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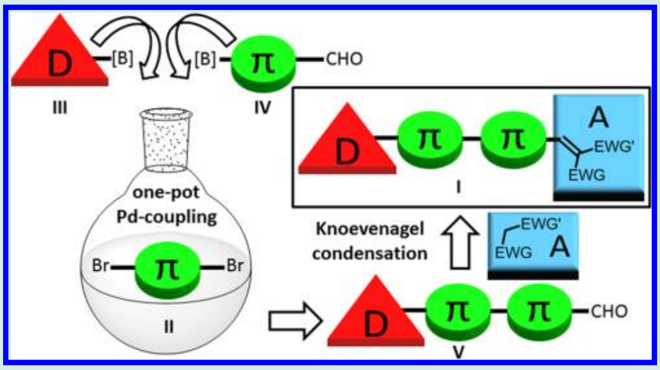
Elucidation of the Structure−Property Relationship of p-Type Organic Semiconductors through Rapid Library Construction via a One-Pot, Suzuki−Miyaura Coupling Reaction

Shinichiro Fuse,*[†] Keisuke Matsumura,[†] Atsushi Wakamiya,[‡] Hisashi Masui,[§] Hiroshi Tanaka,[†] Susumu Yoshikawa,[◇] and Takashi Takahashi[§]

[†]Department of Applied Chemistry, Tokyo Institute of Technology, Tokyo 152-8552, Japan
[‡]Institute for Chemical Research, Kyoto University, Kyoto 611-0011, Japan
[§]Yokohama College of Pharmacy, Kanagawa 245-0066, Japan
[◇]Institute of Advanced Energy, Kyoto University, Kyoto 611-0011, Japan

Ⓢ *Supporting Information*



ABSTRACT: The elucidation of the structure−property relationship is an important issue in the development of organic electronics. Combinatorial synthesis and the evaluation of systematically modified compounds is a powerful tool in the work of elucidating structure−property relationships. In this manuscript, D−π−A structure, 32 p-type organic semiconductors were rapidly synthesized via a one-pot, Suzuki−Miyaura coupling with subsequent Knoevenagel condensation. Evaluation of the solubility and photovoltaic properties of the prepared compounds revealed that the measured solubility was strongly correlated with the solubility parameter (SP), as reported by Fedors. In addition, the SPs were correlated with the J_{sc} of thin-film organic solar cells prepared using synthesized compounds. Among the evaluated photovoltaic properties of the solar cells, J_{sc} and V_{oc} had strong correlations with the photoconversion efficiency (PCE).

KEYWORDS: *p-type semiconductor, structure−property relationship, Suzuki−Miyaura coupling, one-pot*

INTRODUCTION

Elucidating the relationship between the chemical structure of single molecules and the properties of materials/devices is important in the development of organic electronics.[1] Recent dramatic progress in theoretical calculation has made it possible to estimate the properties of single molecules such as the conformation, absorption spectra, and the electron distributions of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).[2] However, because intermolecular interactions dramatically influence the properties of the materials/devices, a rational estimation of these important interactions is not simple. Another method of estimation is the use of structure−property information, which is drawn from extensive past reports.[3,4] However, the extraction of precise structure−property information is also not a simple process, because the procedure for the preparation and evaluation of materials/devices varies depending on the research group.[5] The combinatorial synthesis of systematically modified compounds, and the evaluation of the properties of materials/devices using those synthesized compounds, have been a powerful tool in the work of elucidating the relationship between a single molecule structure and the properties of materials/devices.[6,7]

