Simple BODIPY dyes as suitable electron-donors for organic bulk heterojunction photovoltaic cells

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\textbf{ABSTRACT}

In this work we present the synthesis and characterization (including the report of two new crystal structures) of a series of \textit{meso}-substituted boron-dipyrromethene (BODIPY) molecules. With an accessible synthesis, these simple BODIPYs have characteristics that par with those BODIPY's having more complex structures, what makes them very interesting materials for industrial production. The photovoltaic performance of the synthesized BODIPY's was evaluated in bulk heterojunction organic solar cells, where they were used as electron-donors. We found that the presence of electron-withdrawing groups has a detrimental effect on the photovoltaic performance, while the \textit{meso}-free structure shows an improved efficiency in comparison with the \textit{meso}-substituted BODIPYs. We also studied the origin of the \textit{meso}-unsubstituted derivative, elucidating at least one of its formation processes, which can open a new way of BODIPY synthesis.

1. Introduction

The photovoltaic market is still ruled by the silicon-based solar cells due to their good efficiency and high stability, supported by the well-established modern inorganic semiconductors technology \cite{1,2}. However, high costs, prospects for building integration and environmental concerns about this industry have driven the research into alternative organic photovoltaic technologies, such as, dye-sensitized solar cells and fully organic photovoltaic cells (OPVs). In fact, OPV are now emerging as one of the most viable alternatives due to their low-cost production, mechanical flexibility and lightweight \cite{2–4}.

The organic photovoltaic effect starts by sunlight absorption that promotes electron excitations of the organic material (absorber) forming excitons (bound electron-hole pairs). In order to generate free charges (free electrons and holes) those excitons need to be split. This splitting is achieved by combination with another material that has an adequate energy offset of the frontier orbitals (HOMO and LUMO). The combination of such materials can be made in a bi-layer or in a blend (commonly known as bulk heterojunction (BHJ)), which is the most used approach. Its main particularity is that the active layer presents an interpenetrated biphatic network of the electron-donor and the electron-acceptor organic semiconductors \cite{5,6}.

Many new small molecules and conjugated polymers have been designed and developed for organic solar cells. Initially, polymers were the most tested and efficient materials, but today solar cells based on small molecules show similar, or even better performance, than those based on polymers \cite{7}. Small molecules show smaller batch-to-batch variations and well-defined absorptions spectra due to their uniform and defined molecular structures.

Boron-dipyromethene (BODIPY) molecules constitute an important class of visible light absorbing dyes, with a wide variety of applications \cite{8–14}. BODIPYs are auspicious photosensitizer materials for OPVs due to their properties, such as photochemical and chemical stability, high molar absorption coefficients, excitation/emission wavelengths in the visible and NIR spectral region, good solubility in inorganic solvents and ease of functionalization \cite{15–17}. Despite this, research efforts still remain at a low level if compared with other pyrrolic small molecules like porphyrins or phthalocyanines.

In fact there is a relatively low number of published works relating BODIPY with OPV systems \cite{9,10}. Since the first published data on BODIPY with OPVs in 2009 \cite{18}, there are only a few reports showing power conversion efficiencies (PCE) above 3\% \cite{9,10}, being the highest PCE reported for BODIPY small molecule-based photovoltaic cells of 7.2\% \cite{19}. Generally, the BODIPYs used in OPV are complex α- or β-
functionalized BODIPYs and the most used methods to prepare such derivatives are either the Sonogashira reaction or the Suzuki coupling [20–23]. The preparation of those BODIPYs involves several synthetic steps that increase the cost of the final product. On the other hand, “simple” BODIPYs i.e. BODIPY made in a one pot reaction without any post-functionalization were never reported as electron-donor and, consequently, their photovoltaic performance was not yet described.

In this work, we present the synthesis, characterization and application as electron-donor materials in OPVs of a series of very simple meso-substituted BODIPYs made in a one-pot process. This work demonstrates that simple BODIPYs can achieve very high open circuit voltages and we propose that these results can be used as “standards” for more complex BODIPYs in order to avoid elaborated synthesis that do not bring significant PCE improvements. We also clarified the appearance of a common contaminant in most of the previously reported BODIPY’s synthesis. The isolation of that BODIPY by-product (meso-free BODIPY) allowed us to discover that its photovoltaic properties are significant, and consequently, it is possible that previous studies may have been unintentionally disturbed by this contaminant. Our findings on the origin of this meso-free BODIPY may be used in a new synthetic method (acid free/aldehyde free) for BODIPYs.

2. Experimental

2.1. Materials and reagents

Reagents and solvents were obtained from Sigma-Aldrich and used without further purification. Solvents for photophysical studies were HPLC grade (CHROMASOLV plus) purchased from Sigma-Aldrich. Analytical thin layer chromatography (TLC) was performed on Merck silica gel plates with F-254 indicator. For visualization, a twin wavelength ultraviolet lamp (254 and 365 nm) was used. Silica gel column chromatography was carried out with silica gel (230–400 mesh) from Fluka.

