π7A1	504	648	23000	1.31	-0.60	D2π7A1	512	622	24900	1.15	-0.84
D1π1A2	495	592	18500	1.29	-0.81	D2π1A2	499	622	28000	1.20	-0.79
D1π2A2	490	605	5800	N.D. ^[d]	N.D. ^[d]	D2π2A2	506	669	44100	1.15	-0.70
D1π3A2	489	587	40700	1.30	-0.81	D2π3A2	501	607	32 400	1.16	-0.88
D1π4A2	489	583	36100	1.31	-0.82	D2π4A2	502	626	33 000	1.15	-0.83
D1π5A2	501	618	11 000	1.20	-0.80	D2π5A2	497	636	12100	1.11	-0.84
D1π6A2	497	593	42 000	1.26	-0.83	D2π6A2	510	609	65 100	1.16	-0.88
D1π7A2	486	640	15700	1.23	-0.70	D2π7A2	495	627	57 200	1.15	-0.82
D1π1A3	350,	563	13000	1.35	-0.85	D2π1A3	471	590	34000	1.15	-0.95
	440										
D1π2A3	447	558	24600	1.25	-0.97	D2π2A3	472	603	31 000	1.13	-0.92
D1π3A3	447	543	21 000	1.34	-0.94	D2π3A3	457	563	26300	1.18	-1.03
D1π4A3	343	538	37700	1.31	-1.00	D2π4A3	444	563	24000	1.14	-1.06
D1π5A3	477	569	26800	1.24	-0.94	D2π5A3	492	606	25 000	1.13	-0.92
D1π6A3	460	565	23 000	1.35	-0.85	D2π6A3	474	572	30 300	1.16	-1.01
D1π7A3	470	570	20 000	1.30	-0.88	D2π7A3	479	601	30 000	1.15	-0.91
D1π1A4	512	640	32000	1.32	-0.61	D2π1A4	526	638	23 600	1.18	-0.77
D1π2A4	513	631	30 000	1.27	-0.69	D2π2A4	526	642	40 200	1.18	-0.75
D1π3A4	505	617	39000	1.33	-0.68	D2π3A4	523	645	30 000	1.15	-0.77
D1π4A4	505	599	39600	1.28	-0.79	D2π4A4	524	649	39000	1.15	-0.76
D1π5A4	536	622	68 500	1.22	-0.77	D2π5A4	560	659	63100	1.13	-0.75
D1π6A4	226, 518	650	15600	1.27	-0.64	D2π6A4	530	632	33 000	1.17	-0.79
D1π7A4	524	618	88 000	1.25	-0.75	D2π7A4	538	636	14000	1.16	-0.79

[a] Absorption maxima in CH₂Cl₂. [b] Molar absorption coefficients in CH₂Cl₂. [c] E_{HOMO} was determined by the cyclic voltammetry of each dye-sensitizer solution (~0.3 mm) with $LiClO_4$ (0.1 m) as a counter electrolyte in DMF (N,N-dimethylformamide) equipped with Pt plate, Pt wire, and Ag/Ag⁺ (0.01 м of AgNO₃ in DMF) as working, counter, and reference electrodes, respectively. Before and after each measurement, the Ag/Ag⁺ reference electrode was calibrated independently by the redox potential of ferrocene (Fe^{III}/Fe^{II}) in DMF referred as + 0.853 [V] (vs. NHE).^[17] $E_{HOMO}-E_{LUMO}$ gap was determined by the edge of absorption spectra defined by the wavelength for which the absorbance revealed 1/10 of peak top; that is, E_{HOMO}-E_{LUMO} gap [eV] was calculated by 1240 [nm]/optical edge [nm]. E_{LUMO} was thus calculated by the summation of HOMO potential and $E_{HOMO}-E_{LUMO}$ gap. [d] Not determined (solubilities of the dyes were not sufficient).

(Scheme 1). The reaction conditions for the first coupling between 1 and 2 were explored. Combinations of bases (Na₂CO₃ and K₂CO₃), Pd ([Pd(PPh₃)₄],^[10] catalysts [Pd₂(dba)₃],^[11] Pd(OAc)₂,^[12] and $[PdCl_2(dppf)]^{[13]}$), phosphine ligands (Xantphos,^[14] DPEphos,^[14] PPh₃, and P(furyl)₃),^[15] and solvents (toluene, EtOH, and THF with H₂O) were examined. As a result, the combination of $1 \text{ mol } \% \text{ [Pd}_2(dba)_3], 2 \text{ mol } \%$ Xantphos, and Na₂CO₃ in toluene/H₂O afforded the best result (68% yield). Then, the one-pot conditions were explored. After confirming the completion of the first coupling reaction by TLC analysis, 5 mol% $[Pd_2(dba)_3],$ 7 mol% [(tBu₃P)H]BF₄,^[16] Na_2CO_3 , and **3** were added. The following workup and silica gel column chromatography afforded the desired product 4 in a 60% yield (one-pot, two-step yield). This result indicated that the remaining compounds in the first step did not suffer the following step. The addition of [Pd₂(dba)₃] and an electron-rich and bulky ligand, [(*t*Bu₃P)H]BF₄, was crucial for a good yield. Otherwise, the reaction was very slow and

