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

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Two new conjugated acceptor−donor−acceptor (A−π-D−π-A) compounds having a Zn-porphyrin acting as donor and linked by ethynlenes to one or two units of thienylenevinylene and capped by dicyano-vinylene 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-toll 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...
(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 ethynlenes to one or two units of thienylenevinylene and capped by dicyanovinylene groups as acceptor units. Ethynlenes 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-thiophenecarboxaldehyde (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: 9.98 (s, 1H), 7.19 (d, 1H, J = 4.5 Hz), 8.91 (d, 4H, J = 4.5 Hz), 7.35 (s, 4H), 2.69 (s, 6H, CH3), 1.85 (s, 12H).13C NMR (100 MHz, CDCl3) δ/ppm: 181.2, 150.5, 148.4, 143.0, 89.7, 123.3, 131.5, 134, 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 C35H55IOS2: 546.09; found: 546.28.

2.2.3. (E)-1-(5-formyl-3,4-dihexyl-2-thiophenecarboxaldehyde (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, 132.1, 118.8, 75.5, 32.3, 31.6, 31.5, 31.4, 31.1, 31.0, 29.8, 29.3, 29.3, 27.9, 27.1, 26.4, 22.6, 22.5, 14.1, 14.0. MALDI-TOF MS (m/z): [M]+ calculated for C15H15NO2: 282.27; found: 283.49.

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

To a solution of 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, 49.3 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).

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 (0.6 mL). 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 (151.1 g, 247 mmol, 99% yield).


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 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.
30 min and quenched with acetone. The solvent was removed by rotary evaporation and the solid was purified by column chromatography (silica gel, hexane–CHCl₃, 7:3). The product [5,15-bis-(dodecyl)-10,20-dimesitylporphyrinato] zinc (II) was obtained as a purple solid (1.11 g, 1.45 mmol, 98% yield). ¹H NMR (400 MHz, CDCl₃) δ/ppm: 9.59 (d, 4H, J = 4.6 Hz), 8.71 (d, 4H, J = 4.6 Hz), 7.80 (s, 4H), 2.65 (s, 6H), 1.80 (s, 12H). ¹³C NMR (100 MHz, CDCl₃) δ/ppm: 150.5, 149.9, 139.1, 138.8, 137.6, 133.3, 132.0, 127.7, 122.3, 120.1, 104.1, 55.4, 21.6, 21.4. MALDI-TOF MS (m/z): [M⁺] calculated for C₃₈H₄₈N₄Si₂Zn: 766.73; found: 766.01. FT-IR (ATR) u/cm⁻¹: 1808, 1604, 1423, 1373, 1315, 1207, 972, 850, 786, 740, 694, 628, 609.

2.2.7. Synthesis of [5,15-bis-(trimethylsilyl)ethyl]-10,20-dimesitylporphyrinato] zinc (II) (2)

In a Schlenk tube under an argon atmosphere, a solution of [5,15-dibromo-10,20-dimesitylporphyrinato] zinc (II) (1.14 mmol, 1.10 g) in 62 mL of THF and 3 mL of Et₃N was added over a mixture of Pd₂(dba)₃ (0.6 eq) (658 mg), zinc (II) (87 mg, 0.6 eq) and CuI (417 mg, 0.06 mmol, 81% yield). M. p. 1489, 1483, 1403, 1330, 1284, 1207, 1150, 995, 937, 848, 790, 709.

