Photovoltaics

Rapid Synthesis of Thiophene-Based, Organic Dyes for Dye-Sensitized Solar Cells (DSSCs) by a One-Pot, Four-Component Coupling Approach

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Abstract: This one-pot, four-component coupling approach (Suzuki–Miyaura coupling/C–H direct arylation/Knoevenagel condensation) was developed for the rapid synthesis of thiophene-based organic dyes for dye-sensitized solar cells (DSSCs). Seven thiophene-based, organic dyes of various donor structures with/without the use of a 3,4-ethylenedioxythiophene (EDOT) moiety were successfully synthesized in good yields based on a readily available thiophene boronic acid pinacol ester scaffold (one-pot, 3-step, 35–61 %). Evaluation of the photovoltaic properties of the solar cells that were prepared using the synthesized dyes revealed that the introduction of an EDOT structure beside a cyanoacrylic acid moiety improved the short-circuit current (J_{sc}) while decreasing the fill factor (*FF*). The donor structure significantly influenced the open-circuit voltage (V_{oc}), the *FF*, and the power conversion efficiency (PCE). The use of a *n*-hexyloxyphenyl amine donor, and our originally developed, rigid, and non-planar donor, both promoted good cell performance ($\eta =$ 5.2–5.6 %).

Introduction

The one-pot, transition-metal-catalyzed, multicomponent coupling approach for oligoheteroaromatic compounds starting from readily available heteroaromatic scaffolds is a powerful method. With this approach, complex oligoheteroaromatic structures can be readily constructed from simple starting materials in one step under ambient reaction conditions without the necessity of purifying synthetic intermediates.[1]

Among the numerous examples of oligoheteroaromatic rings, oligothiophenes make up a particularly important class of compounds because they are valuable elements that are used in organic electronics for applications such as solar cells and field-effect transistors as well as for chemical probes in chemical biology.[2]

Several one-pot, palladium-catalyzed, multicomponent coupling approaches for the synthesis of oligothiophenes based on readily available thiophene scaffolds have been reported in the past decade (Scheme 1). The reported syntheses fall into one of the following three categories: 1) the regioselective coupling approach; 2) the site-selective coupling approach; and 3) the chemoselective coupling approach. In 2007, Handy and co-workers reported a regioselective, one-pot, Suzuki–Miyaura (SM) coupling[3] reaction based on dibromothiophene scaffold **A** (category 1).[4] The intrinsic difference in reactivity between C4–Br and C5–Br bonds against a palladium catalyst was used for C5-selective SM coupling. Dauban, Dodd, and co-workers reported a site-selective, one-pot, SM coupling reaction based on the readily available, symmetric dibromothiophene scaffold **B** in 2009 (category 2, upper scheme).[5] In addition, in 2011, Yamada and co-workers reported a site-selective, one-pot, SM coupling reaction based on a thiophene-2,5-diboronic acid scaffold (category 2, not shown).[6] The approach of category 2[7] allows the use of readily available symmetric scaffolds with two identical reaction sites, but the selective activation of the desired reaction site is generally somewhat difficult compared with that of category 1. There are fewer reports that are based on the chemoselective approach (category 3) compared with those of regio- and site-selective approaches (cate-

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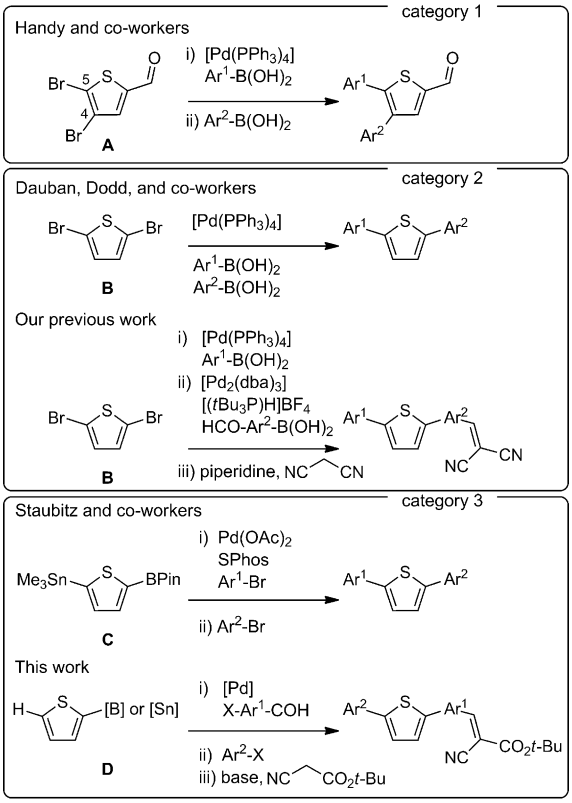


