Tetrahedron xxx (2014) 1–6

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis of EDOT-containing organic dyes via one-pot, four-component Suzuki–Miyaura coupling and the evaluation of their photovoltaic properties

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ARTICLE INFO

Article history:
Received 30 July 2014
Received in revised form 12 September 2014
Accepted 12 September 2014
Available online xxx

Keywords:
Dyes
Suzuki–Miyaura coupling
One-pot
Dye-sensitized solar cell
Thiophene

ABSTRACT

We have developed a one-pot, four-component Suzuki–Miyaura coupling for the synthesis of thiophene-based donor–π-bridge–acceptor (D–π–A) dyes for dye-sensitized solar cells. Two D–π–A dyes, **19** and **20**, retaining 3,4-ethylenedioxythiophene (EDOT) beside a cyanoacrylic acid moiety, and one D–π–A dye **21** without EDOT (reference compound) were rapidly synthesized in accordance with the developed procedure. The measurement of the absorption spectra and the electrochemical properties of synthesized dyes, and the photovoltaic properties of solar cells that were prepared using the synthesized dyes **19**–**21**, revealed that the dyes retaining only one EDOT beside a cyanoacrylic acid moiety would exert a high J_{SC}.

1. Introduction

Oligo-thiophene compounds make up an important class of compounds because they can be used in organic electronics such as in dyes[1–21] for dye-sensitized solar cells (DSSC)[22–29] and in p-type semiconductors for thin-film organic solar cells.[30,31] In the past three decades, many sophisticated synthetic procedures have been developed and utilized for the construction of oligo-thiophene compounds. Nevertheless, the development of divergent, protection/deprotection-free, short synthetic routes remains important.

One-pot, multi-component coupling approaches are very useful methods for the rapid construction of large molecules from simple and small materials. The approaches should meet the following criteria: (1) the multiple components should be sequentially coupled without extra steps such as protection, deprotection, and introduction of activating groups; (2) the number of work-up and purification steps should be minimized; (3) each of the coupling steps should 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, one-pot, Suzuki–Miyaura (SM) coupling[32,33] is attractive.[34–48]

We have reported combinatorial library syntheses for drug and material development based on a palladium-catalyzed cross-coupling reaction.[49–58] Recently, we also reported one-pot, three-component SM coupling procedures for the synthesis of a thiophene-based organic dyes library for dye-sensitized solar cells,[56] p-type organic semiconductors, and bioactive compounds for the inhibition of amyloid-β and phospholilated tau protein aggregations.[58]

Herein, we wish to report a one-pot, four-component SM coupling approach for the synthesis of three thiophene-based organic dyes, and the evaluation of their photovoltaic properties.

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http://dx.doi.org/10.1016/j.tet.2014.09.039
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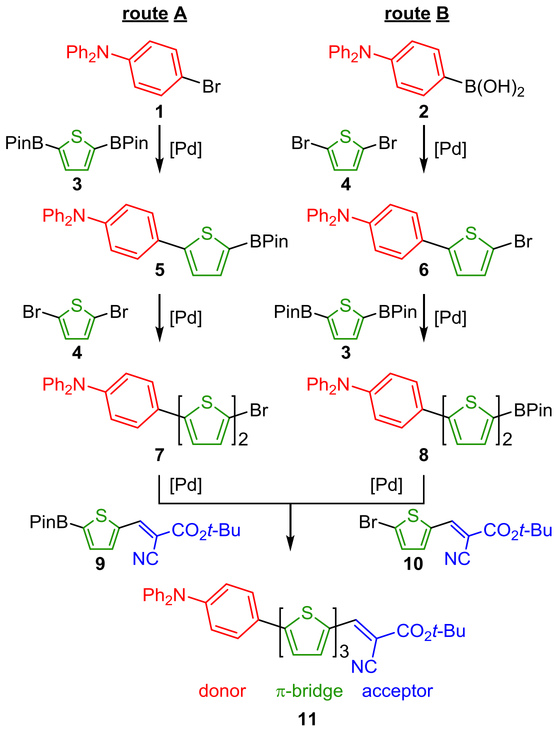
Please cite this article in press as: Fuse, S.; et al., Tetrahedron (2014), http://dx.doi.org/10.1016/j.tet.2014.09.039