Organic solar cells have garnered considerable attention due to their simple fabrication procedures, low production cost, a lightweight construction, and mechanical flexibility.[3,4,8] Bulk heterojunction solar cells now demonstrate remarkable achievements with power conversion efficiencies (PCEs) in excess of 10%.[9] Although the best PCEs have been achieved with polymer p-type organic semiconductors that consist of alternating donor−acceptor (D−A) repeating structures, small-molecule p-type counterparts have recently demonstrated high PCEs. In 2012, Heeger and co-workers reported a symmetric small-molecule with A−D−A structure that exerted a high PCE of 6.7%.[10] In 2013, Chen and co-workers reported a small-molecule with A−D−A structure that exerted a remarkable PCE of 8.1%.[11] Wong and co-workers reported a D−A−A type asymmetric small-molecule that also exerted a high PCE of 6.8%,[12] although this was still lower than the A−D−A symmetric-structure. By comparison with corresponding

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polymers, small-molecule p-type organic semiconductors have predominant advantages such as well-defined molecular structures, easier purification, and better batch-to-batch reproducibility. For the development of novel small-molecule p-type semiconductors with higher PCEs, a fundamental elucidation of the structure−property relationship is important.

We have reported the construction of combinatorial libraries based on palladium-catalyzed cross-coupling reactions.[13−21] Herein, we wish to report the rapid synthesis of asymmetric small-molecules (32 compounds) with D−π−A structures for use as p-type semiconductors of organic thin film solar cells via a one-pot, SM coupling with subsequent Knoevenagel condensation. In addition, the solubility and photovoltaic properties of prepared compounds were evaluated. The relationships between the structures of p-type semiconductors, and the solubility and photovoltaic properties are discussed.

■ RESULTS AND DISCUSSION

The D−π−A structure of organic p-type semiconductor **I** was selected as a target compound (Figure 1). We planned to couple a donor block **III** with the aromatic scaffold of **II** 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 **II**, and, therefore, an undesirable overreaction affording a D−π−D compound would be suppressed. The one-pot Suzuki−Miyaura (SM) coupling with **IV** afforded the desired coupling product **V**. The subsequent Knoevenagel condensation afforded the desired compound **I**.

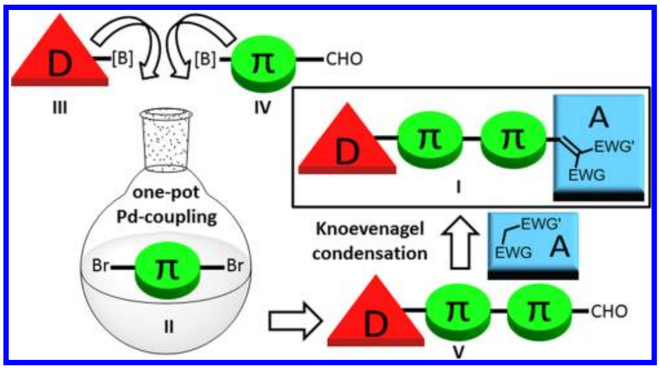
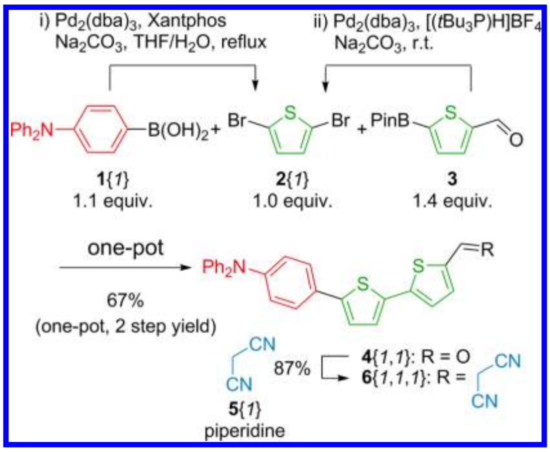


Figure 1. One-pot approach for the synthesis of p-type semiconductors with D−π−A structures that was based on a Suzuki−Miyaura coupling with subsequent Knoevenagel condensation.

