

Short Note

4,4-Bis(2-ethylhexyl)-6-(9-(2-ethylhexyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazol-6-yl)-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde

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Abstract: Dyes with a donor– π –spacer–acceptor (D– π –A) structure containing a dicyanovinyl group as an acceptor have recently been of interest for the production of single-component organic solar cells. The most convenient precursors for their synthesis are the corresponding aldehydes. In this communication, 4,4-bis(2-ethylhexyl)-6-(9-(2-ethylhexyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazol-6-yl)-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde was synthesized by the Suzuki cross-coupling reaction between 4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2,6-dicarbaldehyde and 9-(2-ethylhexyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3,4,4a,9,9a-hexahydro-1H-carbazole in the presence of tetrakis(triphenylphosphine)palladium(0). The structure of the newly synthesized compound was established by means of high-resolution mass spectrometry, ¹H, ¹³C NMR, IR, and UV spectroscopy.

Keywords: small molecules for solar cells; building block for solar cells components; Suzuki cross-coupling reaction; 4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene; 2,3,4,4a,9,9a-hexahydro-1H-carbazole



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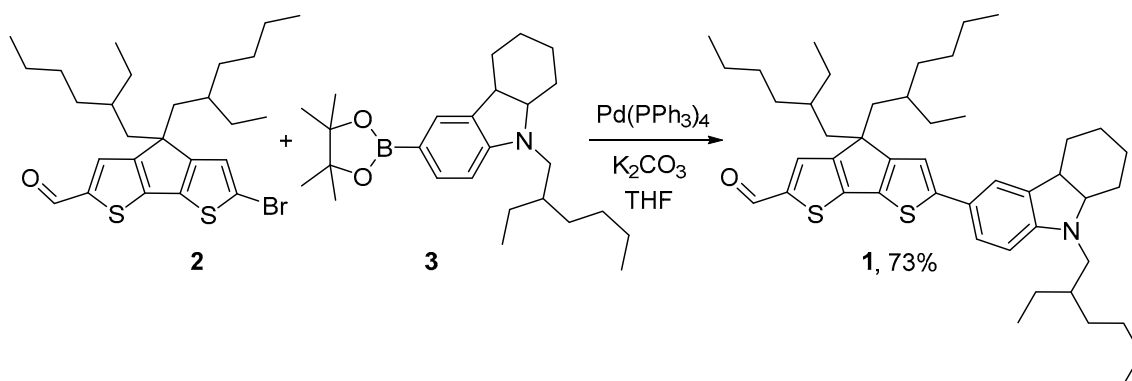
1. Introduction

Organic solar cells (OSCs) have received unrelenting interest over the past 50 years [1]. The development of various solar cell components, such as narrow-gap π -conjugated polymers [2,3], molecular donors [4,5], non-fullerene acceptors [6,7], has made it possible to increase power conversion efficiency (PCE) in donor–acceptor bulk heterojunction OSCs (BHJ) from 1% to 20% over the past two decades [8]. However, the industrial development of OSCs is constrained by issues of cost, synthesis scalability, and stability of organic dyes [1,9,10]. To solve the problem of reducing the cost of OSC production, the efforts of chemists in recent years have been focused on simplifying the structure of active materials and devices, including single-component organic solar cells (SMOSCs) [11,12]. As a rule, such simple molecules have a donor– π –spacer–acceptor (D– π –A) structure, where the dicyanovinyl group acts as an acceptor [11–14]. The main method for introducing this group is the Knoevenagel reaction of malononitrile with the corresponding aldehydes. Therefore, the synthesis of the aldehyde precursor is the most important step in this short reaction scheme. Herein, we report the synthesis of 4,4-bis(2-ethylhexyl)-6-(9-(2-ethylhexyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazol-6-yl)-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde **1** as a key precursor for the preparation of the organic solar cells component.

2. Results and Discussion

π -Spacers containing a thiophene ring have demonstrated their perfect suitability in organic dyes for DSSCs [15]. Among them, one of the most striking examples is the

4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene fragment, the use of which in organic solar cells leads to the highest PCE values [16]. On the other hand, among the donor building blocks, one of the most interesting is 2,3,4,4a,9,9a-hexahydro-1*H*-carbazole, the introduction of which into the dye molecule also gives an increase in the photovoltaic efficiency [17,18]. We hypothesized that the combination of these two building blocks in a sensitizer molecule could lead to interesting results. It was found that Suzuki cross-coupling reaction between 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2,6-dicarbaldehyde **2** [19] and 9-(2-ethylhexyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazole **3** [17] upon prolonged reflux in anhydrous THF and catalysis with tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄) led to 4,4-bis(2-ethylhexyl)-6-(9-(2-ethylhexyl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazol-6-yl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde **1** in a high yield (Scheme 1).



Scheme 1. Synthesis of 4,4-bis(2-ethylhexyl)-6-(9-(2-ethylhexyl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazol-6-yl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde **1**.

We have measured the optical absorption spectra of compound **1** in dichloromethane and hexane solutions. It was found that, regardless of the polarity of the solvent used, two broad absorption bands were observed in the absorption spectra, one of which, located in the short-wavelength region at 250–310 nm, refers to π – π^* transitions of the conjugated system, and the long-wavelength band in the range 400–520 nm due to the presence of intramolecular charge transfer (ICT) [20,21]. As expected, the ICT absorption maximum depended on the polarity of the solvent used: in *n*-hexane solution, it had a red shift relative to this value recorded in a dichloromethane solution (460 nm for CH₂Cl₂ and 430 nm for hexane), which indicates the presence of a solvatochromic effect.