2. Results and discussion

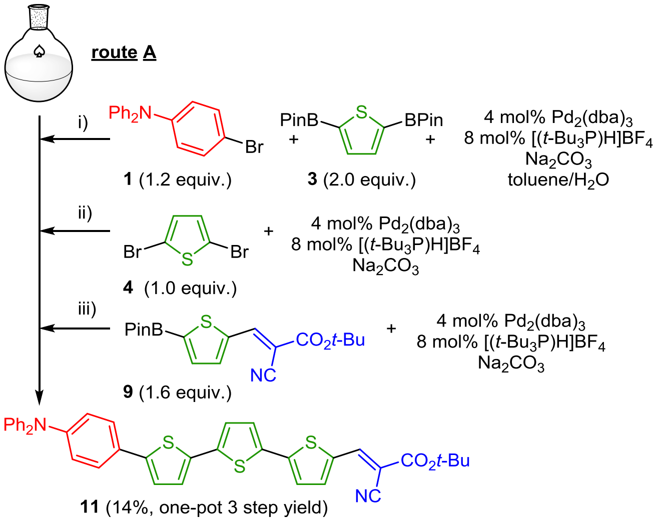
For the development of a one-pot, four-component coupling procedure, a simple and typical donor–π-bridge–acceptor (D–π–A) dye **11**[59–64] was selected as a target. We planned to examine two synthetic routes toward the synthesis of **11**, i.e., routes A and B (Scheme 1). Both routes included three sequential SM couplings for oligo-thiophene chain elongation from the donor side to the acceptor side in accordance with our recently developed, one-pot, three-component SM coupling procedure.[56,65] The combination of aryl bromides and aryl boronic acids or aryl boronic acid pinacol (Pin) esters was switched between routes A and B.



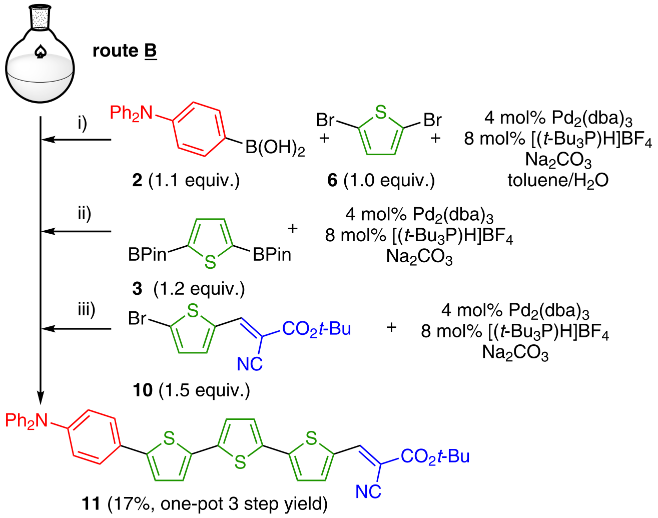
Scheme 1. One-pot, four-component coupling approach to the synthesis of thiophene-based organic dye **11**.

The one-pot, four-component coupling of **1**,[66] **3**, **4**, and **9**[56] in accordance with route A was investigated. Combinations of Pd catalysts [$Pd_2(dba)_3$,[67] and $Pd(OAc)_2$[68]], phosphine ligands {[(*t*-Bu_3P)H]BF_4,[69] Xphos,[70] and Sphos[70]}, temperature, and quantities of substrates were examined. As a result, the combination shown in Scheme 2 afforded the desired coupling product in a 14% yield (one-pot, three-step yield based on **4**).

Next, route B was investigated based on the optimized combination of a Pd catalyst and a phosphine ligand (Scheme 3). To a solution of 4-(diphenylamino)phenylboronic acid (**2**)[56] (1.1 equiv) and 2,5-dibromothiophene (**6**) (1.0 equiv) in toluene/H_2O (1:1) were added Na_2CO_3 (2.0 equiv), 4 mol % of $Pd_2(dba)_3$, and 8 mol % of [(*t*-Bu_3P)H]BF_4 at room temperature. After being stirred at 90 °C for 3 h, to the resultant solution were added 2,5-bis-thiopheneboronic acid pinacol ester (**8**) (1.2 equiv), Na_2CO_3 (2.0 equiv), 4 mol % of $Pd_2(dba)_3$, and 8 mol % of [(*t*-Bu_3P)H]BF_4. After being stirred at 60 °C for 3 h, to the resultant solution were added *tert*-butyl (*E*)-3-(5-bromothiophen-2-yl)-2-cyanoacrylate (**10**) (1.5 equiv), Na_2CO_3 (2.0 equiv), 4 mol % of $Pd_2(dba)_3$, and 8 mol % of [(*t*-Bu_3P)H]BF_4. After being stirred at 60 °C for 5 h, the toluene layer was simply removed from the reaction vessel using a pipette, and was purified by silica gel column chromatography and gel permeation chromatography (GPC) in order to afford the desired coupling product. The desired coupling product, **11**, was obtained in a slightly higher yield (17%, one-pot, three-step yield based on **6**) compared with route A.