For the development of a one-pot, SM coupling-Knoevenagel condensation sequence, a simple and typical compound **6**{*1,1,1*}[22] was selected as the target (Scheme 1). The first SM coupling reaction was carried out using a combination of 1 mol % $Pd_2(dba)_3$,[23] 2 mol % Xantphos,[24] and Na_2CO_3 in THF/H_2O. After confirming the completion of the first SM coupling reaction, **3**, $Pd_2(dba)_3$, $[(tBu_3P)H]BF_4$,[25] and Na_2CO_3 were added to afford the desired coupling product **4**{*1,1*} in a 67% yield (one-pot, 2-step yield). The subsequent Knoevenagel condensation of **4**{*1,1*} with **5**{*1*} proceeded smoothly to afford the desired compound in a good yield.

Scheme 1. Synthesis of the Organic p-Type Semiconductor 6{*1,1,1*} Based on the One-Pot, SM Coupling−Knoevenagel Condensation



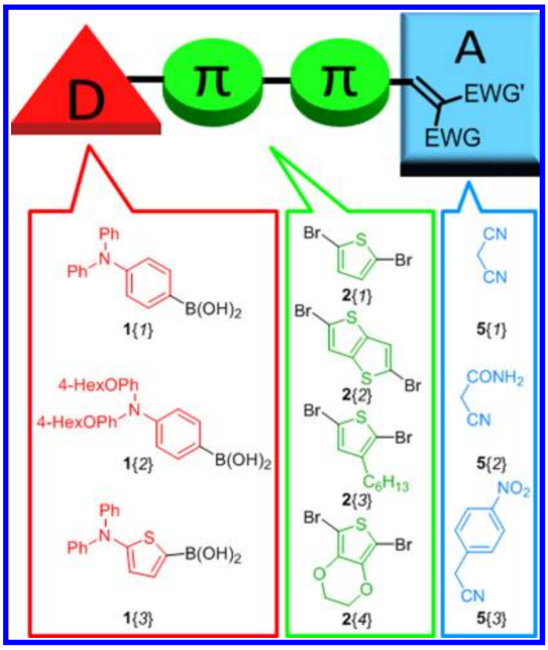


Figure 2. Synthesis of D−π−A small-molecule, p-type organic semiconductors via a one-pot, palladium-catalyzed coupling reaction with subsequent Knoevenagel condensation.

Three donors **1**{*1−3*}, 4 π-bridges **2**{*1−4*}, and 3 acceptors **5**{*1−3*}, were selected for the construction of the asymmetric-structure, small-molecular library (Figure 2). Small-molecules of p-type semiconductors should have a higher planarity that would allow an ordered stacking for a smooth intermolecular electron transfer. On the other hand, generally highly planar molecules are poorly soluble to organic solvents, which are used for the film formation process in preparing organic solar cells. For elucidation of the relationships between the structures of small-molecules, and their solubility and photovoltaic properties, building blocks with different solubilities were used for the library construction.

The building blocks were coupled using the developed one-pot procedure in a parallel fashion. Building block **1**{*3*} was unstable, and attempts at purification using silica-gel column chromatography failed. Therefore, lithiation, borylation, and double SM coupling reaction were performed sequentially in a one-pot. To a stirred solution of 2-(diphenylamino)thiophene in THF, *n*BuLi was added dropwise at −78 °C. then *i*PrOBPin was added to in-situ-generated unstable thiophene boronic acid pinacol ester **1**{*3*}. To a stirred solution of **1**{*3*}, water, **2**{*1*}, $Pd_2(dba)_3$, Xantphos, and Na_2CO_3 were added. After confirmation of the completion of the first SM coupling reaction, **3**, $\text{Pd}_2(\text{dba})_3$, $[(t\text{Bu}_3\text{P})\text{H}]\text{BF}_4$, and Na_2CO_3 were added. To our delight, the desired compound **4**{*3,1*} was obtained in a good yield. It should be noted that although the 2-(diphenylamino)thiophene structure is an attractive building block in materials science,[26−37] the introduction of this useful building block via palladium-catalyzed cross-coupling reactions[28,29,31−37] was not simple because of instability of the coupling precursors: either thienyl boronic acid or thienyl stannane. Recently, Buckwald and co-workers reported an elegant lithiation/borylation/SM coupling sequence of simple thiophenes and aromatic rings in a microflow reactor.[38] Our developed one-pot, lithiation/borylation/SM coupling/SM coupling sequence should be useful for introducing the 2-(diphenylamino)thiophene building block.