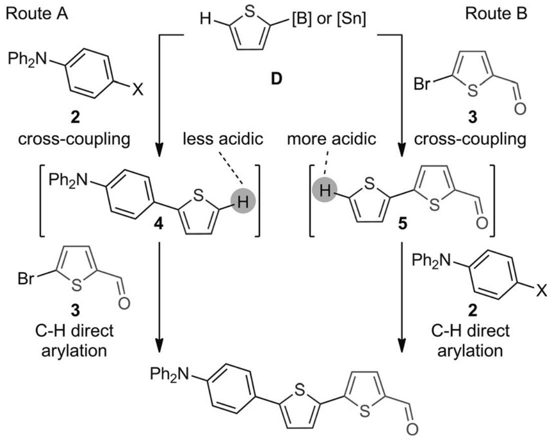
Scheme 1. One-pot, multi-component coupling approaches for the synthesis of oligo-thiophenes. dba = dibenzylideneacetone; Pin = pinacol; SPhos: 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl.

gories 1 and 2). As far as we could ascertain, only Staubitz and co-workers, in 2012, have reported a chemoselective, one-pot, Migita–Kosugi–Stille (MKS) coupling[8]/SM coupling approach based on the unique thiophene scaffold **C** (category 3).[9] Although several useful one-pot approaches have been reported, as described above, the development of high-yielding and mild one-pot approaches based on readily available thiophene scaffolds continues to be important.

We have reported combinatorial library synthesis for drug discovery and materials development using palladium-catalyzed cross-coupling reactions.[10] In addition, we rapidly synthesized thiophene-based organic compounds using a site-selective, one-pot, SM coupling/SM coupling/Knoevenagel condensation approach (category 2, lower scheme).[10i] However, undesired double SM coupling products were usually generated in the first SM coupling step. Based on these results, we decided to investigate either a chemoselective, one-pot, SM coupling or a MKS coupling, and the subsequent C–H direct arylation[11] approach (category 3) based on a scaffold **D**. We anticipated that the selectivity in the first coupling reaction (SM or MKS coupling) would be improved because C–H bonds should not be activated under the first coupling conditions. To further improve synthetic efficiency, we also developed a one-pot, four-component coupling approach for the rapid synthesis of thiophene-based donor-π-bridge-acceptor (D-π-A) dyes. In addition, the photochemical and electrochemical properties of synthesized dyes, as well as the photovoltaic properties of solar cells that were prepared using the synthesized dyes, were evaluated to elucidate the structure–property relationships.

Results and Discussion

For the development of a chemoselective, one-pot, multicomponent coupling procedure, the precursor of a simple and typical D-π-A compound **1**[10i,k,12] was selected as the target. We considered two synthetic routes, A and B, for the synthesis of **1** from the readily available thiophene scaffold **D** (Scheme 2).



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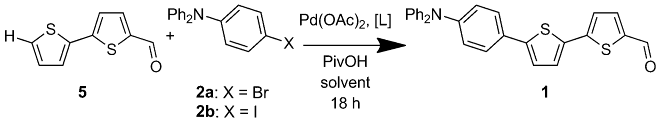
Scheme 2. Chemoselective, one-pot, three-component coupling approaches to the synthesis of **1**.

Both routes included two types (SM coupling or MKS coupling and C–H direct arylation) of coupling reactions. The order of the introduction of building blocks **2** and **3** was switched between routes A and B. Route B was investigated in the present study, because intermediate **5** retained more acidic (reactive) protons compared with the corresponding intermediate **4** in route A. This allowed the activation of the desired C–H bond under mild conditions. The key to success is how to conduct the second C–H direct arylation step in high yields in the presence of the remaining/generating compounds of the first coupling step. This was not simple because the Pd catalysts are generally somewhat susceptible to contaminants.

