



Cyclopentadithiophene-based co-oligomers for solution-processed organic solar cells



Rocío Domínguez^a, Gisela L. Schulz^b, Pilar de la Cruz^a, Peter Bäuerle^{b, **},
Fernando Langa^{a, *}

^a University of Castilla-La Mancha, Institute for Nanoscience, Nanotechnology and Molecular Materials (INAMOL), Campus de la Fábrica, 45071 Toledo, Spain

^b Institute of Organic Chemistry II and Advanced Materials, Ulm University, Albert-Einstein-Alle 11, 89081 Ulm, Germany

ARTICLE INFO

Article history:

Received 15 February 2017

Received in revised form

12 April 2017

Accepted 18 April 2017

Available online 19 April 2017

Keywords:

Cyclopentadithiophene

Thieno[3,2-*b*]thiophene

β -Alkyl substitution

Bulk-heterojunction solar cells

Solvent vapour annealing

ABSTRACT

A new family of low band-gap co-oligomers based on 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT) and thieno[3,2-*b*]thiophene (TT) units as central electron-donor cores has been synthesized and characterized for use as electron-donor materials in solution-processed bulk-heterojunction organic solar cells. An in-depth study into the role played by the hexyl chains linked to the thienylenevinylene-based π -bridge has been carried out. Power conversion efficiencies (PCE) of up to 4% and external quantum efficiencies as high as 50% have been achieved. Experiments carried out after solvent vapour annealing (SVA) as a post-treatment led to a doubling of the fill factor (FF) and PCE.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Bulk heterojunction (BHJ) organic solar cells (OSCs) based on oligomers as electron-donor along with fullerene derivatives as electron-acceptor materials have been widely investigated in recent years owing to their excellent advantages, which include light weight, less marked batch to batch variations, high reproducibility, low-cost, flexibility and large-area applications [1]. Until now, BHJ OSCs based on π -conjugated oligomers, typically denoted as 'small molecules', have reached power conversion efficiencies (PCE) over 10% [2], which is comparable to those of polymer-based OSCs [3]. Π -Conjugated co-oligomers based on alternating electron-donor (D) and electron-acceptor (A) moieties lead to materials with outstanding properties, such as absorption in the visible to near-infrared region, strong charge transfer character, low highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy gap, and good charge carrier mobility [4]. Of these materials, acceptor-donor-acceptor (A-D-A)

oligomers are considered to be among the most promising molecular structures owing to their broad absorption, high hole mobility, suitable electronic levels, controlled solubility, and high open circuit voltage (V_{OC}) of their resulting devices [5], and these have been extensively studied as donor materials in BHJ OSCs [2c,6].

Most of the research into the design of new A-D-A systems has been focused on optimization of the molecular structure of donors and acceptors. Regarding the donor fragments, fused aromatic rings have been widely used due to their extended π -conjugation, high charge carrier mobility, and reduced bandgap according to the enhancement of the π -electron delocalization [7]. The fused ring aromatic structures tend to form π - π stacks with a large overlapping area and this leads to high charge carrier transport through intermolecular hopping, large crystalline domains, and more ordered domain boundaries. Additionally, the position and length of alkyl side chains on the central electron-donor building block play an important role for solubility, π - π stacking, energy levels, and charge transport properties of the oligomers [8]. However, despite the fact that a great deal of effort has been focused on identifying structure-property relationships for these materials, their correlation with device performance parameters remains very difficult and several issues remain unresolved.

* Corresponding author.

** Corresponding author.

E-mail addresses: peter.baehlerle@uni-ulm.de (P. Bäuerle), fernando.langa@uclm.es (F. Langa).

4*H*-Cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT) derivatives have recently been used in organic electronics and optical materials owing to their unique semiconducting and electronic properties, which include high electrical conductivity, low band-gap, and extended π -conjugation [9]. The fused-ring structure of CPDT, which is regarded as a fused-ring analogue of 3-alkylthiophene and a structural analogue of fluorene, has extended π -conjugation in the ground state due to the highly planar molecular geometry. This fused structure leads to a low reorganization energy, a parameter that affects the rate of intermolecular hopping and hence the charge carrier mobility in organic semiconductors. In addition, the increase in the degree of conjugation causes lower HOMO-LUMO separation, facilitates the intramolecular charge transfer process, and enables closer intermolecular interactions [10]. The chemical versatility of CPDT enables a relatively easy modification of the α -positions by different functional groups and the introduction of alkyl substituents at the bridging carbon atom in order to improve the solubility. As a result, the fully coplanar structure and good electron-donating ability of CPDT have boosted its use as a building block in the preparation of electroactive conjugated polymers, especially narrow band gap π -conjugated polymers, as electron-donor materials, π -conjugated spacers, and as materials in organic photovoltaics [11].