4b: Using the general procedure previously described, [5,15-bis-(ethyl)]-10,20-dimesitylporphyrinato] zinc (II) (0.34 mmol, 658 mg), 3b (1.02 mmol, 702 mg), 15 mL of Et₃N in 79 mL of THF were allowed to react. 4b was obtained as a green solid (246 mg, 0.14, 71%). ¹H NMR (400 MHz, CDCl₃) δ/ppm: 9.56 (s, 1H), 9.55 (d, 4H, J = 4.6 Hz), 8.73 (d, 4H, J = 4.6 Hz), 7.32 (s, 4H), 7.32 (d, 2H, J = 15.5 Hz), 7.08 (d, 2H, J = 15.5 Hz), 3.05 (t, 4H, J = 7.2 Hz), 2.79 (t, 4H, J = 7.2 Hz), 2.75 (t, 4H, J = 8.3 Hz), 2.68 (s, 6H), 2.66 (t, 4H, J = 7.2 Hz), 1.91 (t, 4H, J = 7.2 Hz), 1.89 (s, 12H), 1.67—1.13 (m, 60H), 1.00—0.91 (m, 18H), 0.80 (t, 6H, J = 7.2 Hz). ¹³C NMR (100 MHz, CDCl₃) δ/ppm: 181.7, 153.1, 151.6, 149.7, 146.8, 145.9, 142.7, 141.9, 139.0, 138.3, 137.7, 137.3, 134.6, 131.5, 131.1, 127.7, 132.5, 121.5, 119.0, 118.9, 101.2, 100.8, 90.7, 32.2, 31.8, 31.7, 31.6, 31.2, 30.9, 29.7, 29.4, 29.3, 29.2, 29.1, 27.5, 27.1, 26.4, 22.7, 22.6, 21.5, 21.4, 14.2, 14.1, 14.0, 13.9. MALDI-TOF MS (m/z): [M⁺] calculated for C₄₂H₄₀N₂O₅Si₂Zn: 1764.92; found: 1765.07. FT-IR (ATR) u/cm⁻¹: 2919, 2854, 2175, 1654, 1592, 1500, 1454, 1388, 1338, 1282, 1207, 1095, 998, 929, 852, 790, 709.

2.2.8. General procedure for the Knoevenagel condensations

To a solution of 2a (1 eq) in 25 mL/mmol of CH₂Cl₂, malononitrile (3 eq) and 3 drops of Et₃N were added. The reaction mixture was stirred for 18 h and quenched by the addition of water and extracted with CHCl₃ (3 × 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, hexane–CH₂Cl₂, 1:1) and recrystallized with CH₂Cl₂:MeOH.

1a: Using the general procedure previously described, 4a (0.08 mmol, 100 mg) in 2 mL of CH₂Cl₂ were added to 15 mL of Et₃N (45 mmol/mmol) in THF (230 mL/mmol) was added over a mixture of Pd₂(dba)₃ (0.6 eq) and AsPh₃ (3.8 eq). The reaction mixture was refluxed for 18 h. The solvent was removed by rotary evaporation and the solid was purified by column chromatography (silica gel, hexane–CH₂Cl₂, 7:3) followed by recrystallization from CH₂Cl₂:MeOH.

4a: Using the general procedure previously described, [5,15-bis(ethyl)]-10,20-dimesitylporphyrinato] zinc (II) (1 eq), the corresponding aldehyde (3a–b) (3 eq) and freshly distilled Et₃N (45 mmol/mmol) in THF (230 mL/mmol) was added over a mixture of Pd₂(dba)₃ (0.6 eq) and AsPh₃ (3.8 eq). The reaction mixture was refluxed for 18 h. The solvent was removed by rotary evaporation and the product was purified by column chromatography (silica gel, hexane–CH₂Cl₂, 7:3) followed by recrystallization from CH₂Cl₂:MeOH.

2.2.8.1. General procedure for the Sonogashira coupling reactions

Under an argon atmosphere, a solution of [5,15-bis-(ethyl)]-10,20-dimesitylporphyrinato] zinc (II) (1 eq), the corresponding aldehyde (3a–b) (3 eq) and freshly distilled Et₃N (45 mmol/mmol) in THF (230 mL/mmol) was added over a mixture of Pd₂(dba)₃ (0.6 eq) and AsPh₃ (3.8 eq). The reaction mixture was refluxed for 18 h. The solvent was removed by rotary evaporation and the solid was purified by column chromatography (silica gel, hexane–CH₂Cl₂, 7:3) followed by recrystallization from CH₂Cl₂:MeOH.