2.2. Equipments

Reagents and solvents were obtained from Sigma-Aldrich and used without further purification. Solvents for photophysical studies were HPLC grade (CHROMASOLV plus) purchased from Sigma-Aldrich. The fullerene PC60BM was purchased from Sigma-Aldrich. Analytical thin layer chromatography (TLC) was performed on Merck silica gel plates with F-254 indicator (Merck). Visualization was accomplished by a twin wavelength ultraviolet lamp (254 and 365 nm). Silica gel column chromatography was carried out with silica gel (230–400 mesh) from Fluka.

The isolation of that BODIPY by-product (meso-free BODIPY) allowed us to discover that its photovoltaic properties are significant, and consequently, it is possible that previous studies may have been unintentionally disturbed by this contaminant. Our findings on the origin of this meso-free BODIPY may be used in a new synthetic method (acid free/aldehyde free) for BODIPYs.

Table 1

<table>
<thead>
<tr>
<th>Solvent</th>
<th>TFA</th>
<th>BDP6 yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3Cl</td>
<td>yes</td>
<td>4%</td>
</tr>
<tr>
<td>CH3C2H5</td>
<td>no</td>
<td>4%</td>
</tr>
<tr>
<td>CH3I</td>
<td>no</td>
<td>8%</td>
</tr>
<tr>
<td>CH3Br</td>
<td>no</td>
<td>4%</td>
</tr>
</tbody>
</table>

Automatically corrected for the wavelength response of the system. Fluorescence quantum yields were calculated by a comparative method using rhodamine 6G (Φf (470–555 nm) = 0.88 in ethanol) as reference. Cyclic voltammetric (CV) measurements were carried out with a computer controlled Ivium Compact Stat, with a one-compartment three electrode system consisting of a glassy carbon electrode (GCE) (geometric area of 0.00785 cm²) as working electrode, a platinum wire as counter electrode and an Ag/AgCl (3 M KCl) reference electrode, at a scan rate of 50 mVs⁻¹. Tetrabutylammonium tetrafluoroborate (TBAFBF, 0.1 M) in dichloroethane was used as supporting electrolyte. The results were calibrated using a 1 mM ferrocene/ferrocenium (Fc/Fc⁺) redox couple as internal standard. It is assumed that the redox potential of Fc/Fc⁺ has an absolute energy level of −4.80 eV to vacuum. CV experiments were carried out using 1 mM concentrations of each BODIPY.

UV/Vis absorption spectra of the films were recorded in a Cecil 7200 spectrophotometer. The HOMO/LUMO calculations were performed with the basis set split valence, increased with polarization function type (d) 6-31G*. Lorenz and polarization corrections were applied. A multi-scatter absorption correction was applied using SADABS [25]. The structure was solved by direct methods using SHELXS-97 program and refined on F2s by full-matrix least-squares with SHELXL-97 program [26]. The anisotropic displacement parameters for non-hydrogen atoms were applied. The hydrogen atoms were placed at calculated positions and refined with isotropic parameters as riding atoms. One of the two non-equivalent molecules of BDP4 shows signs of disorder and DFIX constraints had to be used.

Film thicknesses were measured with a Dektak 6 M profilometer. The surface topography of the films was characterized by Atomic Force Microscopy using a Nano Observer Microscope from Concept Scientific Instruments (Les Ulis, France). All images were taken with 256 x 256 pixels resolution and processed with Gwyddion (version 2.26) software.

The photovoltaic devices were prepared on glass substrates coated with 100 nm thick indium-tin oxide (ITO), cleaned under ultrasonics with distilled water and a non-ionic detergent (Derrqm Im 02 neutral phosphate free) followed by washing with distilled water, acetone, isopropanol alcohol and then dried under a N2 stream. The ITO surface was then treated with UV-oxygen plasma for 3 min prior to depositing, by spin coating, a 40 nm layer of poly (3,4-ethylenedioxythiophene):polystyrene sulfonic acid (PEDOT:PSS) (Clevios P VP.AI 4083, from Heraeus), which was then dried on a hot plate at 125 °C for 10 min. The solutions of the blends were spin-coated (1300 rpm, 60 s) on top of the PEDOT:PSS in air. Following the spin coating of the active layers, Ca (20 nm) and Al (80 nm) were thermally evaporated on top, under a base pressure of 10⁻⁶ mbar, defining a device area of 0.24 cm². The current-voltage curves of the photovoltaic cells were measured under inert atmosphere (N2) using a Keithley 2400 Source-Meter unit. The curves under illumination were measured with a solar simulator with simulated AM1.5G illumination at 88 mW/cm² (Oriel Sol 3A, 69920, Newport). At least 16 devices of each series were prepared. The light intensity of the solar simulator was verified using a calibrated solar cell.

External quantum efficiency (EQE) spectra were obtained under short-circuit conditions, using a homemade system with a halogen lamp as light source.
source coupled to a monochromator. Its intensity at each wavelength was determined using a calibrated photodiode. The short-circuit current was measured with a Keithley 2400 Source-Meter.

2.3. Synthesis

BDP1, BDP2, BDP3, BDP4 and BDP5 were prepared according to procedures described previously, using benzaldehyde, 4-formylbenzoic acid, pentafluorobenzaldehyde, 4-nitrobenzaldehyde and 9-anthracencarboxyaldehyde, respectively, as the aldehyde reagents [27].