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Table 3. Absorption maxima (λ_{max}), optical edge, and molar absorption coefficients (ε), E_{HOMO} , E_{LUMO} vs. NHE of the synthesized D- π -A dyes (**D3** and **D4**).

Dye	λ _{max} [nm] ^[a]	Optical edge [nm]	$\varepsilon \ [Lmol^{-1} cm^{-1}]^{[b]}$	Е _{номо} [V] ^[с]	E _{lumo} [V] ^[c]	Dye	λ _{max} [nm] ^[a]	Optical edge [nm]	$\varepsilon \ [Lmol^{-1} cm^{-1}]^{[b]}$	E _{HOMO} [V] ^[c]	E _{LUMO} [V] ^[c]
D3π1A1	528	659	30 000	1.11	-0.78	D4π1A1	508	609	33 500	0.93	-1.10
D3π2A1	519	653	18000	1.08	-0.82	D4π2A1	504	620	11 000	1.19	-0.81
D3π3A1	529	654	36000	1.10	-0.80	D4 π3 A1	506	604	28400	1.22	-0.83
D3π4A1	523	650	33 000	1.13	-0.77	D4π4A1	506	605	33 000	1.22	-0.83
D3π5A1	555	686	31 000	1.04	-0.77	D4π5A1	535	629	41 800	1.14	-0.83
D3π6A1	526	648	20 000	1.09	-0.82	D4π6A1	511	610	29600	1.22	-0.82
D3π7A1	528	650	81 800	1.08	-0.83	D4π7A1	516	695	15800	1.19	-0.60
D3π1A2	518	633	14600	N.D. ^[d]	N.D. ^[d]	D4π1A2	505	608	25 300	1.21	-0.83
D3π2A2	499	631	25 400	0.86	-1.11	D4π2A2	504	657	6550	1.16	-0.73
D3π3A2	512	633	24600	1.09	-0.87	D4π3A2	489	609	26100	1.16	-0.88
D3π4A2	519	630	31 200	1.09	-0.87	D4π4A2	500	604	48 300	1.21	-0.85
D3π5A2	521	662	35 600	1.03	-0.84	D4 π5 A2	535	632	20300	1.12	-0.84
D3π6A2	517	687	21 500	1.10	-0.71	D4π6A2	N.D. ^[d]	N.D. ^[d]	N.D. ^[d]	1.19	N.D. ^[d]
D3π7A2	520	620	12900	1.06	-0.94	D4π7A2	N.D. ^[d]	N.D. ^[d]	N.D. ^[d]	1.13	N.D. ^[d]
D3π1A3	481	589	14400	1.13	-0.98	D4π1A3	467	563	33 800	1.21	-0.99
D3π2A3	483	593	22100	1.11	-0.98	D4π2A3	472	591	42 000	1.17	-0.93
D3π3A3	474	584	18000	1.10	-1.02	D4π3A3	455	560	16500	1.20	-1.01
D3π4A3	473	600	20000	1.10	-0.97	D4π4A3	452	553	22600	1.21	-1.03
D3 π5 A3	511	635	29000	1.04	-0.91	D4π5A3	489	612	37 000	1.14	-0.89
D3π6A3	487	596	20900	1.11	-0.97	D4π6A3	470	600	44 900	1.19	-0.87
D3π7A3	486	604	19100	1.08	-0.97	D4π7A3	478	582	15000	1.14	-0.99
D3π1A4	540	654	20700	1.10	-0.79	D4π1A4	524	623	14800	1.23	-0.76
D3π2A4	533	650	42800	N.D. ^[d]	N.D. ^[d]	D4π2A4	560	623	48 300	1.20	-0.79
D3π3A4	542	677	49000	1.02	-0.81	D4π3A4	522	623	38800	1.19	-0.80
D3π4A4	542	673	40 000	1.09	-0.75	D4π4A4	526	621	14600	1.21	-0.79
D3π5A4	575	704	16300	1.02	-0.74	D4π5A4	558	663	46700	1.11	-0.76
D3π6A4	542	666	19600	1.08	-0.78	D4π6A4	526	653	16600	1.18	-0.72
D3π7A4	540	658	11 000	1.09	-0.79	D4π7A4	525	627	16000	1.20	-0.77
						<i>.</i>	<u> </u>				

