High Photo-Current in Solution Processed Organic Solar Cells Based on Porphyrin Core A-\pi-D-\pi-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 thienylenevinyleneithiophene (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.
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] 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 a 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.

**Figure 1.** Molecules 1a and 1b.
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 $^1$H and $^{13}$C NMR, FT-IR and MALDI-MS (see Supporting Information for synthetic details and full analytical and spectroscopic data). In the $^1$H 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 (Figure S9 and S10); this thermal stability is suitable for photovoltaic applications.

Optical Properties

The optical properties of 1a and 1b in CH$_2$Cl$_2$ (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 $\varepsilon$ = 5.27) and a broad intense intramolecular charge transfer (ICT) band with a maximum at 709 nm (log $\varepsilon$ = 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 $\varepsilon$ = 5.02) and in the ICT band at 716 nm (log $\varepsilon$ = 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 (CH₂Cl₂) and with excitation at 481 and 482 nm, respectively, show emission bands at 727 and 746 nm, respectively (Figure S13 and S14).
Figure 2. (a) UV-Visible spectra of 1a (black) and 1b (red) in DCM solution. (b) Normalized UV-Vis spectra of 1a (black) and 1b (red) and in thin films (red line).

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.
Table 1 UV-Vis,\textsuperscript{a} Fluorescence Emission\textsuperscript{a} and OSWV\textsuperscript{b} data for compounds 1a-b

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{max}}$ sol (nm)</th>
<th>log ($\varepsilon$)</th>
<th>$\lambda_{\text{max}}$ film (nm)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>$E_{0-0}$\textsuperscript{c} (eV)</th>
<th>$E_{\text{ox}}$\textsuperscript{b,d} (V)</th>
<th>$E_{\text{HOMO}}$\textsuperscript{e} (eV)</th>
<th>$E_{\text{LUMO}}$ (eV)</th>
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<td>1a</td>
<td>481</td>
<td>5.16</td>
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<td>727</td>
<td>1.74</td>
<td>0.26</td>
<td>-5.36</td>
<td>-3.62</td>
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<tr>
<td></td>
<td>507</td>
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<td>522</td>
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<td>746</td>
<td>1.69</td>
<td>0.14</td>
<td>-5.24</td>
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<tr>
<td></td>
<td>716</td>
<td>5.02</td>
<td>762</td>
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\textsuperscript{a}~10^{-5}~M in dichloromethane (DCM); \textsuperscript{b}~10^{-3}~M in o-dichlorobenzene (ODCB)-acetonitrile (4:1) versus Fc/Fc$^+$ ($E_{\text{ox}} = 0.04$ V) glassy carbon, Pt counter electrode, 20 °C, 0.1 M Bu$_4$NClO$_4$, scan rate = 100 mV s\textsuperscript{-1}; \textsuperscript{c}~estimated from the intersection between the normalized absorption and normalized emission spectra at $\lambda_{\text{max}}$; \textsuperscript{d}~reversible processes; \textsuperscript{e}~calculated with respect to ferrocene, $E_{\text{HOMO}}$: $-5.1$ eV.

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, Figures 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 $E_{\text{ox}}$ 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 EHOMO 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 (Voc).[30-32] The $E_{\text{LUMO}}$ values of 1a-b are higher than the $E_{\text{LUMO}}$ of PC71BM ($-4.0$ eV), i.e., $-3.62$ and $-3.55$ eV for 1a.
and 1b, respectively. Hence, the LUMO energy levels of these small-molecules (Fig. 3) clearly match the LUMO of PC71BM, thus enhancing charge transfer.

Figure 3. Schematic representation of the HOMO and LUMO energy levels for 1a, 1b and PC71BM.

Theoretical Calculations

In order to gain an insight into the structure and the electronic properties of the materials, theoretical studies were carried out by performing density functional theory (DFT) calculations at the B3LYP/6-31G* level in vacuo using Gaussian 03W.

The optimum geometries obtained for dyes 1a and 1b (Figure S17) show that the π-conjugated system, porphyrin macrocycle and the thienylenevinylene monomers are planar. The dihedral angles for this system are around 4°.