The key C–H direct arylation of **5** with **2** was examined in accordance with a procedure established by Fagnou,[13] as shown in Table 1. Three inorganic bases (K_3PO_4, K_2CO_3, and Cs_2CO_3) were examined (Table 1, entries 1–3). The use of Cs_2CO_3 afforded the best results. Solvent and temperature were critical for the C–H direct arylation (entries 3–6). The condition of entry 6 (1,4-dioxane/reflux) afforded the desired coupling product in the highest yield (74%), whereas the other conditions (THF/reflux, toluene/reflux, DMA/140 °C) all resulted in lower yields (entries 3, 4, and 5). The use of other phosphine ligands including PPh_3 and $[(Cy_3P)H]BF_4$ (entries 7 and 8), or the addition of 1 equivalent of water (entry 9) decreased the yield. Under microwave irradiation conditions, the reaction time was dramatically shortened (18 h to 45 min), although the yield was slightly decreased (entry 10). Interestingly, a proce-

Table 1. Examination of C–H direct arylation for the synthesis of **1**.



5 + **2a**: X = Br, **2b**: X = I → **1**

Entry	2	Ligand	Base	Solvent/T	Yield [%][a]
1	**2a**	[(tBu$_3$P)H]BF$_4$	K$_3$PO$_4$	THF/reflux	–
2	**2a**	[(tBu$_3$P)H]BF$_4$	K$_2$CO$_3$	THF/reflux	–[b]
3	**2a**	[(tBu$_3$P)H]BF$_4$	Cs$_2$CO$_3$	THF/reflux	32
4	**2a**	[(tBu$_3$P)H]BF$_4$	Cs$_2$CO$_3$	toluene/reflux	49
5	**2a**	[(tBu$_3$P)H]BF$_4$	Cs$_2$CO$_3$	DMA/140 °C	$<$12
6	**2a**	[(tBu$_3$P)H]BF$_4$	Cs$_2$CO$_3$	1,4-dioxane/reflux	74
7	**2a**	PPh$_3$	Cs$_2$CO$_3$	1,4-dioxane/reflux	–[c]
8	**2a**	[(Cy$_3$P)H]BF$_4$	Cs$_2$CO$_3$	1,4-dioxane/reflux	–[c]
9[d]	**2a**	[(tBu$_3$P)H]BF$_4$	Cs$_2$CO$_3$	1,4-dioxane/reflux	43
10	**2a**	[(tBu$_3$P)H]BF$_4$	Cs$_2$CO$_3$	1,4-dioxane/160 °C[e]	63
11[f]	**2b**	PPh$_3$	Ag$_2$CO$_3$	H$_2$O/MeCN = 9:1/80 °C	72

[a] Isolated yield. [b] The reaction was very slow. A large amount of substrates were recovered. [c] The complex mixtures were obtained. [d] 1 equiv of water was added. [e] The reaction was carried out under microwave irradiation (200 W) for 45 min. [f] [Pd(dppf)Cl$_2$]·CH$_2$Cl$_2$ was employed as a Pd catalyst instead of Pd(OAc)$_2$. PivOH was not added. DMA = N,N-dimethylacetamide; dppf = 1,1′-bis(diphenylphosphino)ferrocene; PivOH = pivalic acid.