[a] Absorption maxima in CH₂Cl₂. [b] Molar absorption coefficients in CH₂Cl₂. [c] E_{HOMO} was determined by the cyclic voltammetry of each dye-sensitizer solution (~0.3 mM) with LiClO₄ (0.1 M) as a counter electrolyte in DMF equipped with Pt plate, Pt wire, and Ag/Ag⁺ (0.01 M of AgNO₃ in DMF) as working, counter, and reference electrodes, respectively. Before and after each measurement, the Ag/Ag⁺ reference electrode was calibrated independently by the redox potential of ferrocene (Fe^{III}/Fe^{II}) in DMF referred as +0.853 [V] (vs. NHE).^[17] E_{HOMO} - E_{LUMO} gap was determined by the edge of absorption spectra defined by the wavelength for which the absorbance revealed 1/10 of peak top; *that is*, E_{HOMO} - E_{LUMO} gap [eV] was calculated by 1240 [nm]/optical edge [nm]. E_{LUMO} was thus calculated by the summation of HOMO potential and E_{HOMO} - E_{LUMO} gap. [d] Not determined (solubilities of the dyes were not sufficient).

Novel rigid and nonplanar donors D3 and D4 containing norbornane а structure were designed to prevent the undesired aggregation of dyes.^[1c] The building blocks were coupled by using the developed one-pot procedure in a parallel fashion (Table 1). After the completion of the one-pot reaction, the toluene layers containing desired dyes were simply removed from the reaction vessels by using pipettes and were loaded onto disposable silica gel pads. Automated column purification was performed to afford the desired coupling products. In the case of A4, the one-pot coupling yields dropped to 20% probably due to the undesired Pd poisoning by heteroatoms in A4.

Therefore, the readily available boronic acid pinacol ester **6** (**A4**') was used instead of **A4** to improve the yields (Scheme 2). After silica gel column purification, Knoevenagel condensation of the obtained coupling

A dye library (Figure 2). Except for **D3** and **D4**, all blocks are frequently found in high-performance dyes for DSSCs.^[3c,d]

product **7** with **8** was performed to afford the intended dye **9**. Thus, the total number of reaction steps was not changed. Al-



Figure 3. a) The average values for E_{HOMO} vs. NHE of **D1**-containing 27 dyes, **D2**-containing 28 dyes, **D3**-containing 26 dyes, and **D4**-containing 28 dyes. b) The average values for E_{LUMO} vs. NHE of **D1**-containing 27 dyes, **D2**-containing 28 dyes, **D3**-containing 26 dyes, and **D4**-containing 26 dyes. c) The average values for E_{HOMO} vs. NHE of **π1**-containing 15 dyes, π 2-containing 14 dyes, π 3-containing 16 dyes, π 4-containing 16 dyes, π 5-containing 16 dyes, π 6-containing 16 dyes, π 4-containing 16 dyes, π 3-containing 16 dyes, π 4-containing 14 dyes, π 3-containing 16 dyes, π 4-containing 16 dyes, π 3-containing 16 dyes, π 4-containing 16 dyes, π 3-containing 16 dyes, π 4-containing 16 dyes, π 4-containing 16 dyes, π 3-containing 16 dyes, π 4-containing 16 dyes, π 3-containing 16 dyes, π 4-containing 28 dyes, π 4-containing 27 dyes. f) The average values for E_{LUMO} vs. NHE of A1-containing 28 dyes, A2-containing 28 dyes, π 4-containing 27 dyes. The values were expressed as means of \pm standard deviation (SD).