Scheme 2. Synthesis of 4{*3,1*} Based on the One-Pot, Borylation-Double SM Coupling Sequence

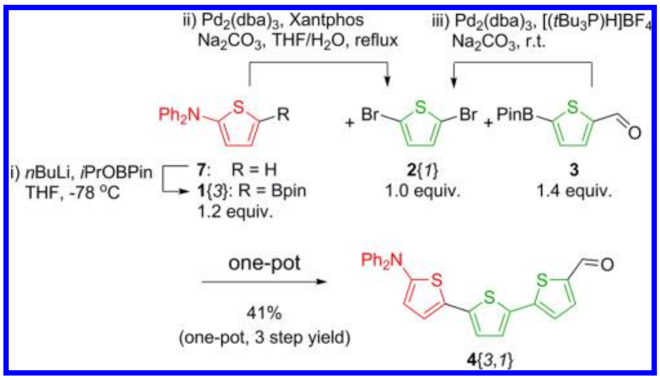
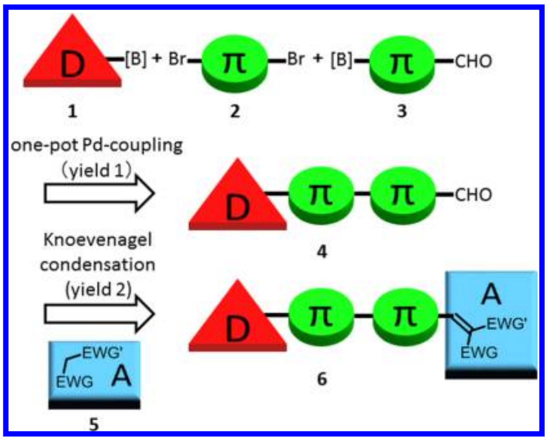


Table 1. Yields of One-Pot, SM Coupling Reactions with Subsequent Knoevenagel Condensations



entry	1	2	product (yield 1)	5	product (yield 2)
1	*1*	*1*	4{*1,1*} (67%)[a]	*1*	6{*1,1,1*} (87%)
2	*1*	*1*		*2*	6{*1,1,2*} (81%)
3	*1*	*1*		*3*	6{*1,1,3*} (74%)
4	*1*	*2*	4{*1,2*} (29%)[a]	*1*	6{*1,2,1*} (69%)
5	*1*	*2*		*2*	6{*1,2,2*} (58%)
6	*1*	*2*		*3*	6{*1,2,3*} (−)[c]
7	*1*	*3*	4{*1,3*} (55%)[a]	*1*	6{*1,3,1*} (91%)
8	*1*	*3*		*2*	6{*1,3,2*} (83%)
9	*1*	*3*		*3*	6{*1,3,3*} (quant.)
10	*1*	*4*	4{*1,4*} (23%)[a]	*1*	6{*1,4,1*} (73%)
11	*1*	*4*		*2*	6{*1,4,2*} (50%)
12	*1*	*4*		*3*	6{*1,4,3*} (61%)
13	*2*	*1*	4{*2,1*} (72%)[a]	*1*	6{*2,1,1*} (72%)
14	*2*	*1*		*2*	6{*2,1,2*} (76%)
15	*2*	*1*		*3*	6{*2,1,3*} (84%)
16	*2*	*2*	4{*2,2*} (50%)[a]	*1*	6{*2,2,1*} (90%)
17	*2*	*2*		*2*	6{*2,2,2*} (95%)
18	*2*	*2*		*3*	6{*2,2,3*} (quant.)
19	*2*	*3*	4{*2,3*} (74%)[a]	*1*	6{*2,3,1*} (69%)
20	*2*	*3*		*2*	6{*2,3,2*} (67%)
21	*2*	*3*		*3*	6{*2,3,3*} (65%)
22	*2*	*4*	4{*2,4*} (40%)[a]	*1*	6{*2,4,1*} (67%)
23	*2*	*4*		*2*	6{*2,4,2*} (68%)
24	*2*	*4*		*3*	6{*2,4,3*} (75%)
25	*3*	*1*	4{*3,1*} (41%)[b]	*1*	6{*3,1,1*} (67%)
26	*3*	*1*		*2*	6{*3,1,2*} (77%)
27	*3*	*1*		*3*	6{*3,1,3*} (−)[c]
28	*3*	*2*	4{*3,2*} (26%)[b]	*1*	6{*3,2,1*} (85%)
29	*3*	*2*		*2*	6{*3,2,2*} (−)[c]
30	*3*	*2*		*3*	6{*3,2,3*} (−)[c]
31	*3*	*3*	4{*3,3*} (52%)[b]	*1*	6{*3,3,1*} (quant.)
32	*3*	*3*		*2*	6{*3,3,2*} (quant.)
33	*3*	*3*		*3*	6{*3,3,3*} (97%)
34	*3*	*4*	4{*3,4*} (19%)[b]	*1*	6{*3,4,1*} (quant.)
35	*3*	*4*		*2*	6{*3,4,2*} (75%)
36	*3*	*4*		*3*	6{*3,4,3*} (84%)