The calculated dihedral angle for the N-ethylrhodanine with the adjacent thiophene ring (θ) is around 1.5°. The planarity of the whole π-conjugated system is responsible for the extended conjugation and this situation is consistent with the calculated wavefunctions of the frontier molecular orbitals.
The HOMO and LUMO are spread over the whole porphyrin and the corresponding thienylenvinylene system. Thus, both orbitals are overlapped and this promotes the HOMO to LUMO electronic transitions (Figure S18).

The theoretical HOMO–LUMO gaps are similar for both dyes, with a slightly lower value for compound 1b (1.72 eV) than for 1a (1.85 eV). These values are of the same order of magnitude as those determined by electrochemical measurements.

The greater extent of the conjugation in dye 1b results in an increase in the HOMO energy level and, as a consequence, a bathochromic shift in the maximum absorption wavelength, which in turn improves the light harvesting behavior.

The differences between the HOMO of the donor (1a or 1b) and the LUMO of the acceptor (PC71BM)[24] (1a: 1.12 eV, 1b: 0.86 eV) point to efficient Voc values. Furthermore, the difference between the LUMO of the dyes 1a and 1b and the LUMO of PC71BM (1a: 0.73 eV, 1b: 0.85 eV) ensures efficient exciton dissociation at the D/A interface.

Device Characterization

The photovoltaic (PV) properties of 1a and 1b were investigated by fabricating solar cells using the conventional sandwich structure of ITO/poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS)/small-molecule:acceptor/Ca/Al. The fabrication method and other details are provided in the Supporting Information. The electrical characterization of all devices was performed under ambient conditions with AM 1.5 G simulated illumination at an intensity of 100 mW cm⁻². The current density-voltage characteristics and the external quantum efficiency (EQE) are shown in Fig. 4 and the performance parameters are summarized in Table 2 as a function of the donor:PC71BM weight ratios. Average values were taken from 12 devices.
The devices based on a 1a:PC71BM blend film with a w/w ratio of 1:2 exhibited an average power conversion efficiency (PCE) above 3%, with an open-circuit voltage (Voc) of 0.85 V, high short-circuit current (Jsc) and poor FF of 30.8% (Fig. 4a). On the other hand, the photovoltaic device with 1b:PC71BM at a blend ratio of 1:4 w/w showed a record PCE of 4.24%, with Voc 0.8 V, a Jsc of 13.2 mA/cm² and a FF of 40.1% (Fig. 4b). Moreover, the EQE values, which are displayed in Figures 4c and 4d, were measured under monochromatic light for 1a:PC71BM and 1b:PC71BM complete devices at different blend ratios. Both spectra exhibit a broad spectral response, ranging from 300 to 800 nm, whereas the mixture of 1b:PC71BM at a 1:4 w/w ratio gave the highest incident photon-to-current efficiency (80%) at 423 nm. This finding is consistent with the devices with the highest Jsc and PCE. Furthermore, the EQE integration against the 1.5 AM G sun spectra results was in good agreement with the measured photocurrents. As can be seen, all the solar cells display fill factor values below 50% (see Table 2). This issue was independent of the donor/acceptor ratio although, for the best solar cells with a ratio of 1:4 we achieved the highest fill factor values. From these results, it is difficult and too speculative to infer the reasons for the low fill factor. Nevertheless, we believe that the low mobility measured for the “only hole devices” and the unbalanced charge transport between holes and electrons are, definitively important factors that effect a change on the fill factor.
Table 2 Main performance parameters for 1a:PC71BM and 1b:PC71BM devices using different ratios. The values in parenthesis correspond to the highest efficiencies reached for each of the ratio conditions.