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Table 4. Photovoltaic properties of solar cells prepared by using 33 randomly selected dyes.													
Dye	E _{HOMO} [V] ^[a]	E _{LUMO} [V] ^[a]	η [%] ^[b]	FF ^(b)	$V_{\rm oc}$ [V] ^[b]	J _{sc} [mAcm ⁻²] ^[b]	Dye	E _{HOMO} [V] ^[a]	E _{LUMO} [V] ^[a]	η [%] ^[b]	FF ^(b)	V _{oc} [V] ^[b]	J _{sc} [mAcm ⁻²] ^[b]
D3π3A4	1.02	-0.81	1.4	0.70	0.57	3.4	D4π3A4	1.19	-0.80	3.1	0.72	0.61	7.3
D3π5A1	1.04	-0.77	0.6	0.53	0.52	2.2	D1π5A2	1.20	-0.80	4.2	0.65	0.61	10.5
D3π5A3	1.04	-0.91	1.6	0.54	0.59	5.2	D2π1A2	1.20	-0.79	3.2	0.68	0.58	8.1
D3π2A1	1.08	-0.82	2.8	0.60	0.58	8.0	D4π2A4	1.20	-0.79	2.4	0.69	0.54	6.3
D3π6A1	1.09	-0.82	2.7	0.55	0.59	8.2	D4π4A4	1.21	-0.79	2.7	0.72	0.62	5.9
D3π4A4	1.09	-0.75	1.6	0.69	0.58	4.0	D1π5A4	1.22	-0.77	1.7	0.62	0.54	5.2
D3π3A1	1.10	-0.80	4.0	0.65	0.64	9.7	D4π4A1	1.22	-0.83	5.2	0.66	0.71	11.3
D3π1A1	1.11	-0.78	3.5	0.58	0.61	10.3	D1π5A1	1.25	-0.74	3.3	0.69	0.60	7.9
D4π5A2	1.12	-0.84	0.9	0.61	0.49	3.0	D2π1A1	1.28	-0.73	2.7	0.63	0.57	7.6
D2π2A3	1.13	-0.92	3.4	0.63	0.64	8.6	D1π7A3	1.30	-0.88	4.8	0.69	0.67	10.2
D4π5A1	1.14	-0.83	3.4	0.62	0.61	9.1	D1π4A2	1.31	-0.82	4.6	0.69	0.68	9.8
D2π1A3	1.15	-0.95	4.0	0.65	0.66	9.4	D1π6A1	1.32	-0.70	4.6	0.64	0.65	11.2
D2π6A1	1.15	-0.87	4.1	0.66	0.64	9.7	D1π3A4	1.33	-0.68	1.9	0.75	0.63	4.1
D2π7A1	1.15	-0.84	3.3	0.65	0.58	8.9	D1π4A1	1.33	-0.79	4.6	0.72	0.70	9.0
D2π7A2	1.15	-0.82	2.3	0.65	0.55	6.3	D1π3A1	1.34	-0.69	4.9	0.71	0.71	9.6
D4π3A2	1.16	-0.88	4.9	0.64	0.66	11.9	D1π6A3	1.35	-0.85	4.5	0.68	0.71	9.5
D2π1A4	1.18	-0.77	1.1	0.64	0.51	3.5							
[a] E _{HOMO}	and ELUI	_{vo} were	estima	ated k	oy usir	ng the poten	tial and a	n optica	al edge o	of dye	sensi	tizers	by means of

[a] E_{HOMO} and E_{LUMO} were estimated by using the potential and an optical edge of dye-sensitizers by means of electrochemical measurements and UV/Vis absorption spectra (see Tables 2 and 3). [b] Average values from three independent experiments. FF, fill factor; V_{or} open-circuit voltage; J_{scr} short-circuit current.

though decreased yields were observed in the case of $\pi 5$ (average one-pot yield 34%) due to the slow oxidative addition of an electron-rich C–Br bond in $\pi 5$, other combinations generally afforded good yields (average one-pot yield 50%). Following either acidic removal of the *t*Bu group or Knoevenagel condensation, all the desired compounds were afforded in

and <i>E</i> _{LUMO} located more positive
than iodine/iodide redox potential (+0.4 V vs. normal hydro-
gen electrode (NHE)), and more negative than the conduction
band edge of TiO ₂ (-0.5 V vs. NHE), respectively.