[a] One-pot, 2-step yield. [b] One-pot, 3-step yield. [c] Pure compounds were not obtained because of their poor solubility.

Thirty-two compounds in 36 trials were obtained in satisfactory to good yields, as shown in Table 1. The obtained compounds were purified by silica-gel column chromatography with subsequent gel-permeation chromatography (GPC) or recrystallization. The one-pot yields tended to decreased when **2**{*2*} or **2**{*4*} building blocks were employed. Four compounds, **6**{*1,2,3*}, **6**{*3,1,3*}, **6**{*3,2,2*}, and **6**{*3,2,3*} were not obtained as pure products due to their poor solubility. Residual palladium reportedly have detrimental effects for their PCEs.[39] Therefore, we measured the residual quantity of palladium in the prepared samples using inductively coupled plasma mass spectrometry (ICP-MS). We selected two compounds, **6**{*1,1,1*} and **6**{*2,1,1*}, that were purified by different methods, that is, either silica-gel column chromatography/recrystallization or silica-gel column chromatography/GPC. As a result, less than 1 ppb of the residual palladium was detected. Thus, our synthesis and purification procedure proved to be sufficient for providing the p-type organic semiconductors library.

The solubilities of 9 randomly selected, solid compounds against chlorobenzene were briefly measured (see Supporting Information for details), and are shown as solubility scores in Figure 3. The compounds with higher scores retained better solubility against chlorobenzene. The solubility parameter (SP) for each compound was calculated in accordance with the Fedors group substitution method,[40] SP = $(\Delta E_\text{v}/V)^{0.5}$, where ΔE_v is the energy of vaporization, and V is the molar volume. The SPs of the compounds were calculated by dividing the compound structures into different fragments, and the corresponding values of vaporization energy (Δe_i) and molar volumes (Δv_i) for each of the fragments were obtained from a previous report.[40] The calculated SPs were compared to the measured solubility scores. The compounds with SPs that were similar to that of chlorobenzene (SP = 10.4) were speculated to retain good solubility against chlorobenzene. The result shown in Figure 3 clearly shows that the measured solubility scores correlated well (R^2 = 0.83) with the calculated SPs. It was found