Table 2

Oak Ridge Thermal Ellipsoid Plot (ORTEP) drawing of the molecular structures Ellipsoids at 50% probability level of the BDP4 and BDP5 structures and crystal data details. Hydrogen atoms were omitted for clarity reasons.

<table>
<thead>
<tr>
<th>Crystal data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
</tr>
<tr>
<td>M.</td>
</tr>
<tr>
<td>Crystal system, space group</td>
</tr>
<tr>
<td>Temperature (K)</td>
</tr>
<tr>
<td>a, b, c (Å)</td>
</tr>
<tr>
<td>a, b, c (Å)</td>
</tr>
<tr>
<td>V(Å³)</td>
</tr>
<tr>
<td>Z</td>
</tr>
<tr>
<td>Radiation type</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
</tr>
</tbody>
</table>

Table 3

Conformation of the ethyl groups, length of the bond between the meso-carbon and the substituent and the dihedral angle between the least-squares plane of the substituent and that of the central core.

<table>
<thead>
<tr>
<th>Entries</th>
<th>Conformation</th>
<th>Bond length (Å)</th>
<th>Dihedral angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIDLIP [32]</td>
<td>trans</td>
<td>1.514 (3)</td>
<td>89.41 (8)</td>
</tr>
<tr>
<td>UNIFIG [33]</td>
<td>trans; cis; trans</td>
<td>1.478(10); 1.515(10); 1.475 (10)</td>
<td>78.22(2); 78.8(2); 84.5(2)</td>
</tr>
<tr>
<td>BDP4</td>
<td>trans; trans</td>
<td>1.486(3); 1.482(3)</td>
<td>87.87(6); 89.89(7)</td>
</tr>
<tr>
<td>BDP5</td>
<td>trans</td>
<td>1.495 (2)</td>
<td>89.99 (5)</td>
</tr>
<tr>
<td>XODGUT [29]</td>
<td>cis</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Scheme 1. General procedure for the preparation of the BODIPY series: i) TFA; ii) DDQ; iii) diisopropylethylamine, BF₃.O(C₂H₅)₂.

Scheme 2. Synthesis of BDP1 using α,α-dichlorotoluene and α,α-di-bromotoluene (1 mmol of 3-ethyl-2,4-dimethylpyrrole, 1 eq. of DDQ and 17 eq. of boron trifluoride etherate and 12 eq. diisopropylamine).
without aldehyde. Further details on the synthesis of BDP6 are presented in Table 1. For the BDP2, BDP3 and BDP4 preparation reaction, the residue was chromatographed on silica gel using CH2Cl2/petroleum ether (1:1) as eluent to separate BDP6 from the others. Preparative thin layer chromatography is necessary to separate BDP6 from BDP1 or BDP5. We used toluene as eluent and 20×20 cm silica gel 60 plates, with fluorescent indicator at 254 nm, from Fluka.

**BDP1**: Yield 18% (BDP1) 5% (BDP6); 1H NMR (400 MHz, CDCl3) (Electronic Supplementary Information (ESI) Fig. S2) δ (ppm): 7.49–7.45 (m; 3H); 7.30–7.26 (m; 2H); 2.53 (s, 6H); 2.30 (q, J = 8 Hz, 4H), 1.26 (s, 6H), 0.98 (t, J = 8 Hz, 6H); 19F NMR (376 MHz, CDCl3) (ESI Fig. S3) δ (ppm): 145.80 (q, J = 33.8 Hz, 2F); 13C NMR (100 MHz, CDCl3) (ESI Fig. S4) δ (ppm): 156.15; 144.2 (d, J = 250.52 Hz), 141.94 (d, J = 262 Hz); 138.19 (d, J = 257.86 Hz); 136.58; 133.91; 130.36; 121.16; 110.32 (d, J = 14.4 Hz, 403 Hz); 17.09; 14.54; 12.74 (t, J = 2.57 Hz); 10.85. HRMS (ESI Fig. S22) m/z [M + H]+ calculated for C24H14BF3N2O2+: 426.2159; Found: 421.2162; BDP5: Yield 13% (BDP5) 6% (BDP6); 1H NMR (400 MHz, CDCl3) (ESI Fig. S14) δ (ppm): 8.56 (s, 1H), 8.03 (dd, J = 8.7, 1.0 Hz, 2H); 7.45 (m, 4H); 6.94 (s; 1H); 2.60 (s, 6H); 2.16 (q, J = 8 Hz, 4H), 0.89 (t, J = 8 Hz, 6H) 19F NMR (376 MHz, CDCl3) (ESI Fig. S15) δ (ppm): 145.57 (q, J = 33.8 Hz, 2F); 13C NMR (100 MHz, CDCl3) (ESI Fig. S16) δ (ppm): 154.02; 138.14; 132.70; 131.35; 129.94; 129.27; 129.05; 128.29; 128.03; 127.67; 125.71; 125.51; 17.02; 14.58; 12.66; 10.54. HRMS (ESI Fig. S24) m/z [M + H]+ calculated for C31H29BF3N2O2+: 481.2621; Found: 481.2624; BDP6: 1H NMR (400 MHz, CDCl3) (ESI Fig. S17) δ (ppm): 6.94 (s; 1H); 2.49 (s, 6H); 2.37 (t, J = 8 Hz, 4H), 2.16 (s, 6H), 1.06 (t, J = 8 Hz, 6H); 19F NMR (376 MHz, CDCl3) (ESI Fig. S18) δ (ppm): 146.31 (q, J = 33.8 Hz, 2F); 13C NMR (100 MHz, CDCl3) (ESI Fig. S19) δ (ppm): 153.63; 135.62; 131.40; 130.60; 117.55; 16.26; 13.56; 11.51 (t, J = 2.20 Hz); 8.35. HRMS (ESI Fig. S25) m/z [M + H]+ calculated for C17H23BF3N2+: 305.1995; Found: 305.2000; 3. Results and discussion