Table 5. Photovoltaic properties of solar cells prepared by using D149 and 21 dyes that fulfil the requirements of HOMO and LUMO levels.											
E _{HOMO} [V] ^[a]	E _{LUMO} [V] ^[a]	η [%] ^[b]	FF ^[b]	$V_{\rm oc} [V]^{\rm [b]}$	J _{sc} [mAcm ⁻²] ^[b]						
-	-	6.1	0.68	0.69	12.9						
1.16	-0.88	2.7	0.68	0.59	6.9						
1.16	-0.88	2.4	0.62	0.56	7.0						
1.16	-1.01	1.9	0.64	0.54	5.5						
1.17	-0.84	4.1	0.66	0.64	9.2						
1.18	-1.03	2.8	0.70	0.62	6.5						
1.20	-1.01	4.2	0.63	0.74	8.9						
1.21	-0.83	2.9	0.65	0.57	7.8						
1.21	-0.99	2.6	0.69	0.57	6.6						
1.21	-0.85	6.2	0.65	0.67	14.3						
1.21	-1.03	4.4	0.65	0.76	8.9						
1.22	-0.82	2.7	0.63	0.60	7.2						
1.22	-0.83	4.2	0.67	0.59	10.5						
1.24	-0.94	5.0	0.71	0.70	10.0						
1.25	-0.97	4.6	0.71	0.69	9.5						
1.26	-0.83	4.8	0.66	0.64	11.5						
1.29	-0.81	4.0	0.65	0.57	10.8						
1.30	-0.81	4.6	0.70	0.66	9.9						
1.31	-1.00	4.9	0.73	0.76	8.9						
1.32	-0.81	5.0	0.57	0.71	12.6						
1.34	-0.94	3.9	0.72	0.76	7.2						
1.35	-0.85	3.4	0.71	0.66	7.2						
	Photovoltaic yes that fulfil E_{HOMO} [V] ^[a] - 1.16 1.16 1.17 1.18 1.20 1.21 1.21 1.21 1.21 1.21 1.21 1.22 1.24 1.25 1.26 1.29 1.30 1.31 1.32 1.34 1.35	Photovoltaic properties yes that fulfil the require E_{HOMO} $VI^{[a]}$ E_{LUMO} - - 1.16 -0.88 1.16 -0.88 1.16 -0.88 1.16 -0.84 1.17 -0.84 1.18 -1.03 1.20 -1.01 1.21 -0.83 1.21 -0.85 1.21 -0.85 1.21 -0.82 1.22 -0.82 1.23 -0.99 1.24 -0.94 1.25 -0.97 1.26 -0.83 1.29 -0.81 1.30 -0.81 1.31 -1.00 1.32 -0.81 1.34 -0.94	Photovoltaic properties of solar yes that fulfil the requirements of E_{HOMO} $VI^{[a]}$ P_{LUMO} N $[\%]^{[b]}$ - - 6.1 1.16 -0.88 2.7 1.16 -0.88 2.4 1.16 -1.01 1.9 1.17 -0.84 4.1 1.18 -1.03 2.8 1.20 -1.01 4.2 1.21 -0.83 2.9 1.21 -0.85 6.2 1.21 -0.85 6.2 1.21 -0.83 4.4 1.22 -0.83 4.2 1.24 -0.94 5.0 1.25 -0.97 4.6 1.26 -0.83 4.8 1.29 -0.81 4.0 1.30 -0.81 4.6 1.31 -1.00 4.9 1.32 -0.81 5.0 1.34 -0.94	Photovoltaic yes that fulfilproperties requirements of $HOMO$ E_{HOMO} $VI^{[a]}$ \mathcal{P} \mathcal{P} \mathcal{P} 6.10.681.16-0.882.70.681.16-0.882.70.681.16-10.11.90.641.17-0.844.10.661.18-1.032.80.701.20-1.014.20.631.21-0.832.90.651.21-0.856.20.691.22-0.822.70.631.22-0.834.20.671.24-0.974.60.711.25-0.974.60.711.26-0.834.80.6651.30-0.814.00.651.31-1.004.90.731.32-0.815.00.571.34-0.943.90.721.35-0.853.40.71	Photovoltaic yes that fulfil the requirements of HOMO and LUM E_{HOMO} $[V]^{[a]}$ E_{LUMO} $[V]^{[a]}$ η $[9_0]^{[b]}$ $FF^{[b]}$ V_{oc} $[V]^{[b]}$ 6.10.680.691.16-0.882.70.680.591.16-0.882.40.620.561.16-1.011.90.640.541.17-0.844.10.660.641.18-1.032.80.700.621.20-1.014.20.630.741.21-0.832.90.650.571.21-0.856.20.690.571.21-0.822.70.630.601.22-0.834.20.670.591.24-0.945.00.710.701.25-0.974.60.710.691.30-0.814.00.650.571.30-0.814.00.650.571.31-1.004.90.730.761.32-0.815.00.571.34-0.943.90.720.76						

[a] $E_{\rm HOMO}$ and $E_{\rm LUMO}$ were estimated by using the potential and an optical edge of dye-sensitizers by means of electrochemical measurements and UV/Vis absorption spectra (see Tables 2 and 3). [b] Average values from three independent experiments.



Figure 4. Correlations between a) ε and η , b) λ_{max} and η , and c) optical edge and η of the 54 dyes.

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good to excellent yields (Table 1). These results clearly indicate the robustness of our developed synthetic procedure.

