



New acceptor– π –porphyrin– π –acceptor systems for solution-processed small molecule organic solar cells



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ABSTRACT

Two new conjugated acceptor–donor–acceptor (A– π –D– π –A) compounds having a Zn-porphyrin acting as donor and linked by ethynylenes to one or two units of thienylenevinylene and capped by dicyanovinylene groups as acceptor units have been synthesized and their photophysical and electrochemical properties were investigated. These compounds were used as donor materials and PC₆₁BM and PC₇₁BM were used as acceptors in solution-processed bulk-heterojunction (BHJ) organic solar cells and the best photoconversion efficiency (PCE) obtained was 3.21%.

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1. Introduction

Efficient production of clean and sustainable energy is one of the most important scientific challenges that the world faces today. Sunlight is the most abundant and one of the cleanest sources of energy, thus the efficient utilization of solar energy to prepare solar cells has attracted much attention from the scientific community [1–3]. The development of efficient organic photovoltaic (OPV) solar cells has attracted considerable interest as potential alternative solar energy sources to silicon-based solar cells, because of their distinct advantages of solution processability, low-cost, flexibility and roll-to-roll production possibilities. The bulk heterojunction (BHJ) approach is the most efficient to date, which consists of a nanometer scale interpenetrating network of an electron-accepting, typically fullerene, phase and a light-harvesting electron-donor phase, such as a polymer or a small molecule. Polymer solar cells (PSCs) underwent significant progress in the past decades, thanks to the judicious design of narrow band-gap copolymers, optimization of the nanoscale morphologies of the photoactive layers and enhanced carriers mobilities, which have

led to power conversion efficiencies (PCEs) of 10% for single-junction PSCs [4,5] and up to 11% for tandem PSCs [6]. Nonetheless, there are issues with the synthesis of conjugated polymers for photovoltaic applications, such as difficult purification, poor batch-to-batch reproducibility and so on.

Solution processed small-molecule organic solar cells (SMBHJ), are an emerging alternative to the polymer counterparts, and these have rapidly developed in recent years, which offer potential advantages, such as better defined structures, easier purification and better reproducibility [6–9]. Thus far, power conversion efficiencies exceeding 9% have been reported for solution-processed small molecule single junction devices [10–15].

Inspired by natural photosynthetic organisms, where chlorophylls absorb light for energy conversion, and because of intense Soret band at around 400 nm and the Q bands close to 600 nm, porphyrins and their derivatives are excellent building blocks for the construction of light harvesting architectures [16]. Porphyrins are among the best sensitizers in Dye Sensitized Solar cells (DSSCs) [17–22] showing performances as high as 12% [23]. However, the utilization of porphyrins as active materials in solution-processed BHJ solar cells has been limited [24–33] despite their natural tendency to form aggregates by π – π stacking interactions [34].

In this article we report the synthesis of two new conjugated acceptor–donor–acceptor (A– π –D– π –A) molecules **1a** and **1b**

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(Fig. 1), along with their photophysical and electrochemical properties, as well as their performance in solution-processed SMBHJ. Both compounds were used as the p type layer with the Zn-porphyrin core acting as a donor linked by ethynylenes to one or two units of thienylenevinylene and capped by dicyanovinylene groups as acceptor units. Ethynylenes were chosen to make the systems planar and hexyl chains were attached on the thiophene units to enhance their solubility. PC₆₁BM and PC₇₁BM were used as acceptor components in the devices.

2. Experimental section

2.1. Experimental details

Experimental details are given in the [Supporting information](#).

2.2. Synthetic procedures

2.2.1. General synthetic procedure for **3a, b** [35]

To a solution of **5a, b** [36] (1 eq) in carbon tetrachloride (CCl₄, 1.25 mL/mmol) was added PhI(OCOCF₃)₂ (0.55 eq) and molecular iodine (I₂, 0.5 eq). The mixture was stirred at room temperature. The reaction was quenched with a saturated solution of sodium thiosulfate (Na₂SO₃ sat.) while stirring for 15 min and extracted with CH₂Cl₂. The combined organic phases were dried over anhydrous MgSO₄ and filtered. The solvent was removed by rotary evaporation.