3.1. Synthesis

The series of BODIPYs presented in Scheme 1 was synthesized by the common method of acid catalyzed condensation of aromatic aldehydes and α-free-pyrroles, followed by the DDQ oxidation step and finished with the complexation with boron trifluoride, in the presence of a base [9,15,27].

All HPLC analyses for purity assessment were performed on a C18 reversed phase column (80% of acetonitrile and 20% of water, under 0.8 ml/min flux). As expected, the most hydrophilic compound BDP2, is the one with the lowest retention time (tR), while BDP5, the most aromatic compound, is the one with the highest tR (ESI Fig. S1). All BODIPYs were synthesized with reasonable yields and isolated with a purity level above 99%.
3.2. Anomalous meso-free BODIPY presence

In the synthesis of all meso-substituted BODIPYs (BDP1-5), the BDP6 was isolated as a by-product in yields ranging from 2% to 6%. This peculiarity was already reported but never explained [28,29]. In fact, the BDP6 by-product can be easily masked by the main BODIPY in terms of visible spectroscopy, but by HPLC it is possible to identify both, and then isolate them, either by column chromatography or preparative thin layer chromatography. This contamination is particularly evident in the synthesis of BDP1 and BDP5, having a direct influence on the lower yields of these BODIPYs due to the consumption competition of pyrrole units with the BPD6 synthesis. Due to its almost identical photophysical properties, BDP6 contamination must be taken seriously on photovoltaic studies, but this has not been referenced in almost all previously reported studies using BODIPYs made by the acid condensation of aldehydes and α-free-pyrroles.

We investigated the possibility of BDP6 result from the reaction of the α-free-pyrrole with the solvent (CH2Cl2). Table 1 shows a few reaction conditions, all without the aldehyde reagent, to study the influence of the solvent on BDP6 formation. In fact, it was possible to synthesize and isolate BDP6 in the total

Table 4
Photophysical properties of the BODIPY series.

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Solvent</th>
<th>λabs (nm)</th>
<th>ε (cm⁻¹ M⁻¹)</th>
<th>λem (nm)</th>
<th>ɸF</th>
<th>SS (cm⁻¹)</th>
<th>Δλ (nm)</th>
<th>E_g (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDP1</td>
<td>Chloroform</td>
<td>525</td>
<td>548</td>
<td>538</td>
<td>98%</td>
<td>460</td>
<td>13</td>
<td>2.28</td>
</tr>
<tr>
<td>Hexane</td>
<td>524</td>
<td>535</td>
<td>388</td>
<td>11</td>
<td>2.28</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>520</td>
<td>533</td>
<td>468</td>
<td>13</td>
<td>2.29</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BDP2</td>
<td>Chloroform</td>
<td>530</td>
<td>539</td>
<td>537</td>
<td>71%</td>
<td>498</td>
<td>14</td>
<td>2.26</td>
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<td>526</td>
<td>539</td>
<td>452</td>
<td>13</td>
<td>2.25</td>
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<tr>
<td>Acetonitrile</td>
<td>520</td>
<td>533</td>
<td>468</td>
<td>13</td>
<td>2.29</td>
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<td></td>
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<tr>
<td>BDP3</td>
<td>Chloroform</td>
<td>544</td>
<td>551</td>
<td>558</td>
<td>98%</td>
<td>461</td>
<td>14</td>
<td>2.19</td>
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<td>543</td>
<td>555</td>
<td>398</td>
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<td>530</td>
<td>542</td>
<td>539</td>
<td>6%</td>
<td>315</td>
<td>9</td>
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<td>549</td>
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<td>532</td>
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<tr>
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<td>Chloroform</td>
<td>532</td>
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<td>209</td>
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<td>538</td>
<td>175</td>
<td>10</td>
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<tr>
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<td>Chloroform</td>
<td>533</td>
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<td>531</td>
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<td>5</td>
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<td>534</td>
<td>78%</td>
<td>8</td>
<td>2.29</td>
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</table>

* Films prepared from chloroform and dichlorobenzene solution.

Fig. 2. Cyclic voltammograms of BDP1 and BDP3 in dichloroethane, containing 0.1 M TBATFB and 1 mM of the BODIPY compound in the presence of 1 mM ferrocene/ferrocenium (Fc/Fc⁺) as internal standard, recorded at 50 mV s⁻¹ in deoxygenated solution (N₂).