4a: Using the general procedure previously described, [5,15-bis(ethyl)]-10,20-dimesitylporphyrinato] zinc (II) (1 eq), the corresponding aldehyde (3a–b) (3 eq) and freshly distilled Et₃N (45 mmol/mmol) in THF (230 mL/mmol) was added over a mixture of Pd₂(dba)₃ (0.6 eq) and AsPh₃ (3.8 eq). The reaction mixture was refluxed for 18 h. The solvent was removed by rotary evaporation and the solid was purified by column chromatography (silica gel, hexane–CH₂Cl₂, 7:3) followed by recrystallization from CH₂Cl₂:MeOH.
trimethylsilyl porphyrin 2. The trimethylsilyl group was quantitatively removed by hydrolysis with TBAF and, without further purification, reacted with the corresponding iodoaldehyde 3a, b under Pd-catalyzed Sonogashira coupling conditions to afford the bisaldehydes 4a, b in 81% and 71% yields, respectively. The 1H NMR spectra of 4a, b show the expected signals for both the porphyrin and the thiénylenevinylene moieties and the aldehyde protons are observed at 9.16 ppm and 9.56 ppm, respectively. Compound 4a, only showed the trans configuration of the double bond, which was confirmed by a coupling constant of 15.6 Hz. Finally, the target compounds 1a, b were obtained by Knoevenagel condensations of 4a, b with malononitrile in the presence of triethylamine in 81% and 79% yields, respectively. In the 1H NMR spectra of 1a, b, the aldehyde hydrogen signals are not observed and new vinylic hydrogens signals were observed at 7.89 ppm and 7.69 ppm, respectively, indicating the successful condensation. The mass spectrum showed the expected signals for both the porphyrin and the thienylenevinylene moieties and the aldehyde protons are observed at 9.16 ppm and 9.56 ppm, respectively. Compound 4b, which was prepared by the reaction of 3a, b with molecular iodine (I₂), and bistri fluorooacetoxiyiodobenzene (PhI(OCOCF₃)₂) in 84% and 62% yield according to Scheme 2 [35].

All compounds were satisfactorily characterized by 1H and 13C NMR, FT-IR and MALDI-MS spectrometry (see the Experimental section and the Supporting information for synthetic details and full analytical and spectroscopic characterizations).

The thermal stabilities of compounds 1a and 1b were evaluated by thermogravimetric analysis (TGA). Compounds 1a, b display excellent thermal stabilities up to 300 °C with Td of 369 °C and 374 °C for 1a and 1b, respectively (Fig. S29), which are appropriate for photovoltaic applications.

### 3.2. Optical properties

The optical properties of 1a and 1b in CH₂Cl₂ solutions as well as of their thin-films are shown in Fig. 1 and the characteristics of semiconductors 1a and 1b are collected in Table 1. The UV–Vis absorption spectra of the precursor aldehydes (4a, b) and of the final compounds 1a, b in solution exhibit a panchromatic absorption in the visible region. These spectra show the Soret band (λ_max = 465 nm and 499 nm respectively) bathochromically shifted, with respect to the Soret band in the precursor porphyrin 2 (λ_max = 435 nm, Fig. S30). New intense broad bands are observed at λ_max = 668 nm for 4a and 698 nm for 4b, assigned to intra-molecular charge transfer (ICT) (Fig. S30). In solution, 1a and 1b show absorption ranges from 400 nm to 750 nm with a valley centered at 600 nm. The introduction of the malononitrile fragments (1a, b) lead to a bathochromic shift of both bands (λ_max = 499 and 698 for 1a and 497 and 705 nm for 1b) with respect to the corresponding aldehydes (4a, b) as a consequence of the extension of the conjugation and due to the strong electron-withdrawing properties of the dicyanomethylene. Increasing the π-conjugation upon increasing the length of the thiénylenevinylene in 1b results in a wider absorbance.

In the solid state, the absorption maximum for 1a is bathochromically shifted relative to those in solution, by 13 nm. 1b shows a pronounced absorbance between of 400–850 nm, with a red-shifted maximum of 33 nm (764 nm). These results suggest that the extended backbone in 1b results in stronger intermolecular π–π stacking interactions than in 1a (Fig. 2). The estimated optical band gaps were calculated from the thin film absorbance onsets, and were 1.57 eV for 1a and 1.50 eV for 1b.

The fluorescence spectra display a red-shift of the emission band for compound 1b in comparison to that for 1a, around 30.2 nm, due
to the increased conjugation by one more thienylenevinylene unit. If the emission spectra compounds 1a, b are compared with those of the precursor aldehydes 4a, b (Fig. S33), a significant quenching of the emission is observed, attributed to more efficient electron transfer processes.

3.3. Electrochemical properties

The electrochemical properties of 1a and 1b were investigated using Cyclic Voltammetry (CV) and Osteryoung Square Wave Voltammetry (OSWV) in o-DCB:acetonitrile (4:1) (Table 1, Fig. 3 and S34). In the anodic scan, both compounds show a first reversible one-electron oxidation wave at 0.40 V for 1a (Fig. 4) and 0.26 V for 1b (vs Fe/Fe⁺ in all cases) which correspond to the first oxidation of the porphyrin. For 1b, the extended conjugation gives rise to a decrease of the $E_{\text{ox}}$ value by 14 mV with respect to 1a. A second reversible oxidation wave is observed at 0.78 V for 1a and at 0.62 V for 1b. Compound 1b shows two more non-reversible oxidation waves at 0.93 and 1.02 V. The estimated $E_{\text{HOMO}}$ values were calculated with respect to ferrocene as reference ($E_{\text{HOMO}}$: −5.1 eV [40]) and were determined to be −5.50 eV for 1a and −5.36 eV for 1b, in good agreement with the onset oxidation potentials.