The structure of 4,4-bis(2-ethylhexyl)-6-(9-(2-ethylhexyl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazol-6-yl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde **1** was confirmed by means of high-resolution mass-spectrometry, ¹H, ¹³C NMR, IR, and UV spectroscopy.

3. Materials and Methods

4,4-Bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2,6-dicarbaldehyde **2** [19] and 9-(2-ethylhexyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3,4,4a,9,9a-hexahydro-1*H*-carbazole **3** [17] were prepared according to the published methods. The solvents and reagents were purchased from commercial sources and used as received. Melting point was determined on a Kofler hot-stage apparatus and is uncorrected. ¹H and ¹³C NMR spectra were taken with a Bruker AM-300 machine (Bruker AXS Handheld Inc., Kennewick, WA, USA) (at frequencies of 300 and 75 MHz) in CDCl₃ solution, with TMS as the standard. *J* values are given in Hz. IR spectrum was measured with a Bruker “Alpha-T” instrument in a KBr pellet. High-resolution MS spectrum was measured on a Bruker micrOTOF II instrument (Bruker Daltonik GmbH, Bremen, Germany) using electrospray ionization (ESI). Solution UV-visible absorption spectra were recorded using a OKB Spektr SF-2000 UV/Vis/NIR spectrophotometer controlled with SF-2000 software. The sample was mea-

sured in the standard 10 mm photometric quartz cells in HPLC grade CH_2Cl_2 and C_6H_{14} in a concentration of 5×10^{-6} M.

Synthesis of 4,4-bis(2-ethylhexyl)-6-(9-(2-ethylhexyl)-2,3,4,4a,9,9a-hexahydro-1H-carbazol-6-yl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde **1** (Supplementary Materials).

Aldehyde **2** (390 mg, 0.76 mmol) and boronic ester **3** (377 mg, 0.92 mmol) were dissolved in anhydrous THF (20 mL), and 2 M K_2CO_3 (10 mL) was added. The mixture was degassed for 20 min with a stream of argon, and $\text{Pd}(\text{PPh}_3)_4$ (50 mg, 40 μmol , 5%) was added in one portion. After refluxing for 10 h in inert atmosphere, the mixture was poured into water (50 mL) and extracted with EtOAc (3×20 mL). The combined organic layers were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (Silica gel Merck 60, eluent ethyl acetate /hexane, 1:25, v/v). Yield 400 mg (73%), orange oil, $R_f = 0.6$ (hexane/ethyl acetate, 10:1, v/v). IR spectrum, ν , cm^{-1} : 2957, 2927, 2855, 1654, 1612, 1481, 1385, 1315, 1224, 1138. ^1H NMR (ppm): δ 9.72 (s, 1H), 7.45 (s 1H), 7.29–7.23 (m, 1H), 7.18 (s, 1H), 6.95 (s, 1H), 6.35 (d, $J = 8.1$, 1H), 3.48 (m, 1H), 3.07 (m, 1H), 2.94–2.75 (m, 2H), 1.92–1.81 (m, 4H), 1.77–1.68 (m, 2H), 1.66–1.58 (m, 2H), 1.53–1.44 (m, 2H), 1.43–1.34 (m, 3H), 1.27 (s, 8H), 0.98–0.80 (m, 22H), 0.72–0.62 (m, 8H), 0.52–0.57 (m, 6H). ^{13}C NMR (ppm): δ 182.1, 163.4, 156.4, 152.9, 151.6, 149.2, 141.9, 134.2, 132.6, 130.6, 125.4, 123.6, 120.3, 116.0, 106.6, 64.9, 64.6, 53.9, 50.3, 49.9, 43.2, 40.4, 38.9, 38.7, 35.3, 34.2, 34.1, 31.4, 31.1, 29.1, 28.9, 28.6, 27.5, 27.3, 27.1, 25.4, 25.3, 24.7, 24.3, 23.2, 22.8, 21.6, 14.0, 11.1, 10.8, 10.6. HRMS (ESI-TOF), m/z : calcd for $\text{C}_{46}\text{H}_{67}\text{OS}_2\text{N}$ $[\text{M}]^+$, 713.4659, found, 713.4669. UV-Vis spectrum, λ_{max} : 460 nm ($\epsilon = 29,160 \text{ M}^{-1} \text{ cm}^{-1}$, CH_2Cl_2), 430 nm ($\epsilon = 29,020 \text{ M}^{-1} \text{ cm}^{-1}$, C_6H_{14}).

Supplementary Materials: The following are available online: copies of ^1H , ^{13}C NMR, IR, UV/Vis, and HRMS-spectra for the compound **1**.

Author Contributions: Conceptualization, E.A.K.; methodology, O.A.R.; software, E.A.K.; validation, O.A.R.; formal analysis, investigation, M.S.M. and O.O.U.; resources, O.A.R.; data curation, M.S.M.; writing—original draft preparation, M.S.M.; writing—review and editing, E.A.K.; visualization, O.O.U.; supervision, O.A.R.; project administration, O.A.R.; funding acquisition, O.A.R. All authors have read and agreed to the published version of the manuscript.

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