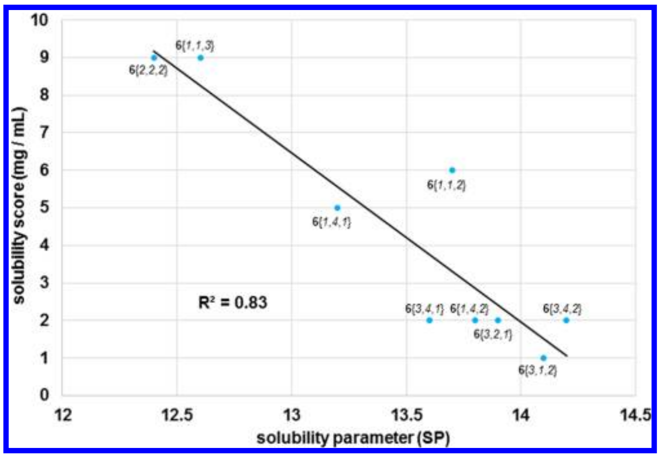


Figure 3. Correlations between measured solubility scores and calculated solubility parameters.

that the SP should be less than 13.5 for the preparation of a sufficient concentration of solutions for the active layers of solar cells.

Organic solar cells were prepared using 10 randomly selected compounds, which fulfilled the requirement of SPs (<13.5) in accordance with standard procedures,[41,42] but did not optimize the fabrication of solar cells. This was because the aim of this study was not to identify the best-performing p-type semiconductor, but rather to elucidate the structure−property relationships. The measured photovoltaic properties of prepared cells are shown along with photoabsorbance properties (film), HOMO and LUMO levels (film), and SPs in Table 2. The calculated LUMO levels of synthesized compounds were sufficiently higher than those of PCBMs (−4.3 eV), and, thus, an electron transfer from a p-type semiconductor to an n-type semiconductor would occur.

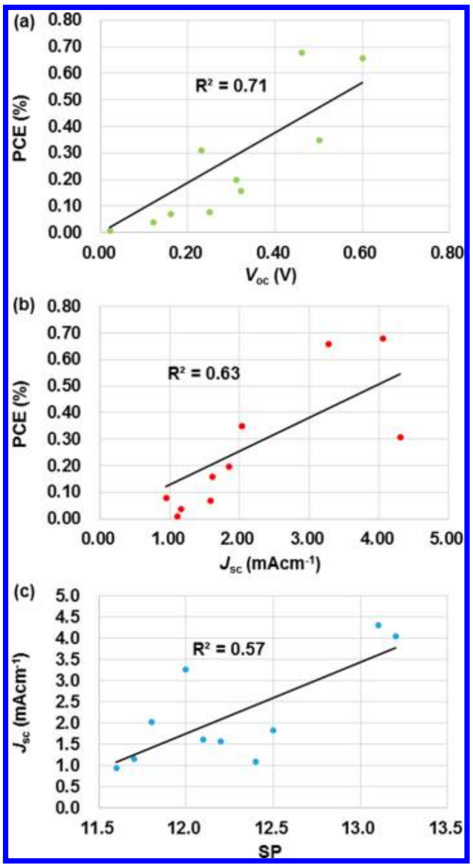


Figure 4. Correlations between (a) PCE vs V_{oc}, (b) PCE vs J_{sc}, and, (c) J_{sc} vs SP.

The correlations between all the shown parameters and PCE were examined (Figure 4). As a result, J_{sc} and V_{oc} correlated well ($R^2 > 0.6$) with PCE. It was noteworthy that the SPs had a fairly strong correlation with the J_{sc}, ($R^2 = 0.57$), and the compounds with higher SPs tended to exert a higher J_{sc}. These obtained results indicated that the compounds retaining an SP of around 13.5 should have a high J_{sc}. Actually, compounds **6**{*1,1,1*} (SP = 13.1), and **6**{*1,4,1*} (SP = 13.2), had SPs that approximated 13.5, and both of these exerted a high J_{sc} (4.30, 4.05 mAcm^{-2}, respectively). The compound **6**{*1,4,1*} exerted the highest PCE of 0.68%.