The absorption spectra and electrochemical properties of all synthesized dyes were measured as shown in Tables 2 and 3. As donors influenced the E_{HOMO} of the dyes, the E_{HOMO} became more positive on the order of $D3 < D2 \le D4 < D1$ (Figure 3a). On the other hand, acceptors influenced the E_{LUMO} of the dyes, and therefore the E_{LUMO} became more negative on the order of A4 < A1 < A2 < A3 (Figure 3f). The HOMO and LUMO levels of all the synthesized dyes met the minimum requirement for a dyesensitizer in DSSCs, that is, E_{HOMO}





Figure 5. Correlations between ε and J_{sc} of a) **D1**-containing 19 dyes (red), **D2**-containing 13 dyes (blue), **D3**-containing 8 dyes (green), and **D4**-containing 14 dyes (yellow), b) π **1**-containing 10 dyes (red), π **2**-containing 5 dyes (blue), π **3**-containing 12 dyes (green), π **4**-containing 8 dyes (yellow). π **5**-containing 8 dyes (orange), π **6**-containing 8 dyes (dark green). π **7**-containing 3 dyes (brown), and c) **A1**-containing 18 dyes (red), **A2**-containing 13 dyes (blue), **A3**-containing 15 dyes (green), **A4**-containing 8 dyes (yellow).

Photovoltaic properties were evaluated for the solar cells that were prepared using 33 randomly selected dyes (Table 4). The $E_{\rm HOMO}$ and $E_{\rm LUMO}$ of the dyes were critical for cell performance. Five of the dyes, **D4** π **3A2**, **D4** π **4A1**, **D1** π **7A3**, **D1** π **4A2**, and **D1** π **6A3**, with $E_{\rm HOMO} > +1.15$ V and $E_{\rm LUMO} < -0.80$ V, exerted a higher cell performance (average of $\eta = 4.8 \pm 0.3$ %). On the other hand, the other 28 dyes exerted a lower cell performance (average of $\eta = 2.9 \pm 1.2$ %).

Photovoltaic properties of the solar cells prepared by using 22 dyes, which fulfilled the requirement of $E_{\rm HOMO}$ > +1.15 V, and $E_{\rm LUMO}$ < -0.80 V, were evaluated (Table 5). Not surprisingly, most of the evaluated dyes exerted high cell performance. These results clearly show that the driving forces of forward interfacial electron transfer are highly important for a high η with respect to organic D- π -A dyes. To our delight, the dye D4 π 4A2, which contained our originally designed D4, exerted the highest efficiency at 6.2%, which was comparable to that of the commercially available high-performance dye, D149 (η = 6.1%).^[3b]

Unexpectedly, no obvious correlation between the ε and the η (R^2 value=0.014) were observed (Figure 4a). Only a very weak correlation between the λ_{max} and the η (R^2 value=0.19) was observed (Figure 4b), and the η tended to decrease as the λ_{max} became longer. A week correlation between the optical edge and η (R^2 value=0.31) was observed (Figure 4c), and the η tended to decrease as the optical edge became longer. It is conceivable that this result also indicated the importance of the proper driving forces.

For a more detailed discussion, the correlations between λ_{max} , ε , optical edge, and J_{sc} for each of the structural components were examined (Figures 5–7). Although strong correla-



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Figure 6. Correlations between λ_{max} and J_{sc} of a) D1-containing 19 dyes (red), D2-containing 13 dyes (blue), D3-containing 8 dyes (green), and D4-containing 14 dyes (yellow), b) π 1-containing 10 dyes (red), π 2-containing 5 dyes (blue), π 3-containing 12 dyes (green), π 4-containing 8 dyes (yellow). π 5-containing 8 dyes (orange), π 6-containing 8 dyes (dark green). π 7-containing 3 dyes (brown), and c) A1-containing 18 dyes (red), A2-containing 13 dyes (blue), A3-containing 15 dyes (green), A4-containing 8 dyes (yellow).



Figure 7. Correlations between optical edge and J_{sc} of a) **D1**-containing 19 dyes (red), **D2**-containing 13 dyes (blue), **D3**-containing 8 dyes (green), and **D4**-containing 14 dyes (yellow), b) π 1-containing 10 dyes (red), π 2-containing 5 dyes (blue), π 3-containing 12 dyes (green), π 4-containing 8 dyes (yellow). π 5-containing 8 dyes (orange), π 6-containing 8 dyes (dark green). π 7-containing 3 dyes (brown), and c) **A1**-containing 18 dyes (red), **A2**-containing 13 dyes (blue), **A3**-containing 15 dyes (green), **A4**-containing 8 dyes (yellow).

tions were not observed in general, correlations between λ_{max} and J_{sc} (R^2 value = 0.56), and optical edge and J_{sc} (R^2 value = 0.53) were observed in the case of π 5-containing dyes. Among all the dyes, π 5-containing dyes retained the longest λ_{max} and

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Figure 8. The average values for a) η , b) FF, c) V_{ocr} and d) J_{scr} of the 19 dyes retaining **D1**, the 13 dyes retaining **D2**, 8 dyes retaining **D3**, and the 14 dyes retaining **D4**. The values were expressed as means of \pm SD.

optical edge. This means that the driving forces of π **5**-containing dyes are not sufficient. Therefore, J_{sc} tended to decrease as the λ_{max} and optical edge became longer in the case of π **5**-containing dyes.

