



High photo-current in solution processed organic solar cells based on a porphyrin core A- π -D- π -A as electron donor material



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ABSTRACT

Two new conjugated acceptor-donor-acceptor (A- π -D- π -A) molecules with a porphyrin core linked by ethynylene bridges to two thiophene (**1a**) or thienylenevinylene thiophene (**1b**) units and both capped by *N*-ethylrhodanine have been synthesized. These compounds were used as the main electron donor moieties for bulk heterojunction small molecule organic solar cells (BHJ-SMOSC). The optimized devices, with PC71BM as the main electron acceptor molecule, show remarkable short circuit currents, up to 13.2 mA/cm², an open circuit voltage of around 0.85 V, and power conversion efficiencies up to 4.3% under 100 W/cm². The External Quantum Efficiency (EQE), Atomic Force Microscopy (AFM), hole mobility, Photo-Induced Charge Extraction (PICE) and Photo-Induced Transient Photo-Voltage (PIT-PV) were analyzed in devices based on **1a** and **1b** in order to account for differences in the final performance of the two molecules. The PIT-PV decays showed slower recombination kinetics for devices fabricated with **1b**. Moreover, the EQE was greater for **1b** and this is ascribed to the better nanomorphology, which allows better charge collection before carrier recombination takes place.

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1. Introduction

Solution processed organic solar cells (OSCs) have improved significantly in recent decades [1–4], due to the judicious design of push-pull low band-gap copolymers, optimization of the nanoscale morphologies of the photoactive layers and enhanced carrier mobility, all of which have led to power conversion efficiencies (PCEs) of 10% for single-junction polymer solar cells (PSCs) [5,6] and up to 11% for tandem PSCs [7]. Moreover, small molecule organic solar cells (SMOSCs) have emerged as complementary systems to the polymeric materials and they have undergone rapid development in recent years as SMOSCs offer potential advantages such as

the possibility of obtaining better-defined molecular structures, easier purification and better batch-to-batch reproducibility [8,9]. Indeed, power conversion efficiencies for bulk heterojunction small molecule organic solar cells (BHJ-SMOSCs) have exceeded 10% and these are expected to be higher for tandem devices [10–13].

Numerous different chemical architectures, especially as donor moieties, have been explored for SMOSCs [11,14–19] and the most promising are the donor-acceptor (D-A) ‘push-pull’ molecules. Within this group, the use of porphyrin moieties (POR) as the main donor has recently been reported but this remains relatively unexplored.

Inspired by natural photosynthetic structures, such as chlorophylls, porphyrins and their derivatives, these excellent building blocks offer efficient light harvesting architectures, high stability, and their large and rigid planar structure allows fine tuning of their energetic and morphological properties [20]. For example, POR-based photosensitizers are among the best sensitizers in dye sensitized solar cells (DSSCs). In recent years, remarkable progress has been made on using POR as the main donor moieties [21–26]

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and efficiencies as high as 8% have been reached in SMOSC [27] devices while in DSSC systems efficiencies close to 12% have been described [28].

Recently, we described two similar conjugated acceptor-donor-acceptor (A- π -D- π -A) compounds that also contained a Zn-porphyrin but were capped by dicyanovinylene groups as acceptor units – these materials gave photoconversion efficiency (PCE) of 3.21% [29]. With the aim of significantly improving the design and thus the performance of the final device, we report here: (a) the synthesis and characterization of two new conjugated POR-based acceptor-donor-acceptor (A- π -D- π -A) ‘push-pull’ molecules **1a** and **1b** (Fig. 1); (b) the device fabrication and performance of these materials in solution-processed SMOSCs using PC71BM as the main electron acceptor moiety and (c) analysis of the carrier recombination kinetics. Compounds **1a** and **1b** were used as electron donor molecules in the blend, with the Zn-porphyrin core acting as a donor linked by ethynylene groups to one or two units of thienylenevinylene and capped by *N*-ethylrhodanine as acceptor units. The strategy for this design is based on the use of the ethynylene units to make the system planar, the thienylenevinylene to extend the π -conjugation and the incorporation of hexyl chains on the thiophene units to enhance solubility. Finally, the use of rhodanine as the acceptor provides a stronger charge transfer character to the molecule and increases the light harvesting efficiency.

2. Synthesis and characterization

Compounds **1a-b** were obtained in 82% and 45% yield, respectively, by Knoevenagel condensation of **2a-b** [28] with *N*-ethylrhodanine and piperidine as base (Scheme 1). Both new compounds were satisfactorily characterized by ^1H and ^{13}C NMR, FT-IR and MALDI-MS (see Supporting Information for synthetic details and full analytical and spectroscopic data). In the ^1H NMR spectra of **1a** and **1b** a new signal was observed at 8.00 ppm and 7.95 ppm, respectively, and this confirms the success of the condensation reaction. The mass spectrum of **1a** showed the molecular ion peak at m/z 1498.75 amu and **1b** gave a molecular ion peak at m/z 2051.69 amu.