Low-lying HOMO levels should result in high open-circuit voltages ($V_{\text{oc}}$) and are, therefore, desired [41–43]. The HOMO – LUMO gaps, optically determined, are as narrow as 1.75 and 1.69 eV for 1a and 1b, respectively. The $E_{\text{LUMO}}$ of the dyes are higher than that of PCBM (−3.9 eV), with values of −3.75 and −3.67 eV for 1a and 1b, respectively. Hence, the LUMO energy levels of these small-molecules match quite well the LUMO energy of PC61BM (−3.9 eV) and PC71BM (−4.0 eV), which suggest an energetically favorable electron transfer from 1a and 1b to the acceptor moiety that should in turn favor the exciton dissociation.

3.4. Theoretical calculations

Theoretical calculations were carried out by density functional (DFT) at the B3LYP 6-31G* level in vacuo using Gaussian 03W to determine the more stable geometries for both dyes 1a and 1b (Fig. 4), the HOMO and LUMO energy levels and their molecular orbital contours.

The optimized structure of both 1a and 1b, show that the core is almost perfectly flat, with the aryl groups bounded to the porphyrin core being perpendicular to the macrocycle (dihedral angle of 90°), while the thienylenevinylene fragments are almost in the same plane with respect to the porphyrin rings with a dihedral angle

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Table 1

<table>
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<th>$\lambda_{\text{max}}$ soln (nm)</th>
<th>log (ε)</th>
<th>$\lambda_{\text{max}}$ film (nm)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>$E_{\text{1ox}}$ (V)</th>
<th>$E_{\text{HOMO}}$ (eV)</th>
<th>$E_{\text{LUMO}}$ (eV)</th>
<th>$E_{0-e^-}$ (eV)</th>
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<td>747</td>
<td>0.26</td>
<td>−5.36</td>
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</tr>
</tbody>
</table>

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10 M, in dichloromethane.

10 M in ODCB:acetonitrile (4:1) versus Fe/Fe⁺ ($E_{\text{ox}}$ = 0.04 V) glassy carbon, Pt counter electrode, 20 °C, 0.1 M Bu4NClO4, scan rate = 100 mV s⁻¹.

Nonreversible processes.

c Calculated with respect to ferrocene, $E_{\text{HOMO}}$: −5.1 eV [40].

$e$ Estimated from the intersection between the normalized absorption and normalized emission spectra at $\lambda_{\text{max}}$.  

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Fig. 2. Normalized UV–Vis spectra of 1a (a) and 1b (b) in DCM solution (black line) and in thin films (red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. CV plot of compound 1a.
around 0.5°. This planarity allows an extension of the conjugation between the porphyrin and the dicyanovinylene fragments. The bond lengths of the π-conjugated bridge between the porphyrin and the acceptor units are around 1.40 Å, both for single and double bonds, revealing a quinoid character. This fact suggests some zwitterionic contribution to the ground state.

The distribution of the orbital coefficients of the HOMO and LUMO states (Fig. 5) show that the charge density of the HOMO of 1a and 1b is delocalized over the whole conjugated system, the porphyrin and thienylenevinylene moieties. Similar to the HOMO, the LUMO spreads over the π-conjugated system. Since both orbitals, HOMO and LUMO (Fig. 5) are somewhat overlapped, this favors the HOMO to LUMO electronic transitions.

The theoretical HOMO – LUMO gaps are similar for both dyes, being slightly lower for compound 1b (ΔE = 1.72 eV) than for 1a (ΔE = 1.87 eV). This fact is mainly due to the more extended conjugation, increasing the HOMO level in 1b and is related to the bathochromic shift of the maximum absorption wavelength of compound 1b with respect to that for dye 1a (according with the experimental data), which shows the light harvesting behavior. Finally, the offset between the LUMO of the donor (1a or 1b) and the LUMO of the acceptor (PC61BM or PC71BM) [41], from 0.54 eV to 1.01 eV, ensures efficient exciton dissociation at the D/A interface.