CONCLUSION

A total of 32 organic p-type semiconductors with D−π−A structures were rapidly synthesized via our originally developed, one-pot, SM coupling with subsequent Knoevenagel condensation. Measurement of the remaining palladium in the synthesized compounds using ICP-MS revealed that our synthesis and purification procedure was sufficient for the removal of palladium. An evaluation of the solubility and the photovoltaic properties of the prepared compounds was

Table 2. Photoabsorption and Photovoltaic Properties of 10 Randomly Selected Compounds (SPs < 13.5)

entry	compound	E_{HOMO}[a] [eV]	E_{LUMO}[b] [eV]	λ_{max}[c] [nm]	optical edge[c] [nm]	ε[c] [L mol^{-1} cm^{-1}]	SP	J_{sc} [mAc m^{-2}]	V_{oc} [V]	FF	PCE [%]
1	**6**{*1,1,1*}	−5.45	−3.40	518	605	36900	13.1	4.30	0.23	0.31	0.31
2	**6**{*1,4,1*}	−5.45	−3.46	545	624	47800	13.2	4.05	0.46	0.37	0.68
3	**6**{*2,1,1*}	−5.47	−3.53	545	639	35100	11.7	1.16	0.12	0.27	0.04
4	**6**{*2,1,2*}	−5.11	−3.05	507	601	30500	12.1	1.61	0.32	0.32	0.16
5	**6**{*2,2,1*}	−5.31	−3.38	548	644	36000	12.0	3.27	0.60	0.34	0.66
6	**6**{*2,2,2*}	−5.34	−3.27	510	599	38100	12.4	1.10	0.02	0.25	0.01
7	**6**{*2,3,2*}	−5.33	−3.24	504	592	34300	11.6	0.95	0.25	0.32	0.08
8	**6**{*2,4,1*}	−5.13	−3.24	570	655	47000	11.8	2.03	0.50	0.35	0.35
9	**6**{*2,4,2*}	−5.12	−3.10	531	614	45100	12.2	1.58	0.16	0.29	0.07
10	**6**{*3,3,1*}	−5.87	−3.94	528	644	26600	12.5	1.84	0.31	0.35	0.20

[a] HOMO levels of the compounds were measured using photoelectron spectroscopy in air (PESA) for thin solid films on glass. [b] The $E_{HOMO}-E_{LUMO}$ gap was determined by the edge of the absorption spectra, as defined by a wavelength where the absorbance revealed 1/10 at its peak top; that is, the $E_{HOMO}-E_{LUMO}$ gap [eV] was calculated by 1240 [nm]/optical edge [nm]. E_{LUMO} was thus calculated by the summation of the HOMO potential and the $E_{HOMO}-E_{LUMO}$ gap. [c] Absorption spectra of thin solid films spin-cast from chlorobenzene solutions.

performed. Among the evaluated photovoltaic properties of the solar cells, J_{sc} and V_{oc} correlated well with the photoconversion efficiency (PCE). The measured solubility had a strong correlation with the solubility parameter (SP), as reported by Fedors. In addition, the SP value had a fairly strong correlation with the J_{sc} of thin-film organic solar cells prepared using synthesized compounds. Our results indicated that a compound with an SP of approximately 13.5 should have a high J_{sc}. The obtained structure−property information should be useful for the development of more efficient p-type semiconductors for organic solar cells.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Analytical data (^{1}H, ^{13}C NMR, and absorption spectra) for the compounds and the details of the measurement of the solubility score and the remaining palladium are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +81-3-5734-2111. Fax: +81-3-5734-2884. E-mail: sfuse@apc.titech.ac.jp.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

dba, dibenzylideneacetone; Xantphos, 9,9-dimethyl-4,5-bis-(diphenylphosphino)xanthene; THF, tetrahydrofuran; Pin, pinacol; J_{sc}, short-circuit current; V_{oc}, open-circuit voltage; FF, fill factor

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