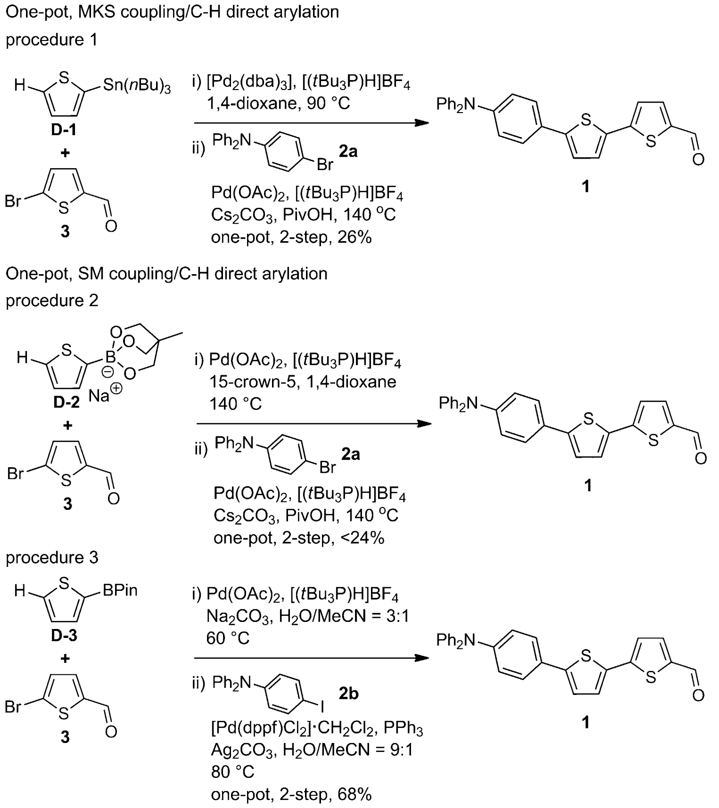
Table 2. Photochemical and electrochemical properties of dyes **16**–**22**.

Entry	Dye	λ_{max}[a] [nm]	ε[b] [L mol^{-1} cm^{-1}]	Optical edge [nm]	E_{HOMO} [V][c] (vs. NHE)	E_{LUMO} [V][c] (vs. NHE)
1	**16**	467[d]	29 000[d]	580[d]	1.32[d]	−0.81[d]
2	**17**	503[d]	29 000[d]	617[d]	1.28[d]	−0.73[d]
3	**18**	520	39 000	623	1.11	−0.88
4	**19**	514	26 000	599	1.30	−0.77
5	**20**	524	40 000	625	1.16	−0.82
6	**21**	528	21 000	630	1.14	−0.82
7	**22**	520	24 000	619	1.11	−0.89

[a] Absorption maxima in DMF. [b] Molar absorption coefficients in DMF. [c] E_{HOMO} was determined by the cyclic voltammetry. $E_{HOMO}-E_{LUMO}$ gap was determined by the edge of the absorption spectra, as defined by the wavelength where the absorbance revealed 1/10 of the 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 the HOMO potential and the $E_{HOMO}-E_{LUMO}$ gap. [d] Data from reference [10k].

dure established by Greaney[14] for the C–H direct arylation of 2H-indazoles was also effective for the synthesis of **1** (entry 11).

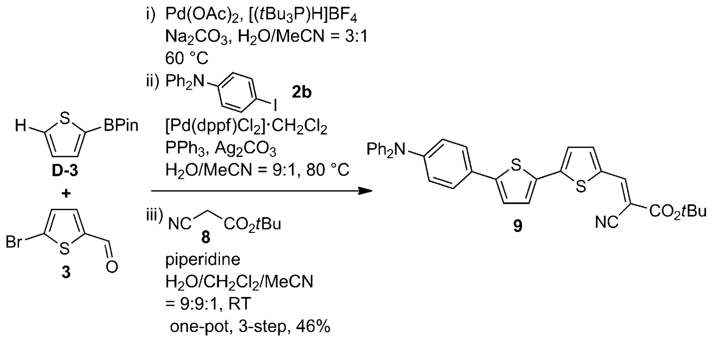
A one-pot, three-component coupling was examined as shown in Scheme 3. As described in the previous paragraph, the water had an adverse effect on our best C–H direct arylation conditions (Table 1, entry 6 vs. 9). Therefore, a MKS coupling/C–H direct arylation procedure was examined (Scheme 3, procedure 1), because MKS coupling required no water. However, the desired product **1** was obtained in an unsatisfactory yield (26 %). We also examined an SM coupling/C–H direct arylation procedure (Scheme 3, procedure 2). The SM coupling of the borate D-**2** with **3** also required no water. However, again, the yield of desired compound **1** was low ($<$24 %). These results turned our attention to employ Greaney's C–H direct arylation[14] using a H$_2$O/MeCN biphasic system (procedure 3). To our delight, procedure 3 afforded the desired compound in a good yield (one-pot, 2-step, 68 %). It should be noted that the developed one-pot procedure 3 could be carried out at ambient temperature.