3.2. Anomalous meso-free BODIPY presence

In the synthesis of all meso-substituted BODIPYs (BDP1-S), the BDP6 was isolated as a by-product in yields ranging from 2% to 6%. This peculiarity was already reported but never explained [28,29]. In fact, the BDP6 by-product can be easily masked by the main BODIPY in terms of visible spectroscopy, but by HPLC it is possible to identify both, and then isolate them, either by column chromatography or preparative thin layer chromatography. This contamination is particularly evident in the synthesis of BDP1 and BDP5, having a direct influence on the lower yields of these BODIPYs due to the consumption competition of pyrrole units with the BDP6 synthesis. Due to its almost identical photophysical properties, BDP6 contamination must be taken seriously on photovoltaic studies, but this has not been referenced in almost all previously reported studies using BODIPYs made by the acid condensation of aldehydes and α-free-pyrroles.

We investigated the possibility of BDP6 be the result of degradation of the main meso-substituted BODIPY products. A series of studies to evaluate the effect of several degradative factors, namely the temperature (room temperature and 50 ºC), light stability (under direct light or in the dark), the pH effect (under acidic conditions (1% of pure HCl) or under basic conditions (1% NaOH solution) and the oxidative conditions (1 equivalent of DDQ) or reductive conditions (1 equivalent of hydrazine) were performed. All experiments were continuously monitored (absorption spectroscopy and HPLC) for 24 h, and under no circumstances the formation of BDP6 was detected. These preliminary results suggested that the formation of BDP6 does not arise from the degradation of the meso-substituted BODIPYs (BDP1-S).

As an alternative hypothesis, we investigated the possibility of BDP6 result from the reaction of the α-free-pyrrole with the solvent (CH₂Cl₂). Table 1 shows a few reaction conditions, all without the aldehyde reagent, to study the influence of the solvent on BDP6 formation. In fact, it was possible to synthesize and isolate BDP6 in the total

Table 5
Electrochemical properties of the six BODIPY compounds.

<table>
<thead>
<tr>
<th>Dyes</th>
<th>E°red (V)</th>
<th>E°ox (V)</th>
<th>E°ox (V)</th>
<th>E_ÖHOMO (eV)</th>
<th>E_LUMO (eV)</th>
<th>E_g (eV)</th>
<th>E_LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDP1</td>
<td>−1.21</td>
<td>1.22</td>
<td>1.43</td>
<td>−5.35</td>
<td>−3.08</td>
<td>2.27</td>
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<tr>
<td>BDP2</td>
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<td>BDP4</td>
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<td>−5.27</td>
<td>−2.99</td>
<td>2.28</td>
<td>2.25</td>
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<tr>
<td>BDP5</td>
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<td>1.25</td>
<td>1.42</td>
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<td>−3.10</td>
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</tr>
<tr>
<td>BDP6</td>
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<td>1.22</td>
<td>1.39</td>
<td>−5.35</td>
<td>−3.08</td>
<td>2.27</td>
<td>2.27</td>
</tr>
</tbody>
</table>

* Estimated from the CV: E_ÖHOMO = [−(E°onset ox₁ − E_Fc/Fc⁺) − 4.8] eV.

* Estimated from the CV: E_LUMO = [−(E°onset red₁ − E_Fc/Fc⁺) − 4.8] eV.

* Estimated as the difference between the HOMO and LUMO obtained from CV measurements.

* Estimated from the onset of absorption spectra in chloroform.

E_LUMO = [E_ÖHOMO + E_g] eV.
absence of aldehyde, which shows that the dichloromethane solvent is the source of the meso-carbon that leads to the unexpected formation of the meso-free BODIPY (BDP6). Under these conditions (absence of aldehyde), BDP6 was the only BODIPY species formed. It was easily purified and isolated by column chromatography.

It was also found that the use of TFA as catalyst is not required, either because hydrochloric acid is formed in situ or because this aliphatic nucleophilic substitution reaction does not require acid catalysis. In summary, these preliminary results indicate that BDP6 must arise from the reaction of pyrrole with the electrophilic carbon of the halogenated solvent and therefore future works must take this in consideration.

To further support our hypothesis of the dichloromethane role in the synthesis of BDP6, we performed the reaction of 3-ethyl-2,4-dimethylpyrrole with α,α-dichlorotoluene and α,α-dibromotoluene, and in both cases we obtained exclusively the BDP1 with 6% and 4% yield, respectively (Scheme 2). This result is consistent with previous studies of reaction of pyrrole with dihalogenated electrophiles reported in 1907 by Pictet and Rilliet [30], and the more recent reaction of pyrroles with a dihalogenated alkanes to synthesize corrole derivatives, by Gross et al. [31].

### 3.3. X-ray diffraction studies and the new structures

The crystallization of all BODIPYs was made through slow evaporation from a dichloromethane/hexane solution. We succeeded at obtaining crystals of BDP3, BDP4, BDP5 and BDP6. Crystals of BDP3 and BDP6 exhibit a unit cell equal to that already reported by Rurack et al. [32] and Beniston et al. [29], respectively, with CCDC codenames FIDLIP and XODGUT.
In the case of BDP4, we have refined a new polymorph, different from that reported previously by Diederich et al. [33] (codename UNIFIG). We report here the first known crystal structure for BDP5.

Table 2 shows the single-crystal X-ray structure of the BDP4 and BDP5 and crystal data details. Data collection and refinement data can be found in the supplementary information (Table S1).