### 3.5. Photovoltaic properties

To explore the potential photovoltaic (PV) properties of 1a and 1b, solar cells were fabricated using the conventional sandwich structure of ITO/poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS)/small molecule: acceptor/Ca/Al. The active layer was spin-coated from chlorobenzene solutions. The ratio of 1a and 1b to PC61BM was adjusted, ranging from 1:1 to 1:4 (w/w), and the optimized value was found to be 1:2 for both of them. The optimized ratio was employed in a blend of 1a and 1b with PC71BM. The photovoltaic devices were measured under an ambient atmosphere employing AM1.5G simulated illumination at an intensity of 100 mW/cm². The current density voltage (J–V) characteristics and the external quantum efficiency (EQE) for the conventional device are shown in Fig. 6a–d and the performance parameters are summarized in Table 2 as a function of the weight ratios of Donor:PC61BM.

Fig. 6b and d illustrates the best photovoltaic performances at varying D/A ratios. Photovoltaic devices containing 1a:PC61BM exhibited high Voc (0.86 V) at the optimized blend ratio of 1:2 w/w, with a short circuit current (Jsc) of 5.72 mA cm⁻², and a fill factor (FF) of 28.4% for an average PCE of 1.45%. Increasing as well as decreasing the amount of PC61BM resulted in a lower PCE. In contrast, photovoltaic devices incorporating a blend of 1b and PC71BM.

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**Fig. 4.** Optimized geometries of dyes 1a and 1b.

**Fig. 5.** Electronic density contours and energy levels for HOMO – 1, HOMO, LUMO, and LUMO + 1 calculated at the B3LYP/6-31G** level for dyes 1a and 1b compared with the energy levels of the PC61BM and PC71BM frontier orbitals.
PC61BM exhibited an average PCE of 2.70%, with a Voc of 0.82 V, FF of 35.2% and a noteworthy Jsc of 9.79 mA cm⁻², because of its more efficient light absorbing properties. Average values were taken from 12 devices. The high values observed for the Voc using 1a are in agreement with the deeper HOMO level of 1a (−5.50 eV) vs 1b (−5.36 eV). The electron acceptor (PC61BM) was replaced by PC71BM due to the broader absorbance and the higher extinction coefficient of the latter in the visible range. SMBHJ devices were fabricated with an architecture of ITO/PEDOT:PSS/1b or 1a:PC71BM (1:2 w/w)/Ca/Al. Photovoltaic devices based on 1b and PC71BM yielded an increased PCE of 3.21%, a remarkable 14% improvement, with an average Jsc of 10.83 mA cm⁻², Voc of 0.82 V and a slightly

### Table 2

Summary of the photovoltaic performance of 1a and 1b blended with PC61BM and PC71BM under the illumination of AM1.5G, 100 mW/cm².

<table>
<thead>
<tr>
<th>Active layer</th>
<th>Voc (V)</th>
<th>Jsc (mA cm⁻²)</th>
<th>FF (%)</th>
<th>PCE [highest] (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a:PC61BM (1:4)</td>
<td>0.78 ± 0.03</td>
<td>5.38 ± 0.33</td>
<td>27.8 ± 0.27</td>
<td>1.16 ± 0.1 [1.26]</td>
</tr>
<tr>
<td>1a:PC61BM (1:2)</td>
<td>0.86 ± 0.01</td>
<td>5.67 ± 0.12</td>
<td>28.1 ± 0.22</td>
<td>1.36 ± 0.1 [1.48]</td>
</tr>
<tr>
<td>1a:PC61BM (1:1)</td>
<td>0.63 ± 0.02</td>
<td>4.62 ± 0.13</td>
<td>29.1 ± 0.21</td>
<td>0.84 ± 0.1 [0.91]</td>
</tr>
<tr>
<td>1b:PC61BM (1:4)</td>
<td>0.79 ± 0.03</td>
<td>8.41 ± 0.21</td>
<td>33.2 ± 0.29</td>
<td>2.21 ± 0.1 [2.34]</td>
</tr>
<tr>
<td>1b:PC61BM (1:2)</td>
<td>0.82 ± 0.02</td>
<td>9.44 ± 0.26</td>
<td>35.0 ± 0.22</td>
<td>2.70 ± 0.1 [2.82]</td>
</tr>
<tr>
<td>1b:PC61BM (1:1)</td>
<td>0.84 ± 0.02</td>
<td>5.84 ± 0.30</td>
<td>27.3 ± 0.21</td>
<td>1.35 ± 0.1 [1.48]</td>
</tr>
<tr>
<td>1a:PC71BM (1:2)</td>
<td>0.84 ± 0.01</td>
<td>5.56 ± 0.12</td>
<td>26.4 ± 0.20</td>
<td>1.24 ± 0.1 [1.34]</td>
</tr>
<tr>
<td>1b:PC71BM (1:2)</td>
<td>0.82 ± 0.01</td>
<td>10.83 ± 0.24</td>
<td>35.7 ± 0.24</td>
<td>3.16 ± 0.1 [3.21]</td>
</tr>
</tbody>
</table>