In terms of the D structure-device parameter (η , FF, V_{oc} , and J_{sc}) relationships, all the parameters became higher in the order of D3 < D2 < D4 < D1 (Figure 8). This tendency was consistent with the E_{HOMO} (Figure 3). Namely, the dyes with a more positive E_{HOMO} exerted higher PCEs. The results corroborated the importance of the driving force.

In terms of the π structure-device parameter relationships, roughly all the parameters became higher in the order of $\pi 5 < \pi 1 \approx \pi 2 \approx \pi 3 \approx \pi 6 \approx \pi 7 < \pi 4$. Similar to the previous report,^[18] π -bridges with long alkyl chains ($\pi 3$ and $\pi 4$) contributed to the high $V_{\rm oc}$ (Figure 9c) and high FF (Figure 9b). On the other hand, the electron-donating $\pi 5$ decreased in all the parameters. This contrasted with recently reported D-A- π -A dyes, which exerted excellent PCEs.^[3g]

In terms of the **A** structure-device parameter relationships, **A1–A3** exerted a similar level of η and Jsc, whereas they were decreased for **A4** (Figure 10a and d). Among **A1–A4**, only the average value for E_{LUMO} of **A4**-containing dyes (-0.75 ± 0.05 V) was less negative than -0.80 V. Therefore, it is conceivable that the driving force was not sufficient in the case of **A4**.^[19]

Although the average values for the E_{LUMO} of A1–A3-containing dyes (A1 = -0.79 ± 0.09 , A2 = -0.83 ± 0.08 , A3 = -0.96 ± 0.06 V) were different from each other (Figure 3f), this did not influence the PCEs. It seemed that the key to high PCEs was the fulfillment of the previously described requirement of $E_{LUMO} < -0.80$ V. No obvious correlation between FF and the A structure was observed (Figure 10b). The V_{oc} became higher in



Figure 9. The average values for a) η , b) FF, c) V_{oc} and d) J_{scr} of the 10 dyes retaining π 1, the 5 dyes retaining π 2, the 12 dyes retaining π 3, the 8 dyes retaining π 4, the 8 dyes retaining π 5, the 8 dyes retaining π 6, and the 3 dyes retaining π 7. The values were expressed as means of \pm SD.



Figure 10. The average values for a) η , b) FF, c) V_{ocr} and d) J_{scr} of the 18 dyes retaining **A1**, the 13 dyes retaining **A2**, 15 dyes retaining **A3**, and the 8 dyes retaining **A4**. The values were expressed as means of \pm SD.

the order of $A4 \le A2 \le A1 < A3$. Tian and co-workers pointed out the possibility that the LUMO level is correlated with V_{oc} .^[1c] It is conceivable that a high V_{oc} of A3-containing dyes can be attributed to their most negative LUMO, and thus the low V_{oc}



Figure 11. Correlations between a) FF and η , b) V_{oc} and η , c) J_{sc} and η , d) J_{sc} and IPCE area of the 54 dyes.

of the **A4**-containing dyes was attributed to their least-negative LUMO.

Reportedly, V_{oc} is the most important factor to achieve high PCEs with organic dyes.^[1c,20] However, it is noteworthy that J_{sc} strongly correlated (R^2 value = 0.87) with η (Figure 11c). The J_{sc} also correlated (R^2 value = 0.74) with IPCE (Figure 11d). On the other hand, only a weak correlation (R^2 value = 0.38) between V_{oc} and η (Figure 11b) was observed. No obvious correlation (R^2 value = 0.073) between FF and η (Figure 11a) was observed. Generally, J_{sc} is correlated with the sensitizer absorption capability and the electron injection efficiency. There was only



Figure 12. Correlation between a) J_{sc} and the average values for the E_{HOMO} of D1-, D2-, D3-, and D4 containing dyes and b) J_{sc} and the average values for the E_{LUMO} of A1-, A2-, A3-, and A4-containing dyes.

a weak or no obvious correlation between spectroscopic properties (λ_{max} , and ε) and cell performance, and, therefore, the injection efficiency seemed to be the most important factor for high PCEs with respect to the organic D- π -A dyes. The injection efficiency was correlated with the HOMO and LUMO levels of dyes, and these were influenced by D and A structures, respectively (Figure 3a and f).