BDP4 molecules, crystallize in a non-centrosymmetric unit cell in a triclinic space group. In UNIFIG, there are three symmetry-independent molecules while in the new polymorph (BDP4), reported here, there are only two. In UNIFIG, two molecules have the ethyl groups in a trans-conformation and the third one has the ethyl groups in a cis-conformation. The angles between the least-squares plane of the meso-substituent and the central planar molecular core are 78.9(2), 78.8(2)

and 84.5 (2°) for the three molecules. In the new polymorph, both molecules show a trans-conformation and the angle between the meso-substituent group and the core is 89.17 (6)° and 86.81 (7)°.

BDP5 crystallizes also in a triclinic unit cell with an inversion centre. The angle between the anthracene substituent and the central core of the molecule is 89.99 (5)°.

They pack efficiently without any solvent accessible voids (Table 3). Table 3 gathers information about BODIPY’s angle and distance between the meso-carbon and the substituent carbon to which it is bonded.

3.4. Absorption and fluorescence spectroscopy

The absorption and emission spectra of all presented BODIPYs, in chloroform solution, are presented in Fig. 1 (A and B respectively), and the corresponding optical data is summarized in Table 4. The absorption spectra of BDP1-6 series cover a broad range of the visible spectrum. All six spectra are characterized by a strong S0–S1 (π-π*) transition (525–544 nm) with a higher energy vibrionic shoulder at about 30 nm from the main peak and a weaker broad band (340–420 nm) arising from the S0–S2 (π-π*) transition. As it has been reported previously, the presence of an aromatic group at the meso-position has a weak effect on the absorption/emission characteristics [15,17,28]. This is due to the negligible electronic interaction between the meso-aromatic ring and the BODIPY core, since the two moieties are almost perpendicular to each other. However, BDP3 presents a small red-shift if compared with the remaining members of the series, which can be explained by the inductive effect of the strong electron-withdrawing properties of the meso-C₆F₅ group.

Independently of the solvent, all BODIPY show high extinction coefficients (ranging from 5.4×10⁴ to 1.0×10⁵ cm⁻¹M⁻¹), which confirms their excellent light-harvesting ability.

Apart from BDP4, the various BODIPY dyes present high fluorescence quantum yields, and their emission spectra are mirror images of the S0–S1 transition of the absorption spectra. Excitation spectra match the absorption spectra allowing us to conclude that the emitted light originates from the singlet excited state without any contribution of any charge transfer or other excited state. The small Stokes shift is a typical characteristic of these compounds, and it is an indication of a similar S1 and S0 configuration.

The emission of BDP4 (p-nitro-phenyl substituted BODIPY) is significantly affected by solvent polarity. In hexane, it shows fluorescence emission (at 549 nm) but in chloroform the fluorescence quantum yield becomes very weak, and in acetonitrile the fluorescence quantum yield

![Fig. 3. Emission spectra of the films of BDP6 and BDP6:PC60BM blend.](image1)

![Fig. 4. Current density-voltage characteristics of BODIPY dyes:PC60BM-based OPVs, under AM 1.5G illumination at 88 mWcm⁻².](image2)

![Fig. 5. EQE curves of the optimized BDP1:PC60BM, BDP5:PC60BM and BDP6:PC60BM-based OPV cells.](image3)

Table 7 Photovoltaic parameters from the BDP1-6:PC₆₀BM-based OPVs, under AM 1.5 G illumination at 88 mW/cm². All the solar cells were made under the optimized conditions for BDP6:PC₆₀BM solar cell (Table S2).

<table>
<thead>
<tr>
<th>Dye</th>
<th>Active layer thickness (nm)</th>
<th>JSC (mA/cm²)</th>
<th>VOC (V)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>maximum</td>
<td>average¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BDP1</td>
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<td>0.54</td>
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<td>BDP4</td>
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<td>0.53</td>
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<td>BDP5</td>
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<td>BDP6</td>
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<td>2.27</td>
<td>0.67</td>
<td>0.27</td>
<td>0.47</td>
</tr>
</tbody>
</table>

¹ Average values calculated from at least 8 devices.
becomes residual and a new band at 650 nm arises (Fig. 1 (C)). The quenching of the emission in polar media and the appearance of new red-shifted bands are usually associated with the formation of intramolecular charge transfer (CT) states [34]. Thus, the BDP4 emission in polar solvents can be rationalized as a mixture of local fluorescence and CT excited states, formed from intramolecular electron transfer.

The absorption spectra of the BODIPY thin films show a clear bathochromic shift of the absorption maximum accompanied by a broadening of the peaks (Fig. S27), due to the interactions between adjacent molecules, possibly involving π-orbitals.

3.5. Electrochemical properties

Cyclic voltammetry (CV) was used to study the electrochemical properties of the BODIPY dyes in the presence of 0.1 M TBATFB in dichloroethane, as supporting electrolyte. The ferrocene/ferrocenium (Fc/Fc+) couple was used as internal reference and it is assumed that the redox potential of Fc/Fc+ has an absolute energy level of 4.80 eV in relation to vacuum. Solutions were degassed with N2 for 5 min before CV measurements. Fig. 2 illustrates the cyclic voltammograms of BDP1 and BDP3 (all cyclic voltammograms can be found in the support information (Figs. S28–S33). The electrochemical properties of all these BODIPYs are summarized in Table 5.