<table>
<thead>
<tr>
<th>Active layer</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a:PC71BM (1:4)</td>
<td>0.79 ± 0.04</td>
<td>11.03 ± 0.31</td>
<td>31.4 ± 0.2</td>
<td>2.73 ± 0.2 (2.86)</td>
</tr>
<tr>
<td>1a:PC71BM (1:3)</td>
<td>0.87 ± 0.01</td>
<td>11.48 ± 0.25</td>
<td>30.2 ± 0.1</td>
<td>3.01 ± 0.1 (3.04)</td>
</tr>
<tr>
<td>1a:PC71BM (1:2)</td>
<td>0.85 ± 0.01</td>
<td>11.36 ± 0.21</td>
<td>30.8 ± 0.3</td>
<td>3.01 ± 0.1 (3.05)</td>
</tr>
<tr>
<td>1b:PC71BM (1:4)</td>
<td>0.80 ± 0.04</td>
<td>13.2 ± 0.21</td>
<td>40.1 ± 0.29</td>
<td>4.24 ± 0.1 (4.35)</td>
</tr>
<tr>
<td>1b:PC71BM (1:3)</td>
<td>0.82 ± 0.02</td>
<td>12.45 ± 0.24</td>
<td>38.5 ± 0.24</td>
<td>3.91 ± 0.1 (3.98)</td>
</tr>
<tr>
<td>1b:PC71BM (1:2)</td>
<td>0.84 ± 0.03</td>
<td>12.12 ± 0.37</td>
<td>34.7 ± 0.26</td>
<td>3.55 ± 0.1 (3.63)</td>
</tr>
</tbody>
</table>

![Graphs](image-url)
Figure 4 (a) Current density-voltage (J-V) characteristics of 1a:PC71BM devices; (b) 1b:PC71BM devices, both at different ratios; (c) EQE of 1a:PC71BM and (d) EQE of 1b:PC71BM devices.

![Figure 4](image)

Figure 5. AFM images of (a) 1a:PC71BM and (b) 1b:PC71BM in the most efficient devices.

Once the solar cells had been evaluated, the morphologies of the active layer were characterized by atomic force microscopy (AFM) in tapping mode in order to gain an insight into the differences in device performance, using the best composition for each device, as shown in Figure 5. The surface topographies of the film of the 1b:PC71BM (1:4) blend displays rather uniform nanometer-sized features with a root-mean-square roughness (rms) value of 0.53 nm. In contrast, the blend containing 1a with PC71BM exhibited a coarser topography, with higher rms values of 0.62 nm. The surface of the former is smoother than that of the latter and it also has better-defined morphological features. This is often related to better phase intermixing, which in turn leads to better phase separation and is beneficial for efficient exciton diffusion and charge transport.

The effect that the blend nano-morphology has on the solar cell parameters was analyzed further by measuring the hole carrier mobility in complete devices with the appropriate selective contacts (see Supporting Information). The mobility was calculated using the Space Charge
Limited Current method (SCLC) as described in the Supporting Information (Figure S19). Values for 1a and 1b of $1.25 \pm 0.8 \times 10^{-5}$ V cm$^{-2}$ s$^{-1}$ and $1.53 \pm 0.3 \times 10^{-5}$ V cm$^{-2}$ s$^{-1}$, respectively, were obtained. It should be noted that, in contrast to previous publications,[33-40] the effect of the alkyl chains in these molecules on the hole carrier mobility is less critical. Moreover, it was determined that the hole carrier mobility is not responsible for the difference between the two porphyrin-based devices and, more importantly, this physical characteristic is not considered to be a determinant factor for the final device performance.

Finally, the carrier losses were evaluated by measuring the interfacial carrier recombination kinetics as reported previously.[33, 34, 41-48]

The charge extraction of 1a-b is depicted in Figure 6a and was determined by subtracting the contribution of the geometrical capacitance. The total extracted charges are shown in the Supporting Information (Figure S20), where the geometric contribution is indicated by a straight line and the calculated values are 80 and 64 nF cm$^{-2}$ for 1a and 1b, respectively. Hence, the charge values shown in Figure 6b correspond to the photo-induced charge, which can either be stored at the contacts, in the bulk of the device or both. As can be seen in Figure 6a, there is a shift in the exponential in devices made with 1a and this finding is in good agreement with the 5–10 mV increase in Voc observed in the IV curves.