Scheme 2. Examination of route A.



Scheme 3. Examination of route B.

Palomares, De Angelis and co-workers reported attractive D–π–A dyes retaining 3,4-ethylenedioxythiophene (EDOT) beside a cyanoacrylic acid moiety.[71] Inspired by this report, two EDOT-containing organic dyes, **19** and **20**, and the reference compound **21**[72–75] were selected as target dyes.

The necessary building blocks **13** and **15** were prepared as shown in Scheme 4. The building block **13** was prepared from a readily available aryl bromide **12**[10] via a lithiation/borylation sequence. The building block **15** was prepared from a commercially available aldehyde **14** via Knoevenagel condensation.

Protected oligo-thiophene dyes **16**–**18** were obtained in accordance with the developed procedure (route B) in one-pot as shown in Scheme 5, although the yields of the desired products were low. The following acidic removal of the *tert*-butyl group afforded the desired dyes **19**–**21** in good yields.

The absorption spectra and electrochemical properties of the three dyes were measured, as shown in Figs. 1 and 2, and Table 1. The absorption maxima of **20** and **21** in CH_2Cl_2 solution were 530 nm and 489 nm, respectively, as shown in Fig. 1 and Table 1. The 41 nm red-

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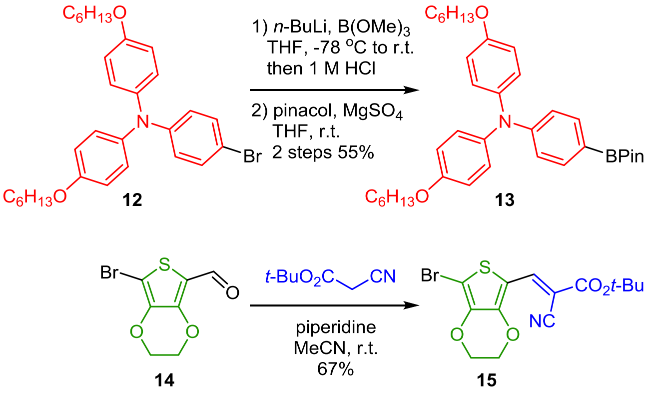
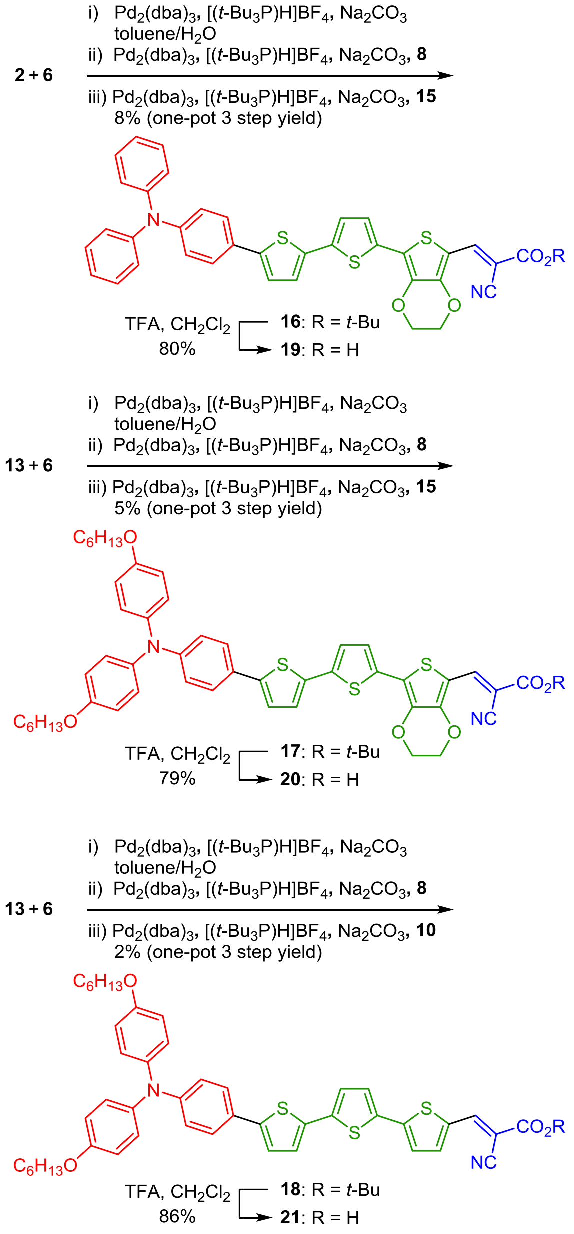


Scheme 4. Preparation of building blocks **13** and **15**.