All BODIPYs present quasi-reversible redox processes with very similar cyclic voltammograms, with two oxidations processes (E_{ox}^1 and E_{ox}^2) and one reduction process (E_{red}). These processes can be assigned almost exclusively to the BODIPY core, not only because the HOMO of meso-BODIPY dyes is generally delocalized over the BODIPY core.

BDP3 oxidation and reduction potentials are slightly shifted to more positive potentials, which can be attributed to the stabilization effect of the pentafluoro withdrawing groups.

The HOMO and LUMO energy levels were calculated using the onset of the first oxidation peak and the first reduction peak respectively. The LUMO energies were also calculated using the optical energy gap (Table 4) as reported by several authors [21,35–38]. The differences between the LUMO energies and energy gaps obtained from cyclic voltammetry and those calculated from the optical energy-gap are minimal or non-existent.

The calculated HOMO and LUMO energies indicate that all six BODIPYs are suitable candidates to be used as electron-donors with
respect to PC_{60}BM in BHJ photovoltaic cells because their HOMO and LUMO lie above the corresponding levels of PC_{60}BM i.e. −6.1 eV and −3.7 eV, respectively, thereby forming a type II heterojunction.

3.6. Theoretical calculations

To better understand the change of photophysical and electrochemical properties among the various BODIPIYs, the structures and energies of the frontier orbitals were calculated by Density Functional Theory (DFT) in vacuum. The optimized ground-state geometries and electronic distribution in HOMO-LUMO levels are presented in Table 6. All calculations were carried out using the B3LYP method and a 6–31 G* basis set.

The π-electrons in the HOMOs are delocalized over the entire BODIPIY backbone π-systems. Similarly, the LUMO orbitals in all BODIPIYs, with the exception of BDP4, are delocalized also within the BODIPIY backbone but with higher intensity at the meso carbon. Due to the less perpendicular symmetry of meso group on BDP3 there is a very small delocalization between the backbone and the meso-substituting group. In the case of BDP4, the LUMO is entirely localised in the nitrrophenyl substituent. The absence of spatial overlap between HOMO and LUMO of BDP4, indicates that the HOMO – LUMO transition has a charge transfer character, which is in line with the fluorescence results discussed above.

The HOMO energies obtained from cyclic voltammetry are very similar to the theoretical ones. However, a somewhat higher deviation is found for the LUMO energy. The dissimilarity between the experimental LUMO energy and the calculated can be justified by the lack of solvent stabilisation effects. Nevertheless, the experimental and calculated data follows the same trend, in what concerns HOMO, LUMO and energy-gap, and confirm that all the six BODIPIYs are suitable candidates to be used as electron donors in OPVs when blended with PC_{60}BM.

3.7. Photovoltaic performance evaluation and surface morphology

All BODIPIYs exhibit the fundamental requirements to be used as electron-donor materials in PC_{60}BM-based OPVs. Fluorescence studies of the film prepared with the BDP6:PC_{60}BM blend (Fig. 3) reveal a complete quenching of the BODIPIY emission, which is consistent with an excited state electron transfer from BODIPIY to fullerene, thereby providing good perspectives for application in OPVs.

Solution-processed bulk heterojunction OPVs were manufactured with a typical multilayer structure: ITO/PEDOT:PSS/active layer/LiF/Al. The PEDOT:PSS layer was spin-coated at 1800 rpm and dried for 10 min at 125 °C to obtain a film thickness of about 40 nm. Several conditions of the active layer were tested, aiming to achieve the best power conversion efficiency (PCE). The optimization procedures, Table S2 (Supplementary Information), were carried out with BDP6-based devices and then replicated in the OPVs based on the remaining BODIPIYs. The adjusted parameters were: donor/acceptor weight ratio, active layer solution concentration and back (top) electrode (Ca/Al or LiF/Al).

The optimized BDP6-based OPV was prepared from a BDP6:PC_{60}BM blend with a weight ratio of 1:3, dissolved in dichlorobenzene at 40 mg/ml, and deposited by spin-coating at 1200–1300 rpm with LiF/Al top electrode.

Devices based on BDP2 were poorly characterized due to the BDP2 low solubility, which led to films with poor quality and irregular current-voltage (J–V) curves. For this reason, BDP2 was not included in the photovoltaic studies.

The parameters characterizing the photovoltaic cells performance are given in Table 7 and the J–V curves are shown in Fig. 4. For the optimized conditions, the best PCE values were obtained with the BDP6-based devices. Devices based on BDP1 and BDP5 showed a slightly lower efficiencies. BDP3 and BDP4 led to OPV with much worst performance. The current density versus voltage, in the dark and under illumination, for the best BODIPIYs:PC_{60}BM cells are shown in the supplementary information (Fig. S34).

As mentioned above, the optimization process showed that the best thickness of the active layer should be around 70 nm. However, under the optimal conditions, BDP3 has 110 nm of active layer thickness. When the active layer thickness was reduced to 77 nm (using 35 mg/ml solution concentration) the PCE remained at 0.01%. The thinner layer caused a small increase in short circuit current (J_Sc) but also a decrease of open circuit voltage (V_OC).