As shown in Figure 12a and b, the dyes with a more positive $E_{\rm HOMO}$, and with an $E_{\rm LUMO} < -0.80$ V, exerted a higher $J_{\rm sc}$. Based on the obtained structure-property information, the combinations of D1, π 3, or π 4 and A1, A2, or A3 were supposed to exert a high η , because the average value for E_{HOMO} of D1 was the most positive. The $\pi 3$ and $\pi 4$ contributed to the high FF and $V_{\rm oc}$. The average values for $E_{\rm LUMO}$ of A1, A2, and A3 were either equal to, or more negative than, the value of -0.80 V. In accordance with speculation, most of the combinations actually exerted a high η (Table 4 and 5). However, it was interesting to note that the best dye was not found in the supposed best combinations of D, π , and A blocks. The combination of D4, π 4, and A2 exerted the highest PCE. Here, we considered the reason for the high η of **D4** π **4A2**. The photocurrent-voltage curve and the incident photon-to-current conversion efficiency (IPCE) spectra of $D4\pi 4A2$ were compared with those of the simplest structure D- π -A dye (D1 π 1A1), and D149 as references (Figure 13). $D4\pi 4A2$ efficiently converted UV/Vis light to a photocurrent in the region from 350 to 660 nm, similar to D149. Compared with D1 π 1A1, the IPCE of D4 π 4A2 in the region from 300 to 590 nm was lower, and that of in the region from 590 to 750 nm was higher. An advantage of $D4\pi 4A2$ seemed to be that the dye exerted a somewhat high IPCE in the wide region from 350 to 660 nm.

For the evaluation of the electron injection efficiency of **D4**π**4A2**, and **D1**π**1A1** in the film, a time-resolved microwave conductivity (TRMC) measurement was carried out (see the Supporting information for details). TRMC is a type of transient absorption spectroscopy that measures the conductivity σ of mobile charges produced by pulsed-light excitation.^[21] The obtained results indicated that the electron injection efficiency for **D4**π**4A2** was lower than that for **D1**π**1A1** (electron injection efficiencies, N719: 1,^[21b] **D1**π**1A1**: 0.9, **D4**π**4A2**: 0.7).

We have described the importance of the proper driving forces (HOMO and LUMO levels) for smooth forward interfacial electron transfer for the creation of high PCE dyes in this

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Figure 13. Photocurrent-voltage curves obtained with DSSCs based on D4 π 4A2, D1 π 1A1, and D149 under standard AM1.5 solar conditions (a) and in the dark (b). c) Incident photon-to-current conversion efficiency spectra for DSSCs based on D4 π 4A2, D1 π 1A1, and D149. $_{\odot}$: D4 π 4A2; $_{\odot}$: D149; $_{\odot}$: D1 π 1A1.

manuscript. However, the electron injection efficiency of the best dye, **D4** π **4A2**, was not the highest among the synthesized dyes. In fact, the electron injection efficiency of **D4** π **4A2** was lower than that of **D1** π **1A1**. These results indicated that the criteria of the more positive E_{HOMO} , and $E_{LUMO} < -0.80$ V should be useful for creating high PCE dyes. Nevertheless, that was not sufficient for identifying the best combination of D, π , and A blocks. Our results indicated that combinatorial synthesis and evaluation were important for identifying the best dye.

Conclusion

In summary, a large-scale (112-membered) D- π -A dye library was rapidly constructed by a one-pot, three-component SM coupling procedure. The evaluation of absorption spectroscopic and electrochemical measurements of all synthesized dyes, and cell performance of the selected 54 dyes were performed. No obvious correlations between ε , and the η were observed. On the other hand, the HOMO and LUMO levels of the dyes

were critical for cell performance. The dyes with a more positive $E_{\rm HOMO}$, and with an $E_{\rm LUMO} < -0.80$ V, exerted higher PCEs. This indicated that the proper driving forces were crucial for smooth forward interfacial electron transfer, which directly influences the $J_{\rm sc}$. The $J_{\rm sc}$ was the most important parameter for η in the case of organic D- π -A dyes. The above criteria of $E_{\rm HOMO}$ and $E_{\rm LUMO}$ should be useful for creating high PCE dyes. However, is interesting that the best dye, **D4** π **4A2** that contained our originally designed, rigid, and nonplanar **D4** was not found in the supposed combinations of D, π , and A blocks based on the above criteria of $E_{\rm HOMO}$ and $E_{\rm LUMO}$. This clearly indicated the importance of combinatorial synthesis and evaluation for identifying the best dye.

Experimental Section

Experimental details are given in the Supporting Information. These include synthetic, photophysical and electrochemical procedures, and the characterization of the synthesized compounds.

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

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