Moreover, on using 1b the organic blend is capable of storing more charges at a given photo-induced voltage (the so-called light bias) and, as shown above, can extract these charges more efficiently when compared to 1a. The Photo-Induced Transient Photo-Voltage (PIT-PV) technique was also applied to compare the charge lifetime of devices based on 1a and 1b. A clear difference can be seen between these two materials. Firstly, 1b clearly has a slower carrier lifetime than 1a. The slower carrier recombination dynamics, in addition to the observed shift in
the exponential charge density measurement, explain the higher Voc observed for 1b. It is known that the Voc of a solar cell is closely related to the carrier recombination dynamics under illumination. The slower the carrier recombination the higher the Voc for devices with similar charge density.

![Graph showing charge density vs potential for 1a and 1b](image-url)
Figure 6. (A) Charge density at different light intensities (light bias) of 1a (red line) and 1b (green line). The charges correspond to the extracted charges under different illumination conditions. (B) The carrier life-time of 1a (red line) and 1b (green line) at different charge values.

The results described above indicate that the molecular structure of 1b favors better film nano-morphology and thus improved charge collection and slower carrier recombination dynamics.

Conclusions

Two conjugated molecules bearing a Zn-porphyrin, which act as an electron donor, linked by ethynylene units to one or two thienylenevinylene moieties and capped by ethylenerhodanine groups as acceptor units have been synthesized and characterized for solution processed small
molecule solar cells. The design strategy was based on the incorporation of electron-accepting ethylenerhodanine moieties through the thiophene based bridges, which shift the absorption profiles bathocromically to the NIR due to a more intense intramolecular charge transfer band. Compounds 1a and 1b exhibit excellent light harvesting properties, good thermal stability and have low-lying HOMO levels of -5.36 and -5.24 eV, respectively. Complete SMOSCs were fabricated using 1a and 1b donors combined with PC71BM as the electron acceptor molecule. Compound 1b gave a PCE of 4.3%. The EQE measurements are consistent with the Jsc values obtained, with an incident photon-to-current efficiency of 80% at 430 nm for the 1b:PC71BM device with a 1:4 ratio. The hole carrier mobility was also measured and values of 1.25±0.8×10^-5 Vcm^-2s^-1 and 1.56±0.4×10^-5 Vcm^-2s^-1 were obtained, respectively. Finally, photo-induced charge extraction and photo-induced transient photo-voltage experiments were carried out in order to determine the origin of the difference in performance between devices based on 1a and 1b. The PICE showed a shift that mirrored the difference in Voc and very similar distribution of charges versus applied light bias, although 1b can store more charge at the same voltage. Moreover, the PIT-PV showed a marked difference between the two molecules; In the case of 1b the carrier lifetime was considerably shorter than that of 1a. Thus, for 1b the presence of the thiophene groups not only improves the light absorption but also changes the nano-morphology and, hence, the carrier extraction and recombination. This is achieved without a substantial decrease in the device Voc, as expected due to the reduced bandgap of 1b.

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Notes and references


Supplementary Information.

High Current Porphyrin Core Based A-π-D-π-A Small Molecule for Solution Processed Organic Solar Cells

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TABLE OF CONTENTS

1. Experimental details S2
2. \(^1\)H-NMR, \(^{13}\)C-NMR, FT-IR and MALDI-TOF MS spectra S6
3. Thermogravimetric analysis S12
4. Absorption and emission spectroscopies S13
5. Cyclic and Square Wave voltammetry plots S15
6. Hole mobility measurement S17
7. Charge Extraction and Transient Photo-Voltage details S18
1. Experimental details

Synthetic procedures were carried out under inert argon atmosphere, in dry solvent unless otherwise noted. All reagents and solvents were reagent grade and were used without further purification. Chromatographic purifications were performed using silica gel 60 SDS (particle size 0.040-0.063 mm). Analytical thin-layer chromatography was performed using Merck TLC silica gel 60 F254. $^1$H-NMR spectra were obtained on Bruker TopSpin AV-400 (400 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak (CDCl$_3$, 7.27 ppm). $^{13}$C-NMR chemical shifts (δ) are reported relative to the solvent residual peak (CDCl$_3$, 77.0 ppm).