The presented BODIPIY-based OPVs show high V_OC values, some of which are similar to those of the best BODIPIY-based solar cells, but the main limitation factors in these systems are J_Sc and fill factor (FF). These parameters are related to light harvesting ability, recombination, charge transport and collection. Since the proposed BODIPIY dyes show high absorption coefficients and absorbance in a favourable range of the spectrum, we believe that the main restriction of this system is related to a non-optimal active layer morphology or to a poor charge transport.

Among the five tested BODIPIYs, the largest difference between the corresponding devices is in the current. The best BODIPIY is the one with the free-meso-position and the worst (BDP3 and BDP4) are the BODIPIYs with electron-withdrawing groups at the meso-position. These results show that the nature of the group at the meso position significantly affects the photovoltaic performance. Since the meso group is perpendicular to the BODIPIY core and it does not have a considerable influence on the optical-electronics properties, the differences in device performance are likely related to the intermolecular interactions and molecular packing.

The external quantum efficiencies (EQE) were also measured for BDP1:PC_{60}BM, BDP5:PC_{60}BM, BDP6:PC_{60}BM (Fig. 5). The EQE profiles are similar to the corresponding absorption spectra of the films, with a broad response in the 375–600 nm range. This response is mainly due to the BODIPIY absorption profile but some contribution of PC_{60}BM at 300–400 nm is also detected. The stronger response of the BDP6-based OPV is consistent with a higher short-circuit current.

The morphology of the OPVs’ active layers can provide valuable information about the photoelectronic response, being related with exciton dissociation efficiency and, consequently, with the obtained photocurrent. For that reason, the film’s surface of BDP1:PC_{60}BM, BDP3:PC_{60}BM, BDP4:PC_{60}BM, BDP5:PC_{60}BM and BDP6:PC_{60}BM were characterized by AFM (Fig. 6 and Fig. S35). All films exhibit very similar surface topography without noticeable phase domains or aggregates. They are very flat (root mean squared (RMS) inferior to 0.40 nm). Usually low roughness and small phase domains are indicators of good miscibility between the donor and the acceptor and are associated with good photovoltaic efficiencies. These results demonstrate that there is a good miscibility between the BODIPIY dyes and the PC_{60}BM, with a good donor:acceptor interpenetrating network within the blend films.

The AFM results show a good intermixing of the two active layer materials (BODIPIY and PCBM). This morphology facilitates the exciton dissociation (by virtue of a large donor:acceptor interface) but tends to limit the charge transport, as it does not allow the formation of percolation paths for the generated charges to reach the electrodes.

The hole mobility in films of neat BODIPIYs was calculated from the current-voltage characteristics of hole-only devices, with the structure ITO/PEDOT:PSS/BODIPIY/MoO_3/Al in the space charge limited current (SCLC) regime [39]. The calculated values were BDP1: 3 × 10^{-7} cm²/V.s; BDP3: 6 × 10^{-7} cm²/V.s; BDP4: 6 × 10^{-7} cm²/V.s; BDP5: 1 × 10^{-6} cm²/V.s. In case of BDP5, we could not observe such SCLC regime, and the mobility could not be calculated using this method. Despite the similarity of the calculated mobilities to some reported BODIPIY-based OPVs [40,41], these values are much lower than both
values we obtained, by the same method, for P3HT ($2 \times 10^{-3}$ cm$^2$/V.s) and the electron mobility reported in PCBM ($4 \times 10^{-3}$ cm$^2$/V.s) [39]. These results suggest that the hole mobility in the BODIPY phase does limit the performance of the OPVs.

4. Conclusions

In this work we report the synthesis and characterization of a series of simple meso-BODIPY molecules, as well as two new crystal structures. We showed that the synthesis of the unexpected meso-free-BDP6 results from the reaction of the pyrrole with the solvent (dichloromethane). Therefore, the use of halogenated solvents in these reactions implies a rigorous evaluation of by-products. But equally important those studies show that we can produce BODIPYs by allaphatic nucleophilic substitution over halogenated molecules. Despite being a reaction that is more than a century old, it was never exploited in BODIPY chemistry and our results show that it may be a valuable alternative to acid sensitive BODIPY targets.

From our studies some noticeable effects on the photovoltaic properties can be drawn. The best photovoltaic performance was obtained with BDP6 (BODIPY without meso groups), pointing to the fact that the substitution at this position can negatively influence the photovoltaic cells efficiency. Among the meso-substituted BODIPYs, BDP1 (phenyl group at the meso position) and BDP5 (anthracyl group at meso position) have a similar photovoltaic response, and they are around 3 times better than BDP4 (para-nitrophenyl group at meso position) and 27 times better than BDP3 (pentfluorophenyl group at the meso position). This variation indicates that the strong electron withdrawing groups at meso-position can cause large drop in OPV performance. Despite the low hole mobility, the Voc of our tested BODIPY-based OPV cells are comparable to the values of some of the best OPV cells. The AFM studies of the active layer blend show a very good miscibility between our tested BODIPYs and PC$_{61}$BM, with the blend films showing very flat surfaces. These results can be used as standard results for validation of further BODIPYs functionalization and their application in photovoltaics.

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Appendix A. Supplementary data

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