Scheme 5. Synthesis of three thiophene-based organic dyes **19**–**21**.

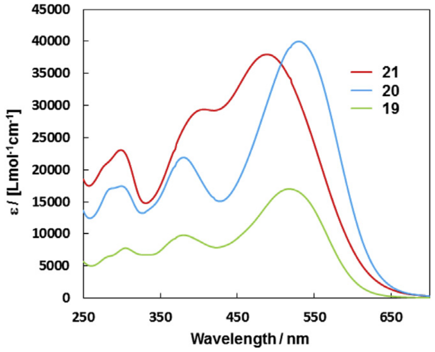


Fig. 1. Absorption spectra of synthesized dyes **19**–**21** in CH_2Cl_2.

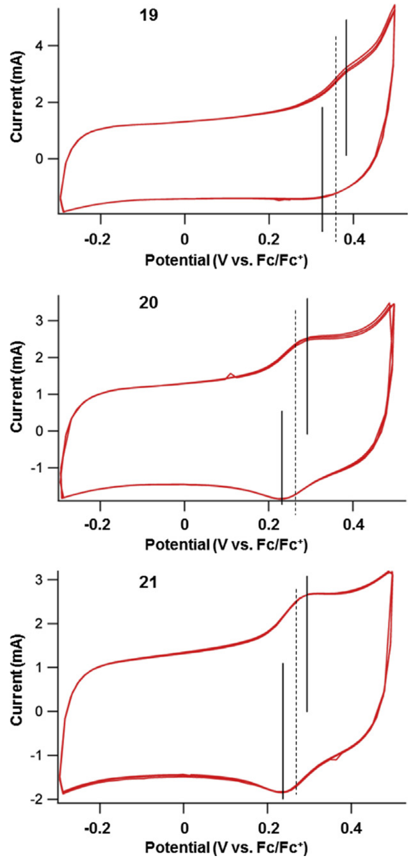


Fig. 2. Cyclic voltammograms of solutions (~0.3 mM) of synthesized dyes **19**–**21** with $LiClO_4$ (0.1 M) as a counter electrolyte in DMF equipped with Pt plate, Pt wire, and Ag/Ag^+ (0.01 M of $AgNO_3$ in DMF) as working, counter, and reference electrodes, respectively. Before and after each measurement, the Ag/Ag^+ reference electrode was calibrated independently by the redox potential of ferrocene (Fe(III)/Fe(II)) in DMF referred to as +0.853 [V] (vs NHE).[76] Since **20** and **21** revealed peak separation of approximately 60 mV between oxidation and reduction, the peak separation was also assumed as 60 mV for **19**, although the reduction peak was not clearly observed with **19**.

shift for **20** compared with that of **21** can be ascribed to the lower E_{LUMO} of the EDOT-containing dye **21**. The dyes **20** and **21**, which contained a hexyloxy chain on their donor moiety exerted higher molar absorption coefficients than dye **19**, which had no hexyloxy chain. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the three dyes met the minimum requirement for a dye-sensitizer in DSSCs: i.e., E_{HOMO} and E_{LUMO} 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[77]).

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Table 1
Photochemical and electrochemical properties of the dyes **19**–**21**, and photovoltaic properties of solar cells prepared using the three dyes

Dye	λ_{max}[a] [nm]	Optical absorption edge [nm]	ε[b] [L mol^{-1} cm^{-1}]	E_{HOMO}[c] [V] (vs NHE)	E_{LUMO}[c] [V] (vs NHE)	η[d] [%]	FF[d]	V_{oc}[d] [V]	J_{sc}[d] [mA cm^{-2}]
19	518	608	17,000	1.20	−0.83	3.6	0.57	0.58	11.0
20	530	632	40,000	1.12	−0.84	5.4	0.63	0.63	13.4
21	489	621	38,000	1.12	−0.88	2.6	0.61	0.57	7.6

[a] Absorption maxima in CH_2Cl_2.
[b] Molar absorption coefficients in CH_2Cl_2.
[c] E_{HOMO} was determined by the cyclic voltammetry (Fig. 2). E_{HOMO}−E_{LUMO} gap was determined by the edge of absorption spectra defined by the wavelength where the absorbance revealed 1/10 of the peak top; i.e., 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 E_{HOMO}−E_{LUMO} gap.
[d] Average values from three or four independent experiments. FF, fill factor; V_{oc}, open-circuit voltage; J_{sc}, short-circuit current.