UV-Vis measurements were carried out on a Shimadzu UV 3600 spectrophotometer. For extinction coefficient determination, solutions of different concentration were prepared in CH$_2$Cl$_2$ (HPLC grade) with absorption between 0.1-1 of absorbance using a 1 cm UV cuvette. The emission measurements were carried out on Cary Eclipse fluorescence spectrophotometer. Mass spectra (MALDI-TOF) were recorded on a VOYAGER DE$^{TM}$ STR mass spectrometer using dithranol as matrix. Melting points are uncorrected.

The molecular geometries and frontier molecular orbitals of these new dyes have been optimized by density functional theory (DFT) calculations at the B3LYP/6-31G* level.$^1$ Cyclic and Square Wave voltammetries were performed in ODCB-acetonitrile (4:1) solutions. Tetrabutylammonium perchlorate (0.1 M as supporting electrolyte) were purchased from Acros and used without purification. Solutions were deoxygenated by...

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argon bubbling prior to each experiment which was run under argon atmosphere. Experiments were done in a one-compartment cell equipped with a platinum working microelectrode (\(\Omega = 2\) mm) and a platinum wire counter electrode. An Ag/AgNO\(_3\) (0.01 M in CH\(_3\)CN) electrode was used as reference and checked against the ferrocene/ferrocenium couple (Fc/Fc\(^+\)) before and after each experiment.

The thermal stability was evaluated by TGA on a Mettler Toledo TGA/DSC Start\(^e\) System under nitrogen, with a heating rate of 10 °C/min. Heating of crystalline samples leads to melting of the solids, but no recrystallization was observed.

**SM BHJ device preparation**

PC\(_{71}\)BM were purchased from American Dye Source and used as received. The ITO-coated glasses (Delta technologies, 5-15 \(\Omega\)) were pre-cleaned stepwise by ultracentrifugation 15 minutes in detergent, deionized water, methanol, acetone and isopropanol and then by a 30 minutes UV-ozone treatment. A thin layer of PEDOT:PSS (Clevios P VP AI 4083, 5000 rpm, 30 seconds, \(\approx 30\) nm) was spin-coated onto the ITO and baked at 150 °C for 15 minutes in air. Subsequently, the active layer (1a-b:PC\(_{61}\)BM, 30 mg/mL) with varying weight ratios (1:4, 1:2 and 1:1) was spin-coated at 1500 rpm from chlorobenzene solutions. 1a or 1b, 1a-b:PC\(_{71}\)BM (1:2, 30 mg/mL) was spin-coated at 1500 rpm. Then the devices were transferred to a N\(_2\) filled glove box (<0.1 ppm O\(_2\) and < 0.1 ppm H\(_2\)O) for further processing. The photoactive layer was annealed at 80 °C for 10 minutes followed by thermal evaporation of 20 nm of calcium and 80 nm of aluminum (1 x 10\(^{-6}\) mbar) with a shadow mask of 0.4 cm\(^2\).

**Device characterization.**

The \(J_{sc}\)-\(V_{oc}\) values were recorded with a Keithley 2420 source unit. CE and TPV measurements were carried out using a white LED ring LUXEON® Lumileds and the signal measured in an oscilloscope Yokogawa DLM2052 registering the drops in voltage.
**Synthetic Procedure**

**General method for the Knoevenagel condensations.** To a solution of 2a-b (1 eq) in 75 mL/mmol of CHCl₃, 3-ethylrhodanine (10 eq) and 3 drops of piperidine were added. The reaction mixture was refluxed and stirred for 12 h and quenched by the addition of water and extracted with CHCl₃ (3 x 150 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, CHCl₃) and recrystallized with CH₂Cl₂: MeOH.