Scheme 3. Examination of one-pot, three-component coupling reactions for the synthesis of **1**.

To further improve the synthetic efficiency, a one-pot, four-component coupling approach (SM coupling/C–H direct arylation/Knoevenagel condensation) was examined (Scheme 4). A solution of bromothiophene **3**, thienylboronic acid pinacol ester D-**3**, Pd(OAc)$_2$, [(tBu$_3$P)H]BF$_4$, and Na$_2$CO$_3$ in a mixed solvent of H$_2$O and MeCN (3:1) was stirred at 60 °C under an argon atmosphere. After the mixture had been cooled to room temperature, aryl iodide **2b**, [Pd(dppf)]Cl$_2$·CH$_2$Cl$_2$, PPh$_3$, Ag$_2$CO$_3$, and H$_2$O were added. After being stirred at 80 °C under an argon atmosphere, the mixture was cooled to room temperature, and $tert$-butyl cyanoacetate (**8**), piperidine, and CH$_2$Cl$_2$ were added. It should be noted that the use of $tert$-butyl ester improved the solubility of the product and enabled ready purification.[10k] After being stirred at room temperature under an argon atmosphere, the mixture was poured into saturated aq. NH$_4$Cl. The following standard workup procedure afforded the desired product **9** in a 46 % yield.

To examine the scope of our developed synthetic methodology, seven protected dyes, **9**–**15**, containing different donor moieties with/without an EDOT



Scheme 4. Examination of the one-pot, four-component coupling for the synthesis of **9**.

moiety[10h,15] were rapidly synthesized, as shown in Figure 1. All the dyes were obtained in satisfactory to good yields (for the synthetic details of the building blocks, see the Supporting Information). The subsequent removal of a *tert*-butyl group using trifluoroacetic acid (TFA) afforded the desired dyes **16**–**22** in high yields.

The absorption spectra and electrochemical properties of the seven dyes, **16**–**22**, were measured, as shown in Table 2. The 8–47 nm redshift of the absorption maxima for EDOT containing dyes **19**–**21** compared with those of dyes **16**–**18** without the EDOT was observed (Figure 2). This tendency was consistent with our previous observation.[10h] The HOMO and LUMO levels of the seven dyes met the minimum requirement for a dye-sensitizer in DSSCs, that is, E_{HOMO} and E_{LUMO} were located more positive than the iodine/iodide redox potential (+0.4 V vs. normal hydrogen electrode (NHE)) and more negative than the conduction band edge of TiO_2 (−0.5 V vs. NHE[16]).