Photovoltaic properties were evaluated for the solar cells that were prepared using the three dyes **19**–**21** (Table 1 and Fig. 3). The EDOT-containing dyes **19** and **20** exerted a higher J_{sc} than dye **21** without an EDOT moiety. Palomares, De Angelis and co-workers reported that the D–thiophene–EDOT–A dye exerted a higher J_{sc} than the D–EDOT–EDOT–A dye.[71] Quite recently, we reported that the D-EDOT-π-A dye exerted an adverse effect on J_{sc}, V_{oc}, and FF.[56] From these previous reports and our obtained results, it was indicated that the dyes that contained only one EDOT beside a cyanoacrylic acid moiety would exert a high J_{sc}.

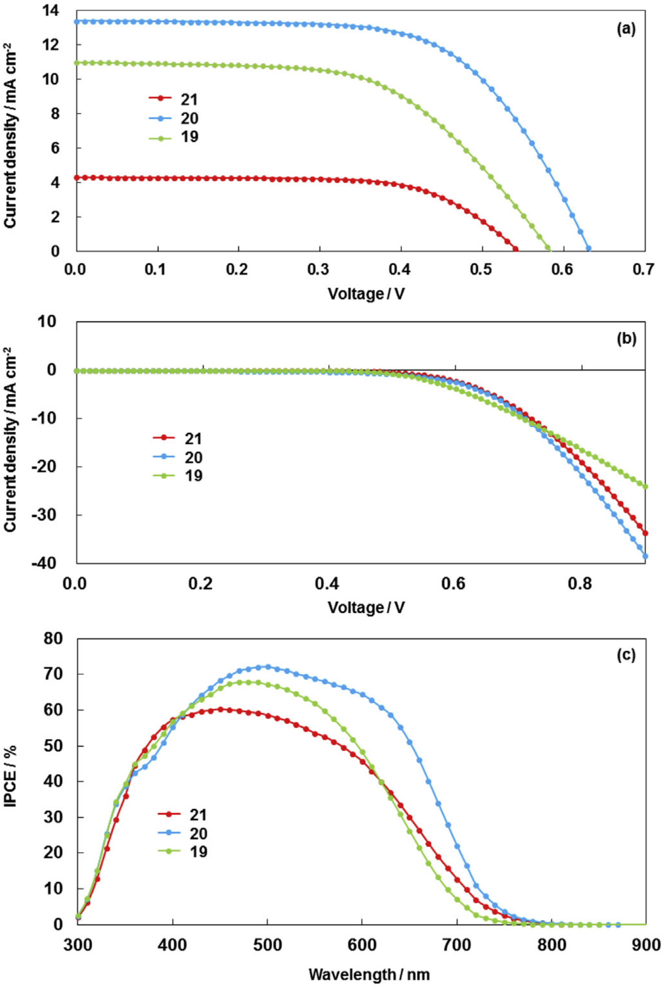

Fig. 3. Photocurrent–voltage curves obtained with DSSCs based on **19** (green line), **20** (blue line), and **21** (red line) under standard AM1.5 solar conditions (a) and in the dark (b). (c) Incident photon-to-current conversion efficiency (IPCE) spectra for DSSCs based on **19** (green line), **20** (blue line), and **21** (red line).

The hexyloxy group-containing dye **20** exerted a higher J_{sc}, V_{oc}, and FF than dye **19** without a hexyloxy group. The lower J_{sc} and V_{oc} of **19** can be ascribed to the low molar absorption coefficients and larger dark current of the dye (Table 1 and Fig. 3b). The best-performing dye **20** exerted high incident photon-to-current conversion efficiency (IPCE) in a somewhat wide region that ranged from 350 to 670 nm.

3. Conclusion

In summary, the framework of thiophene-based D–π–A organic dyes was rapidly assembled based on a one-pot, four-component SM coupling procedure. The measurement of the absorption spectra and electrochemical properties of synthesized dyes, and the photovoltaic properties of solar cells that were prepared using the synthesized dyes revealed that the dyes, which contain only one EDOT beside a cyanoacrylic acid moiety would exert a high J_{sc}.