2.2.2. 5-Iodo-3,4-dihexyl-2-thiophencarboxaldehyde (**3a**)

Using the general procedure previously described, **5a** (1.8 mmol, 500 mg) was reacted with PhI(OCOCF₃)₂ (1.0 mmol, 416 mg) and I₂ (0.9 mmol, 226 mg) in 2.2 mL of CCl₄. The product was purified by column chromatography (silica gel, hexane–CHCl₃, 7:3). **3a** was obtained as a yellow oil (610 mg, 1.51 mmol, 84% yield). ¹H NMR (400 MHz, CDCl₃) δ/ppm: 9.90 (s, 1H), 2.94–2.90 (m, 2H), 2.57–2.53 (m, 2H), 1.64–1.57 (m, 4H), 1.39–1.31 (m, 12H), 0.93–0.88 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ/ppm: 181.2, 150.5, 148.4, 143.0, 89.7, 32.3, 31.5, 31.4, 30.6, 29.7, 29.3, 29.3, 27.8, 22.6, 22.5, 14.1, 14.0. MALDI-TOF MS (*m/z*): [M]⁺ calculated for C₁₇H₂₇IOS: 406.08; found: 406.08. FT-IR (ATR) ν/cm⁻¹: 2923, 2854, 1654, 1523, 1461, 1427, 1365, 1222, 1126, 1079, 721, 674.

2.2.3. (*E*)-1-(5-formyl-3,4-dihexyl-2-thienyl)-2-(5-iodo-3',4'-dihexyl-2'-thienyl)ethylene (**3b**)

Using the general procedure previously described, **5b** (0.6 mmol, 338 mg) was reacted with PhI(OCOCF₃)₂ (0.3 mmol, 142 mg), I₂ (0.3 mmol, 77 mg) in 0.75 mL of CCl₄. The product was purified by column chromatography (silica gel, hexane–CHCl₃, 3:2). **3b** was obtained as a yellow oil (255 mg, 0.37 mmol, 62% yield). ¹H NMR (400 MHz, CDCl₃) δ/ppm: 9.98 (s, 1H), 7.19 (d, 1H, *J* = 15.5 Hz),

6.97 (d, 1H, *J* = 15.5 Hz), 2.84 (t, 2H, *J* = 7.7 Hz), 2.64 (t, 2H, *J* = 7.7 Hz), 2.58 (t, 2H, *J* = 7.7 Hz), 2.49 (t, 2H, *J* = 7.7 Hz), 1.50–1.27 (m, 32H), 0.94–0.88 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ/ppm: 181.9, 153.0, 147.7, 146.6, 141.8, 141.6, 141.0, 134.8, 123.1, 118.8, 75.5, 32.3, 31.6, 31.5, 31.4, 31.1, 31.0, 29.8, 29.3, 27.9, 27.1, 26.4, 22.6, 22.5, 14.1, 14.05. MALDI-TOF MS (*m/z*): [M]⁺ calculated for C₃₅H₅₅IOS₂: 682.27; found: 683.49. FT-IR (ATR) ν/cm⁻¹: 2923, 2850, 1654, 1600, 1523, 1461, 1403, 1375, 1249, 1211, 933, 725, 678, 663.

2.2.4. Synthesis of 5,15-dimesitylporphyrin [37]

A solution of corresponding dipyrromethane [38] (14.4 mmol, 2.10 g) and 2,4,6-trimethylbenzaldehyde (14.4 mmol, 2.1 mL) in 1.40 L of CHCl₃ was treated with BF₃O(C₂H₅)₂ (4.7 mmol, 0.6 mL). The mixture was stirred for 3 h. DDQ (21.5 mmol, 4.9 g) was added and the reaction mixture was stirred for 1 h. Et₃N (2.0 mL) was added and stirred during 30 min. The solvent was removed by rotary evaporation and the solid was purified by column chromatography (silica gel, hexane–CHCl₃, 1:1). 5,15-Dimesitylporphyrin was obtained as a purple solid (1400 mg, 2.56 mmol, 35% yield). ¹H NMR (400 MHz, CDCl₃) δ/ppm: 10.25 (s, 2H), 9.35 (d, 4H, *J* = 4.5 Hz), 8.91 (d, 4H, *J* = 4.5 Hz), 7.35 (s, 4H), 2.69 (s, 6H), 1.87 (s, 12H), –3.04 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ/ppm: 146.8, 145.4, 139.5, 137.8, 137.6, 131.8, 130.0, 127.8, 117.3, 104.6, 21.7, 21.5. MALDI-TOF MS (*m/z*): [M]⁺ calculated for C₃₈H₃₄N₄: 546.09; found: 546.28. FT-IR (ATR) ν/cm⁻¹: 3305, 1828, 1604, 1411, 1373, 1319, 1234, 1052, 950, 852, 782, 736, 694, 617.