Compounds **1a-b** showed excellent thermal stability up to 300 °C, with Td values of 377 °C and 355 °C for **1a** and **1b**, respectively (Figs. S9 and S10); this thermal stability is suitable for photovoltaic applications.

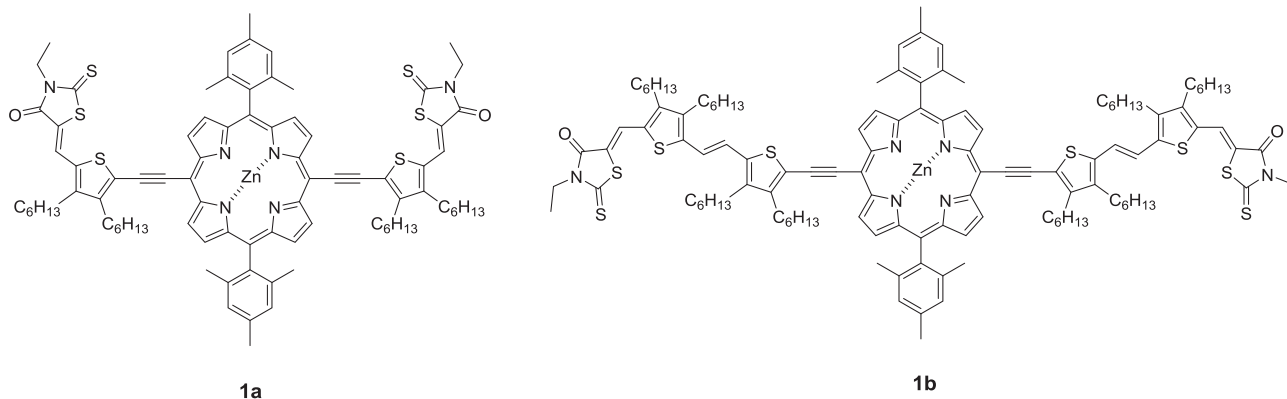


Fig. 1. Molecules **1a** and **1b**.

3. Optical properties

The optical properties of **1a** and **1b** in CH_2Cl_2 (DCM) solutions and in thin films are shown in Fig. 2 and the characteristics of semiconductors **1a** and **1b** are collected in Table 1.

The absorption spectra in DCM solution of both compounds exhibit a panchromatic absorption in the visible region. Compound **1a** shows the characteristic absorption pattern of a Zn-chelated porphyrin with an intense Soret band (B band) at 507 nm ($\log \epsilon = 5.27$) and a broad intense intramolecular charge transfer (ICT) band with a maximum at 709 nm ($\log \epsilon = 5.09$). Extension of the conjugation on the bridge by the introduction of a new thienylenevinylene unit had a significant impact on the absorption spectrum of **1b**. This change led to a broader absorption, which is bathochromically shifted, for the Soret band to 547 nm ($\log \epsilon = 5.02$) and in the ICT band at 716 nm ($\log \epsilon = 5.02$). Comparison of the corresponding absorptions in films shows that the absorption bands became broader and red-shifted as a consequence of the closer intermolecular interactions in solution.

The fluorescence spectra of **1a-b**, measured in DCM (CH_2Cl_2) and with excitation at 481 and 482 nm, respectively, show emission bands at 727 and 746 nm, respectively (Figs. S13 and S14).

From absorbance and emission data, the E_{0-0} values were calculated. The HOMO-LUMO gaps are as narrow as 1.74 and 1.69 eV for **1a** and **1b**, respectively.

4. Electrochemical properties

The electrochemical properties of **1a** and **1b** were investigated by Cyclic Voltammetry (CV) and Osteryoung Square Wave Voltammetry (OSWV) in *o*-dichlorobenzene (ODCB)-acetonitrile (4:1) (Table 1, Figs. S15 and S16). On the cathodic side, both compounds showed a first reversible one-electron oxidation wave at 0.26 V for **1a** and 0.14 V for **1b** (vs Fc/Fc^+ in all cases). This first oxidation potential is ascribed to the oxidation of the porphyrin core; it can be remarked that the extended conjugation in **1b** gives rise to a decrease in the E_{ox} value by 12 mV with respect to **1a**. A second reversible oxidation wave was observed at 0.65 V for **1a** and at 0.42 V for **1b**, and this is attributed to the thienylenevinylene units. Compound **1b** showed two more non-reversible oxidation waves at 0.63 and 0.88 V, which are attributed to oxidation of the thienylenevinylene moieties. The estimated E_{HOMO} values were determined to be -5.36 eV for **1a** and -5.24 eV for **1b**.

Low-lying HOMO levels should result in high open-circuit voltages (V_{oc}) [30–32]. The E_{LUMO} values of **1a-b** are higher than

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