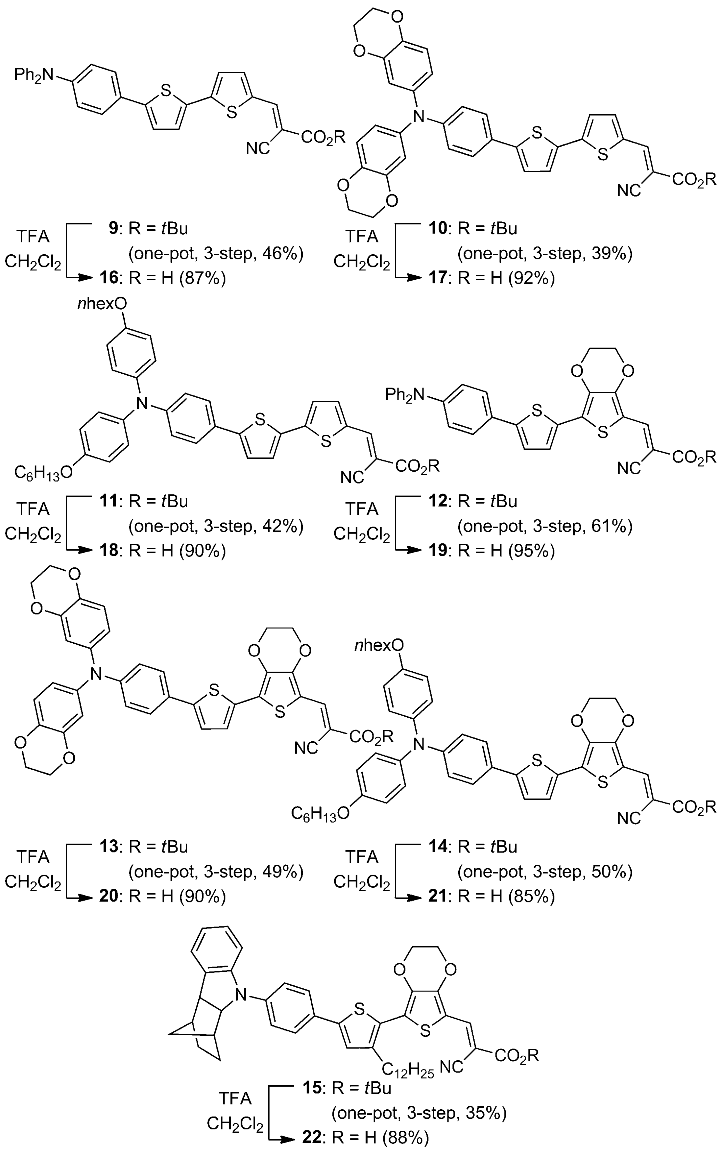


Figure 1. Synthesis of 7 thiophene-based organic dyes **16**–**22** by a one-pot, four-component coupling approach.

The photovoltaic properties were evaluated for solar cells that were prepared using the seven dyes, **16**–**22** (Table 3 and Figure 3). Dyes **19**–**21** had an EDOT moiety and exerted an equal or higher J_{sc} and IPCE compared with dyes **16**–**18** that were without the EDOT moiety (Table 3, entry 1 vs. 4, 2 vs. 5, and 3 vs. 6 and Figure 3c). This tendency was consistent with our previous observation.[10 h] However, interestingly, the best dye was not found from dyes **19**–**21** that contained the EDOT moiety (Table 3, entries 4–6). This was because the *FF* was decreased by introducing the EDOT moiety (Table 3, entry 1 vs. 4, 2 vs. 5, and 3 vs. 6).

The donor moiety in the dyes had a significant influence on the cell performance of the DSSCs. Dyes **17** and **20** had an ethylenedioxyphenyl amine donor and exerted the lowest values for PCE and V_{oc} (Table 3, entries 2 and 5). The observed low V_{oc} can be ascribed to a large dark current (Figure 3b). It should be noted that dyes **17** and **20** caused a larger dark current than dyes **16** and **19**, although dyes **17** and **20** had a sterically larger donor moiety than dyes **16** and **19**. Based on these results, the ethylenedioxyphenyl amine donor might have had a detrimental effect on the increase in the dark current. Dyes **16** and **19** had a triphenyl amine donor and exerted the highest V_{oc} (Table 3, entries 1 and 4). However, the observed cell performance was not the highest because of a low *FF*. On the other hand, dyes **18** and **21**, which contained a *n*-hexyloxyphenyl amine donor (Table 3, entries 3 and 6), and dye **22**, which contained our originally developed, rigid, and nonplanar donor (Table 3, entry 7), exerted a good PCE ($\geq$5.2%), V_{oc} ($\geq$0.68 V), and *FF* ($\geq$0.64).

Conclusion

We successfully developed a one-pot, four-component coupling approach (SM coupling/C–H direct arylation/Knoevenagel condensation) based on a readily available thiophene boronic acid pinacol ester scaffold. Seven dyes were successfully synthesized in

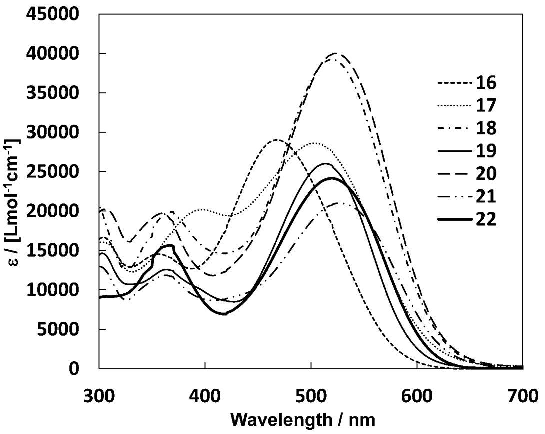


Figure 2. Absorption spectra of synthesized dyes **16**–**22** in CH_2Cl_2.