**1a:** Using the general procedure previously described from 2a (0.06 mmol, 80 mg) in 5 mL of CHCl₃, 3-ethylrhodanine (0.65 mmol, 110 mg). 1a was obtained as a green solid (81 mg, 0.05 mmol, 82% yield). M. p. > 300°C. ¹H NMR (400 MHz, CDCl₃) δ/ppm: 9.57 (d, 4H, J = 4.8 Hz), 8.78 (d, 4H, J = 4.4 Hz), 8.00 (s, 2H), 7.33 (s, 4H), 4.22 (d, 4H, J = 5.7 Hz), 3.11 (m, 4H), 2.88 (m, 4H), 2.67 (s, 6H), 1.88 (s, 12 H), 1.65 (m, 8H), 1.54-1.52 (m, 12H), 1.39-1.30 (m, 18), 0.95 (m, 6H), 0.81-0.77 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ/ppm: 192.4, 167.6, 151.7, 150.2, 149.2, 148.4, 139.1, 138.0, 133.7, 132.0, 131.3, 128.0, 127.7, 123.6, 122.3, 120.7, 40.1, 32.0, 31.9, 31.7, 31.0, 29.9, 29.6, 29.4, 28.1, 22.8, 21.7, 21.6, 14.2, 14.1, 12.5. MALDI-TOF MS (m/z): [M]⁺ calculated for C₈₆H₇₄N₆S₆O₂Zn: 1498.51; found: 1498.75. FT-IR (ATR) υ/cm⁻¹: 2924, 2855, 1700, 1677, 1565, 1500, 1400, 1322, 1234, 1203, 1130, 998, 883, 794, 709.

**1b:** Using the general procedure previously described from 2b (0.04 mmol, 80 mg) in 5 mL of CHCl₃, 3-ethylrhodanine (0.45 mmol, 72 mg). 1b was obtained as a green solid (42 mg, 0.05 mmol, 45% yield). M. p. > 300°C. ¹H NMR (400 MHz, CDCl₃) δ/ppm: 9.58 (d, 4H, J = 4.1 Hz), 8.74 (d, 4H, J = 3.4 Hz), 7.95 (s, 2H), 7.36 (d, 2H), 7.32 (s, 4H), 7.18 (d, 2H, J = 15.4 Hz), 4.22 (d, 4H, J = 6.8 Hz), 3.35, (m, 2H), 3.08 (t, 4H, J = 6.8 Hz), 2.82-2.67 (s, 14H), 2.18 (s, 12H), 1.95-1.85 (m, 14H), 1.67 (t, 4H, J = 5.79 Hz), 1.55 (s, 12H), 1.43-1.26 (m, 30H), 0.97-0.80 (m, 18H), 0.08 (t, 18H, J = 4.3 Hz). ¹³C NMR (100 MHz, CDCl₃) δ/ppm: 192.7, 167.7, 151.9, 151.0, 149.9, 149.0, 145.7, 142.8, 142.6, 139.3, 138.1, 137.8, 131.8, 131.4, 130.9, 128.0, 121.8, 119.3, 101.6, 101.1, 40.2, 32.1, 31.9, 31.9, 31.8, 31.7, 31.4, 31.2, 30.0, 29.6, 29.6, 27.7, 22.9, 22.8, 21.8, 14.5, 14.4, 14.3, 12.6. MALDI-TOF MS (m/z): [M]⁺ calculated for
C_{122}H_{150}N_6O_2S_8Zn: 2050.89; found: 2051.69. FT-IR (ATR) $\nu$/cm$^{-1}$: 2958, 2919, 2850, 1700, 1565, 1496, 1457, 1434, 1392, 1322, 1261, 1230, 1130, 1091, 998, 925, 883, 794, 736.
2. $^1$H NMR, $^{13}$C NMR, FT-IR and MALDI-TOF or MS spectra

Figure S1. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 1a.
Figure S2. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 1a.
Figure S3. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 1b.

Figure S4. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 1b.
Figure S5. FT-IR spectrum of compound 1a.