4. Experimental section

4.1. General

NMR spectra were recorded on a JEOL Model EX-270 (270 MHz for ^{1}H, 67.8 MHz for ^{13}C) or a JEOL Model ECP-400 (400 MHz for ^{1}H, 100 MHz for ^{13}C) instrument in the indicated solvent. Chemical shifts are reported in units of parts per million (ppm) relative to the signal for internal tetramethylsilane (0 ppm for ^{1}H) for solutions in $CDCl_3$. NMR spectral data are reported as follows: chloroform (7.26 ppm for ^{1}H), DMSO-d_6 (2.50 ppm) or chloroform-d (77.1 ppm for ^{13}C), DMSO-d_6 (49.8 ppm). Multiplicities are reported by using the following abbreviations: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; tt, triplet of triplets; m, multiplet; br, broad; and, *J*, coupling constants in hertz (Hz). IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrophotometer. Only the strongest and/or structurally important absorption is reported as the IR data in cm^{-1}. All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254) with UV light, visualized by *p*-anisaldehyde solution, ceric sulfate or 10% ethanolic phosphomolybdic acid. Merck silica gel 60N (0.063–0.200 mm) was used for column chromatography. ESI-TOF mass spectra were measured with Waters LCT Premier™ XE. HRMS (ESI-TOF) were calibrated with leucine enkephalin (SIGMA) as an internal standard.

4.2. General procedure for one-pot, four-component SM coupling

To a solution of donor block **2** or **13** (1.1 equiv) and π-bridge block **6** (1.0 equiv) in toluene/H_2O (1:1) were added Na_2CO_3 (2.0 equiv), 4 mol % $Pd_2(dba)_3$, and 8 mol % $[(t\text{-}Bu_3P)H]BF_4$ at room temperature. After being stirred at 90 °C for 3 h, to the resultant solution were added π-bridge block **3** (1.2 equiv), Na_2CO_3 (2.0 equiv), 4 mol % $Pd_2(dba)_3$, and 8 mol % $[(t\text{-}Bu_3P)H]BF_4$. After being

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stirred at 60 °C for 3 h, to the resultant solution were added acceptor block **10**[56] or **15** (1.5 equiv), Na_2CO_3 (2.0 equiv),s 4 mol % of $Pd_2(dba)_3$, and 8 mol % of $[(t\text{-}Bu_3P)H]BF_4$. After being stirred at 60 °C for 5 h, the toluene layer was simply removed from the reaction vessel using pipette, and was purified by silica gel column chromatography (elution solvent: toluene) in order to remove polar undesired compounds and GPC to afford the desired coupling products **16**–**18**.

*4.2.1. Synthesis of **16**.* The dye **16** was prepared as a black solid from **2**, **6**, **8**, and **15**. Yield 8%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.45 (d, J=8.7 Hz, 2H), 7.38 (d, J=3.9 Hz, 1H), 7.27 (dd, J=8.2, 7.7 Hz, 4H), 7.17 (d, J=3.9 Hz, 1H), 7.15–7.11 (m, 6H), 7.07–7.03 (m, 4H), 4.42 (s, 4H), 1.56 (s, 9H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 162.4, 148.0, 147.5, 147.3, 144.0, 140.3, 139.6, 136.7, 135.0, 131.5, 129.3, 127.6, 127.1, 126.4, 125.2, 124.6, 123.7, 123.3, 123.2, 123.0, 117.1, 109.8, 94.9, 82.6, 65.4, 64.8, 28.0; FTIR (solid) 2927, 2212, 1706, 1582, 1487, 1450, 1251, 1155, 1075, 756, 697 cm^{-1}; HRMS (ESI-TOF); $[M+H]^+$ calcd for $C_{40}H_{33}N_2O_4S_3$, 701.1602; found 701.1608.

*4.2.2. Synthesis of **17**.* The dye **17** was prepared as a black solid from **6**, **8**, **13**, and **15**. Yield 5%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.39–7.36 (m, 3H), 7.15 (d, J=3.9 Hz, 1H), 7.12 (d, J=3.9 Hz, 1H), 7.09 (d, J=3.9 Hz, 1H), 7.06 (d, J=8.7 Hz, 4H), 6.90 (d, J=8.7 Hz, 2H), 6.83 (d, J=8.7 Hz, 4H), 4.41 (s, 4H), 3.93 (t, J=6.8 Hz, 4H), 1.81–1.74 (m, 4H), 1.56 (s, 9H), 1.49–1.43 (m, 4H), 1.36–1.34 (m, 8H), 0.91 (t, J=6.8 Hz, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 162.5, 155.7, 148.6, 148.0, 144.6, 140.3, 140.2, 139.9, 136.6, 134.4, 131.3, 127.1, 126.8, 126.2, 125.5, 125.2, 123.5, 123.1, 122.4, 120.1, 117.1, 115.3, 109.7, 94.9, 82.7, 68.2, 65.4, 64.8, 31.6, 29.3, 28.1, 25.7, 22.6, 14.0; FTIR (solid) 2930, 2211, 1708, 1580, 1558, 1507, 1450, 1239, 1156, 1075, 828 cm^{-1}; HRMS (ESI-TOF); $[M+H]^+$ calcd for $C_{52}H_{57}N_2O_6S_3$, 901.3379; found 901.3367.