PC61BM due to the broader absorbance and the higher extinction coefficient of the latter in the visible range. SMBHJ devices were fabricated with an architecture of ITO/PEDOT:PSS/1b or 1a:PC71BM (1:2 w/w)/Ca/Al. Photovoltaic devices based on 1b and PC71BM yielded an increased PCE of 3.21%, a remarkable 14% improvement, with an average Jsc of 10.83 mA cm⁻², Voc of 0.82 V and a slightly

### Fig. 6

EQE and J–V characteristics of the SMBHJ for 1a and 1b blending with PC61BM at different ratios.

### Fig. 7

EQE (a) and J–V (b) characteristics of the SMBHJ for 1b blending with PC61BM and PC71BM in a 1:2 ratio.
improved FF (Fig. 7). Surprisingly, no improvement was observed employing 1a:PC71BM (1:2 w/w) as the photoactive layer (see Fig. S36). In order to support the performances of the above devices, incident photo-to-current efficiency (IPCE) measurements were also conducted. As shown in Fig. 6b, the IPCE response of 1a with PC61BM covers the visible spectrum ranging from 300 nm to 800 nm, which matches the absorption spectra. The devices incorporating 1b exhibited more efficient photoconversion efficiency than those based on 1a, due to broader and higher IPCE response in the 300–600 nm range. Therefore, the addition of an extra unit of thienylenevinylene leads to a stronger light-harvesting small-molecule which results in a significant improvement in the power conversion efficiency. In addition, the IPCE values were further improved for a 1b:PC71BM blend with a remarkable IPCE of 60% at 427 nm (Fig. 7). The theoretical $J_{sc}$ values integrated from the EQEs are in good agreement with those experimentally observed in all cases (±5% mismatch).

Inspecting the morphology of the photoactive layers by atomic force microscopy using the tapping mode (AFM) provided some explanation for lower power conversion efficiencies obtained for the photovoltaic devices [44] incorporating 1a and 1b when blended with PC61BM and PC71BM (Fig. 8). The topography images for PC61BM and PC71BM reveal the formation of coarse morphologies with faceted islands features showing a root-mean-square roughness (rms) of 1.9 and 1.7 nm, respectively. Large aggregates of several hundred nanometers were observed which limit the exciton dissociation efficiencies and the charge transport, explaining the lower FF and $J_{sc}$ values measured for these devices. On the other hand, the surface morphology of devices containing 1b:PC71BM and 1b:PC71BM exhibit a smoother surface topography (rms of 1.0 and 0.9 nm, respectively) with smaller aggregate sizes indicating better morphological features for exciton dissociation at the donor–acceptor interfaces, which correlate with the higher FF and $J_{sc}$ and higher power conversion efficiencies observed.

4. Conclusions

In conclusion, we have synthesized two new conjugated acceptor–donor–acceptor ($A−\pi−D−\pi−A$) compounds having a Zn-porphyrin acting as donor and linked by ethynlenes to one or two units of thienylenevinylene and capped by dicyanovinylene groups as acceptor units. Incorporation of electron-accepting dicyanovinylene moieties through the thiophene based bridges shift the absorption profiles bathochromically to the NIR due to an intense intramolecular charge transfer band. 1a and 1b exhibit not only excellent light harvesting properties but also thermal stability and low-lying HOMO levels at $−5.50$ and $−5.36$ eV. Photovoltaic devices incorporating 1b blended with PC71BM displayed a moderate PCE of 3.21% compared to that of 1a (PCE of 1.4%). Extension of the conjugation in 1b results in a significantly much higher $J_{sc}$ and FF compared to that of 1a. In order to chase higher efficiencies, further variations in the molecular structure are currently underway in our laboratories.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2015.04.037.

References