2.2.5. Synthesis of [5,15-dimesitylporphyrinato] zinc (II) [39]

To a solution of 5,15-dimesitylporphyrin (2.5 mmol, 1.35 g) in 209 mL of CHCl₃, was added a solution of Zn(OAc)₂·2H₂O (12.3 mmol, 2.26 g) in 6.2 mL of MeOH. The mixture was stirred 18 h. The reaction was quenched with water and extracted with CHCl₃ (3 × 100 mL). The combined organic extract was dried over anhydrous MgSO₄ and filtered. The solvent was removed by rotary evaporation. The product was purified by column chromatography (silica gel, hexane–CHCl₃, 1:1). The product [5,15-dimesitylporphyrinato] zinc (II), was obtained as a purple solid (1.51 g, 2.47 mmol, 99% yield). ¹H NMR (400 MHz, CDCl₃) δ/ppm: 10.27 (s, 2H), 9.41 (d, 4H, *J* = 4.4 Hz), 9.00 (d, 4H, *J* = 4.4 Hz), 7.35 (s, 4H), 2.69 (s, 6H), 1.85 (s, 12H). ¹³C NMR (100 MHz, CDCl₃) δ/ppm: 149.8, 149.4, 139.3, 138.8, 135.7, 132.1, 131.3, 127.7, 118.2, 105.5, 21.7, 21.5. MALDI-TOF MS (*m/z*): [M]⁺ calculate for C₃₈H₃₂N₄Zn: 608.57; found: 608.19. FT-IR (ATR) ν/cm⁻¹: 1816, 1608, 1438, 1388, 1318, 1211, 1052, 856, 786, 728, 701, 617.

2.2.6. Synthesis of [5,15-dibromo-10,20-dimesitylporphyrinato] zinc (II)

To a solution of [5,15-dimesitylporphyrinato] zinc (II) (1.5 mmol, 920 mg) in 80 mL of CHCl₃, *N*-bromosuccinimide (NBS) (3.0 mmol, 536 mg) and 1 mL of pyridine were added. The mixture was stirred

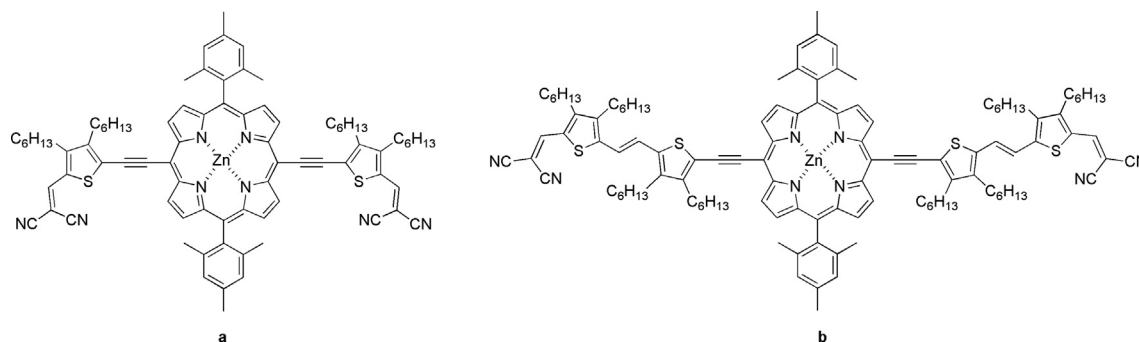


Fig. 1. Structures of **1a** and **1b**.

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