Figure S6. FT-IR spectrum of compound 1b.
Figure S7. MALDI-MS spectrum of compound 1a (Matrix: Dithranol).
Figure S8. MALDI-MS spectrum of compound 1b (Matrix: Dithranol).
3. Thermogravimetric analysis

**Figure S9.** Thermogravimetric analysis of 1a.

**Figure S10.** Thermogravimetric analysis of 1b.
4. Absorption and emission spectroscopy

![Absorption and emission spectroscopy graph]

**Figure S11.** Normalized UV-Vis absorption spectra of compounds 1a (—) and precursors 2 (···), 2a (→) in dichloromethane.

![Absorption and emission spectroscopy graph]

**Figure S12.** Normalized UV-Vis absorption spectra of compounds 1b (—) and precursors 2 (···), 2b (---) in dichloromethane.
**Figure S13.** Emission spectra of compound 1a (λ<sub>ex</sub> = 417 nm) (—) and normalized UV-Vis absorption spectra of 1a (—) in dichloromethane (10<sup>-5</sup> M).

**Figure S14.** Emission spectra of compound 1b (λ<sub>ex</sub> = 483 nm) (—) and normalized UV-Vis absorption spectra of 1b (—) in dichloromethane (10<sup>-5</sup> M).
5. Cyclic and Square Wave voltammetry plots

Figure S15. Cyclic Voltammetry of compound 1a and 1b (referred to Fc/Fc').
Figure S16. Square Wave Voltammetry of compound 1a and 1b (referred to Fc/Fc⁺).
6. Hole mobility measurement.

Figure S17. Current density vs. Voltage plots for hole mobility measurements of compound 1a and 1b.
The hole mobility was calculated using the Space Charge Limited Current method (SCLC). The IV curves in Figure S17 were then fitted to the following equation:

$$J_{SCLC} = \frac{9}{8} \frac{V_{eff}^2}{d^3} \exp \left( \frac{0.89 \sqrt{V_{eff}}}{d} \right)$$

Where $\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$) is the mobility coefficient, $d$ (cm) is the film thickness, $V_{eff}$ (V) is the applied voltage, $\beta$ (cm$^{1/2}$ V$^{1/2}$) is the Poole-Frenkle factor and $\varepsilon$ ($\varepsilon_0\varepsilon_r \approx 3$) is the media permittivity.

7. Charge Extraction and Transient Photo-Voltage details.

The Charge Extraction method (CE) consist of a LED ring that apply the desired light intensity; devices are connected to a DC power supply and a function generator TGP110 to reach a background illumination from 1 sun to dark. The LEDs are typically turned on for approximately few seconds in order to allow the device to reach steady state conditions without overheating. Devices are placed before LEDs and held at open circuit conditions during the illumination, once steady state is reached, the light is turned off and simultaneously the device is switched to short circuit conditions allowing it to discharge. The Signal is measured in an oscilloscope that registers the drop in voltage between a resistance of 50 Ω. Finally, the voltage drop was converted to current and integrated over time to calculate charge density at every applied bias.
**Figure S18.** Total charge density at different applied potentials of 1a (red) and 1b (green) including geometric capacitance contribution from the electrodes (straight line).

**Transient photovoltage** (TPV) use the same setup as in CE in which the device is held at open circuit under steady state conditions while a small short-lived perturbation to the illumination level is applied to the device. The TPV transients allow the measurement of the lifetime of the charge carrier in a complete device. In TPV measurements, devices are connected to the 1 MΩ input terminal of the oscilloscope and the background illumination was obtained from the same LED ring. The perturbation (10-20 mV) was applied through a light pulse (N₂ laser nominal wavelength, 50 ns pulses). The transients are recorded in the oscilloscope.

The fundamental of this technique is that, at open circuit conditions, a potential is created to the quasi-Fermi levels of the involved materials reaching a steady state; The generated pulse provides an extra amount of charges and consequently an increase of the potential that immediately starts to recombine in a period of time and the potential drops to the initial V_{oc} directly indicating the lifetime of the charge carrier.