Thieno[3,2-*b*]thiophene (TT) is also an aromatic fused ring system that is widely employed as a key component in different molecular architectures [12] due to its symmetric configuration and high charge carrier mobility [13] originated from its high tendency to form strong intermolecular interactions and packing [14]. TT, a structure with two fused thiophene rings, exhibits excellent properties including a stable quinoidal structure and narrow energy band gap. Although the TT unit has been extensively employed in conjugated polymers to obtain high performance OPVs [15], it has rarely been used as a central electron-donor core in oligomers or 'small molecules' for solution-processed organic solar cells with high performance [16].

In the work described here, we have synthesized a new series of co-oligomers taking advantage of the outstanding properties displayed by the CPDT unit, *i.e.*, fully planar structure and electron-rich nature, and those exhibited by the TT structure. The synthesis and characterization of this new family of acceptor- π -donor- π -acceptor (A- π -D- π -A) co-oligomers based on CPDT- (1–3) and TT-units (4) are described along with their use as electron-donor materials in solution-processed bulk-heterojunction solar cells (BHJSC). Dicyanovinylene (DCV) was used as the electron-acceptor group and differently substituted thienylenevinylene (TV) moieties were employed as the π -conjugated bridge. These structural variation enabled a study of the effect of the alkyl chains on optical and electrochemical properties, morphology, and device performance parameters.

2. Experimental section

2.1. Synthesis and characterization

2.1.1. General procedure for the Horner-Wadsworth-Emmons reaction

In a round-bottomed flask, under an argon atmosphere, the corresponding phosphonate (2 eq) and the corresponding dialdehyde (1 eq) were dissolved in dry THF. ^tBuOK (8 eq) was added and the mixture was stirred overnight at room temperature. After consumption of the dialdehyde (monitored by TLC), the crude product was extracted with diethyl ether. The organic phase was dried over MgSO₄, concentrated in vacuo and purified by chromatography column (silica gel, hexane).

2.1.2. Synthesis of (E,E)-2,6-bis[2-(2-thienylvinyl)]-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophene (11)

From 174 mg of **8** [20] (0.74 mmol) and 150 mg of **5** [17] (0.37 mmol) reacted as per the general procedure gave 200 mg of **11** as red oil (0.36 mmol, 96% yield). ¹H NMR (400 MHz, CDCl₃) δ /ppm: 7.18–7.17 (m, 2H), 7.04–7.00 (m, 8H), 6.88 (s, 2H), 1.83–1.79 (m, 4H), 1.16–1.14 (m, 12H), 0.98 (m, 4H), 0.84–0.81 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ /ppm: 158.8, 143.2, 142.8, 135.9, 127.7, 125.6, 124.0, 122.5, 120.8, 119.4, 53.8, 37.8, 31.6, 31.0, 29.7, 24.5, 22.6, 14.0; FT-IR (ATR) ν /cm⁻¹: 2924, 2850, 1416, 1392, 930, 852, 825, 686; UV-Vis (CH₂Cl₂) λ_{\max} /nm (log ϵ): 460 (4.66), 485 (4.62); MS (*m/z*) (MALDI-TOF): calculated C₃₃H₃₈S₄: 562.19; found: 562.30 (M⁺).