*4.2.3. Synthesis of **18**.* The dye **18** was prepared as a black solid from **6**, **8**, **10**, and **13**. Yield 2%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.63 (d, J=3.9 Hz, 1H), 7.39 (d, J=8.7 Hz, 2H), 7.31 (d, J=3.9 Hz, 1H), 7.21 (d, J=3.9 Hz, 1H), 7.16 (d, J=3.9 Hz, 1H), 7.12–7.10 (m, 2H), 7.06 (d, J=8.7 Hz, 4H), 6.91 (d, J=8.7 Hz, 2H), 6.83 (d, J=8.7 Hz, 4H), 3.94 (t, J=6.8 Hz, 4H), 1.80–1.74 (m, 4H), 1.57 (s, 9H), 1.48–1.45 (m, 4H), 1.36–1.34 (m, 8H), 0.91 (t, J=6.8 Hz, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 161.9, 155.9, 149.1, 147.5, 147.0, 145.3, 140.1, 138.7, 133.8, 133.3, 127.5, 126.9, 126.4, 124.9, 123.7, 122.7, 119.8, 116.4, 115.4, 98.9, 83.3, 68.3, 31.6, 29.3, 28.0, 25.7, 22.6, 14.0; FTIR (solid) 2931, 2217, 1713, 1585, 1505, 1438, 1283, 1153, 758 cm^{-1}.

4.3. General procedure for removal of *tert*-butyl group

A solution of *tert*-butyl ester **16**, **17**, or **18** was treated with CH_2Cl_2/TFA (4:1) at room temperature under Ar. After being stirred at the same temperature for 1–24 h (monitored by TLC), the mixture was filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel, eluting with 0.01% AcOH and 10% MeOH in CH_2Cl_2 to afford carboxylic acid **19**, **20**, or **21**.

*4.3.1. Synthesis of **19**.* The dye **19** was prepared as a black solid from **16**. Yield 80%; mp 238–240 °C;^{1}H NMR (400 MHz, DMSO-d_6) δ 8.16 (s, 1H), 7.56 (d, J=8.7 Hz, 2H), 7.46 (d, J=3.9 Hz, 1H), 7.42 (d, J=3.9 Hz, 1H), 7.39 (d, J=3.9 Hz, 1H), 7.36 (d, J=3.9 Hz, 1H), 7.32 (dd, J=7.7, 7.2 Hz, 4H), 7.10–7.04 (m, 6H), 6.95 (d, J=8.7 Hz, 2H), 4.51 (s, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.9, 149.0, 147.1, 146.7, 143.2, 139.7, 138.5, 137.4, 133.8, 130.7, 129.6, 127.6, 126.8, 126.4, 126.2, 124.6, 124.4, 124.0, 123.6, 122.7, 120.9, 117.0, 108.1, 93.6, 65.8, 65.2; FTIR (solid) 2946, 2214, 1682, 1535, 1480, 1445, 1174, 1037, 851, 772 cm^{-1}; HRMS (ESI-TOF): $[M+H]^+$ calcd for $C_{36}H_{25}N_2O_4S_3$, 645.0976; found 645.0963.

*4.3.2. Synthesis of **20**.* The dye **20** was prepared as a black solid from **17**. Yield 73%; mp 217–219 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.16 (s, 1H), 7.48–7.45 (m, 3H), 7.40 (d, J=3.9 Hz, 1H), 7.35 (d, J=3.9 Hz, 1H), 7.32 (d, J=3.9 Hz, 1H), 7.03 (d, J=8.7 Hz, 4H), 6.90 (d, J=8.7 Hz, 4H), 6.74 (d, J=8.7 Hz, 2H), 4.51 (s, 4H), 3.92 (t, J=6.8 Hz, 4H), 1.72–1.65 (m, 4H), 1.44–1.36 (m, 4H), 1.32–1.28 (m, 8H), 0.87 (t, J=6.8 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.0, 155.4, 148.8, 148.2, 143.7, 139.6, 139.4, 138.7, 137.2, 133.2, 130.5, 127.4, 126.9, 126.1, 124.5, 124.2, 123.1, 121.0, 118.9, 117.1, 115.4, 108.2, 93.6, 79.1, 67.6, 65.8, 65.1, 31.0, 28.7, 25.2, 22.0, 13.9; FTIR (solid) 2930, 2214, 1681, 1535, 1506, 1421, 1220, 1071, 827, 772 cm^{-1}; HRMS (ESI-TOF): $[M+H]^+$ calcd for $C_{48}H_{49}N_2O_6S_3$, 845.2753; found 845.2756.