Table 3. Photovoltaic properties of solar cells prepared using dyes **16**–**22**.

Entry	Dye	η[a] [%]	FF[a]	V_{oc}[a] [V]	J_{sc}[a] [mAcm^{-1}]
1	**16**	5.0±0.5[b]	0.57±0.06[b]	0.71±0.01[c]	12.6±0.1[c]
2	**17**	1.7±0.1	0.67±0.01	0.57±0.01	4.4±0.2
3	**18**	5.6±0.3	0.68±0.01	0.70±0.01	11.7±0.4
4	**19**	4.9±0.1	0.53±0.01	0.72±0.01	12.9±0.1
5	**20**	4.3±0.2	0.57±0.04	0.63±0.00	11.9±0.4
6	**21**	5.2±0.3	0.64±0.03	0.68±0.01	12.0±0.3
7	**22**	5.2±0.0	0.69±0.01	0.70±0.00	10.7±0.1

[a] Average values from two or three independent experiments. FF = fill factor; V_{oc} = open-circuit voltage; J_{sc} = short-circuit current. [b] Data from ref. [10k].

good yields (one-pot, 3-step, 35–61%) under mild reaction conditions. Evaluation of photovoltaic properties of the solar cells that were prepared using the synthesized dyes revealed that the introduction of an EDOT structure beside a cyanoacrylic acid moiety improved the J_{sc}, but it decreased the FF. The donor structure significantly influenced the V_{oc}, the FF, and the PCE. An ethylenedioxyphenyl amine donor exerted low cell performance due to a large dark current. On the other hand, both an *n*-hexyloxyphenyl amine donor and our originally developed, rigid, and nonplanar donor resulted in good cell performance. The developed synthetic methodology and structure–property relationships would be a valuable aid for rapid materials development.

Experimental Section

Experimental details are given in the Supporting Information.

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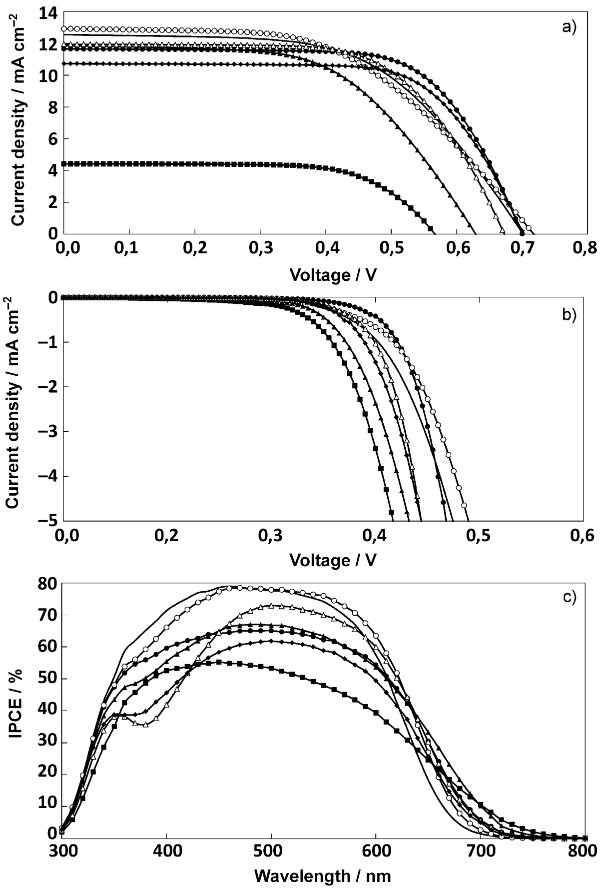

Figure 3. Photocurrent-voltage curves obtained with DSSCs based on **16**–**22** under standard AM 1.5 (1 sun) solar conditions (a) and in the dark (b). c) Incident photon-to-current conversion efficiency (IPCE) spectra for DSSCs based on **16**–**22**. ——: **16**, ■: **17**, ●: **18**, ○: **19**, ▲: **20**, △: **21**, ◆: **22**.

Keywords: C–H activation · cross-coupling · dyes/pigments · dye-sensitized solar cells · one-pot reactions

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