2.1.3. Synthesis of (E,E)-2,5-bis[2-(3,4-dihexyl-2-thienylvinyl)]thieno[3,2-*b*]thiophene (16)

From 927 mg of **6** [18] (2.30 mmol) and 226 mg of **15** [22] (1.15 mmol) reacted as per the general procedure gave 230 mg of **16** as an orange oil (0.33 mmol, 29% yield). ¹H NMR (400 MHz, CDCl₃) δ /ppm: 7.09 (s, 2H), 7.05 (d, 2H, ³J = 15.6 Hz), 6.99 (d, 2H, ³J = 15.6 Hz), 6.79 (s, 2H), 2.64–2.60 (m, 4H), 2.51–2.47 (m, 4H), 1.70–1.59 (m, 4H), 1.54–1.47 (m, 4H), 1.40–1.32 (m, 24H), 0.93–0.90 (m, 12H); ¹³C NMR (100 MHz, CDCl₃) δ /ppm: 145.2, 143.4, 140.7, 138.0, 136.2, 120.8, 120.6, 118.6, 118.0, 31.8, 31.6, 31.0, 29.6, 29.4, 29.3, 29.0, 27.0, 22.6, 14.1; FT-IR (KBr) ν /cm⁻¹: 2954, 2920, 2852, 1466, 922, 876, 831, 729; UV-Vis (CH₂Cl₂) λ_{\max} /nm (log ϵ): 432 (4.77), 457 (4.68); MS (*m/z*) (MALDI-TOF): calculated C₄₂H₆₀S₄: 692.36; found: 692.91 (M⁺).

2.1.4. General procedure for the Vilsmeier-Haack formylation

In a round-bottomed flask, under an argon atmosphere, POCl₃ (4.5 eq) was added to a solution of the corresponding co-oligomer (1 eq) and DMF (6.3 eq) in dry DCE. The mixture was stirred overnight at room temperature. 1 M aqueous sodium acetate solution was added to neutrality and then the mixture was stirred vigorously for 1 h. The solution was extracted with dichloromethane and the organic phase was dried over MgSO₄. After evaporation of the solvent, the product was purified by chromatography column (silica gel, hexane: CHCl₃ 2:3).

2.1.5. Synthesis of (E,E)-2,6-bis[2-(5-formyl-2-thienylvinyl)]-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophene (14)

0.11 mL (1.20 mmol) of POCl₃ were added to a solution of 150 mg of **11** (0.27 mmol) and 0.13 mL (1.68 mmol) of DMF in dry DCE (25 mL) under the same conditions as described in the general procedure. The dialdehyde **14** was obtained in 42% yield as a violet solid (71 mg, 0.11 mmol). ¹H NMR (400 MHz, CDCl₃) δ /ppm: 9.85 (s, 2H), 7.66 (d, 2H, ³J = 3.8 Hz), 7.27 (d, 2H, ³J = 15.6 Hz), 7.10 (d, 2H, ³J = 3.8 Hz), 6.99 (d, 2H, ³J = 15.6 Hz), 7.01 (s, 2H), 1.86–1.82 (m, 4H), 1.21–1.14 (m, 12H), 0.98–0.94 (m, 4H), 0.84–0.81 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ /ppm: 182.4, 159.8, 152.4, 143.0, 141.1, 137.8, 137.5, 126.8, 126.2, 122.8, 118.5, 54.0, 37.8, 31.6, 29.7, 24.5, 22.6, 14.0; FT-IR (KBr) ν /cm⁻¹: 2951, 2926, 2852, 2794, 1651, 1597, 1522, 1448, 1387, 1228, 1047, 924, 822, 667; UV-Vis (CH₂Cl₂) λ_{\max} /nm (log ϵ): 512 (4.77); MS (*m/z*) (MALDI-TOF): calculated C₃₅H₃₈O₂S₄: 618.18; found: 618.28 (M⁺).

2.1.6. Synthesis of (E,E)-2,5-bis[2-(5-formyl-3,4-dihexyl-2-thienylvinyl)]thieno[3,2-*b*]thiophene (17)

0.10 mL (1.14 mmol) of POCl₃ were added to a solution of 175 mg of **16** (0.25 mmol) and 0.12 mL (1.59 mmol) of DMF in dry DCE (25 mL) under the same conditions as described in the general procedure. The dialdehyde **17** was obtained in 69% yield as a red solid (130 mg, 0.17 mmol). ¹H NMR (400 MHz, CDCl₃) δ /ppm: 9.98 (s, 2H), 7.22 (d, 2H, ³J = 15.6 Hz), 7.18 (s, 2H), 7.01 (d, 2H,

Download English Version:

<https://daneshyari.com/en/article/4765872>

Download Persian Version:

<https://daneshyari.com/article/4765872>

[Daneshyari.com](https://daneshyari.com)