*4.3.3. Synthesis of **21**.* The dye **21** was prepared as a black solid from **18**. Yield 86%; mp 149–151 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.43 (s, 1H), 7.93 (d, J=3.9 Hz, 1H), 7.55 (d, J=3.9 Hz, 2H), 7.45 (d, J=8.7 Hz, 2H), 7.38 (d, J=3.9 Hz, 1H), 7.33 (d, J=3.9 Hz, 1H), 7.30 (d, J=3.9 Hz, 1H), 7.01 (d, J=8.7 Hz, 4H), 6.89 (d, J=8.7 Hz, 4H), 6.73 (d, J=8.7 Hz, 2H), 3.91 (t, J=6.8 Hz, 4H), 1.70–1.64 (m, 4H), 1.42–1.37 (m, 4H), 1.39–1.27 (m, 8H), 0.86 (t, J=6.8 Hz, 6H); FTIR (solid) 2930, 2216, 1683, 1599, 1220, 1050, 826, 772 cm^{-1}. The observed spectral data were in good accordance with those of the previously reported.[72,74]

4.4. Fabrication of DSSCs

A photoanode of dye-sensitized solar cell (DSSCs) was fabricated using Ti-Nanoxide D/SP paste (Solaronix, SA) on Fluorene doped Tin-oxide (FTO) transparent conducting oxide glass (Nippon Sheet Glass Co. Ltd.) by employing the doctor blade technique. After drying at room temperature, the substrate was then baked at 500 °C for 30 min to fabricate a 12 μm thick, mesoporous TiO_2 layer. An FTO-coated TiO_2 substrate was then dipped into a 0.2 mM dye solution containing 5 mM of chenodeoxycholic acid in CH_2Cl_2 (DCM) solution for 12 h at room temperature. After the dye absorption, this photoanode was then rinsed three times with CH_2Cl_2 at room temperature to remove un-adsorbed dyes on the substrate. A Pt-sputtered (Shibaura Mechatronics, CFS-4EP-LL) FTO-coated glass was employed as the counter electrode. A 25 μm-thick Himilan film (Mitsui-DuPont Polychemical Co. Ltd.) was used as spacer and sealant. Finally the fabrication of the DSSCs was completed by injecting an electrolyte solution consisting of LiI (500 mM), iodine (50 mM), 4-*tert*-butylpyridine (580 mM), and ethyl-methyl-imidazolium dicyanoimide (600 mM) in MeCN. The cell area was 0.25 cm^2 and was precisely defined by a black metal mask.

4.5. DSSC characterization

Photovoltaic measurement of the fabricated DSSCs was conducted using a solar simulator (Yamashita Densho YSS-50A) equipped with a Xenon lamp for light exposure and a source-measurement unit (Keithley, model 2400). The spectrum of the solar simulator and its power were adjusted to 100 mW/cm^2 at AM 1.5 using a spectro-radiometer (LS-100, Eiko Seiki). Current–voltage characteristics were measured after the simulated solar irradiation to estimate the photovoltaic parameters such as short-circuit current density (J_{sc} in mA/cm^2), open-circuit voltage (V_{oc}), and the fill factor in order to estimate the photoconversion efficiency (η) of the relationship.

$$\eta(\%) = Jsc\left(\mathrm{mA/cm^2}\right) \times V_{oc}(V) \times \mathrm{FF}$$

Please cite this article in press as: Fuse, S.; et al., Tetrahedron (2014), http://dx.doi.org/10.1016/j.tet.2014.09.039

Incident photon-to-current conversion efficiency (IPCE) was measured by using CEP-2000 (Bunko Keiki) equipped with 300 W Xe lamp. Monochromatic light was exposed by DC mode and the current was taken every 100 ms after the light exposure (10 nm interval). The monochromatic photon flux density was adjusted to 1×10^{16}, which was monitored by Si photodiode. IPCE was calculated by the following equation. IPCE=N_e/N_p where N_e and N_p stand for exposure light dose and photocurrent, respectively.

Supplementary data

Procedures for the preparation of building blocks **10**, **13** and **15**, ^{1}H and ^{13}C NMR spectra are provided. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.09.039. These data include MOL files and InChiKeys of the most important compounds described in this article.

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Please cite this article in press as: Fuse, S.; et al., Tetrahedron (2014), http://dx.doi.org/10.1016/j.tet.2014.09.039