Synthetic strategies for modifying dielectric properties and the electron mobility of fullerene derivatives
Jahani Bahnamiri, Fatemeh

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In this chapter, the synthesis, characterization and electrochemical properties of fullerene derivatives with permanent dipole groups in the side chain (PCBDN and PPP) and their reference analogues without a permanent dipole (PCBBz and PP) are described. In the next step, influences of installing permanent strong dipoles on the dielectric constant and charge separation properties of the synthesized compounds are investigated by experimental and theoretical analysis, respectively.

The experimental measurements suggest that the incorporation of these dipole groups does not have a considerable effect on the dielectric constant of the compounds. However, theoretical analyses show an enhanced charge separation in these compounds due to the reorientation of the dipoles, which can lead to, improved OPV devices.
2.1 Introduction

As the OPV technology is expanding, many research efforts have been attracted towards optimizing the efficiency of the OPV devices by tuning the optical and electronic properties of the associated organic materials as well as controlling the nano-scale morphology of the materials in the device. In this scope, a large amount of novel p-type donor materials have been successfully synthesized while development of high-performance n-type acceptors have been less regarded.

Up to now, fullerenes $C_{60}$ and $C_{70}$ and their derivatives are recognized as one of the best candidates for acceptor material for use in OPV devices [2, 3]. This is mainly due to their favorable LUMO energy level, reversible reduction leading to stable reduced species, excellent electron transport properties -because of their spherical shape which allows for three-dimensional charge transport- and compatibility with the hole transport properties of conjugated polymers.

Several synthetic efforts are reported in which different properties of fullerene derivatives were tuned for use in photovoltaic devices and increase their efficiencies. These efforts mainly concern properties such as controlling the LUMO energy level, broadening the absorption coverage and improving solubility (see Figure 2.1). For example, in order to tune LUMO for achieving an enhanced open circuit voltage ($V_{OC}$) and charge separation, one strategy was the incorporation of electron donating and withdrawing groups on the phenyl ring of PCBM (i.e., see Figure 2.1a and b) [4]. $C_{60}$ bis-adducts were developed to directly raise the LUMO energy level (i.e., see Figure 2.1c and d) [5, 6]. To broaden the absorption coverage, a strategy was to introduce a dye attached to the fullerene (i.e., see Figure 2.1f) [7, 8]. But as long as the added dye moiety is not electronically integrated with the fullerene moiety, this approach is of limited use. A modified version of [70]PCBM bearing cyanovinylene 4-nitrophenyl moiety is also reported to show increased absorption (i.e., see Figure 2.1e) [9]. The issue of solubility in a variety of nontoxic solvents is of great importance, especially when it comes to large-scale industrial production. In order to improve the solubility of [60]PCBM in organic solvents, several analogues are reported with different ester alkyl chains (i.e., see Figure 2.1g) [10, 11]. The quality and morphology of the film can be tuned by variation in solubility of the acceptors.

In spite of all of these attempts to improve different properties of fullerenes as an acceptor material, there are no synthetic attempts reported in the literature for improving the dielectric properties of fullerene derivatives. Since dielectric constant of the acceptor material has a direct effect on the efficiency of the OPV devices [12], developing synthetic ways for increasing the
dielectric constant of fullerene derivatives would be the next challenge for the OPV community towards fabrication of more efficient solar cells.

Figure 2.1: Several fullerene derivatives for OPV applications.

As it was discussed in the introduction chapter, the Debye equation accounts for three different
microscopic mechanisms of polarization that can contribute to the dielectric properties of a material: the electronic, ionic and dipolar orientation polarization. The last one only exists in polar molecules with permanent dipole moments. However, as Heitzer et al. [13] indicate, these equations are inappropriate for many materials, especially for molecule based systems [13]. Therefore these classical descriptions should rather be used as guidelines to understand the origin of dielectric response at the molecular scale.

Here, instead of optimizing molecular properties like relative alignments of frontier molecular orbital [14–16], the effect of installing strong permanent dipolar groups and polarizable side chains on the dielectric constant of fullerene derivatives was studied. Ideally, it is preferred that in this process the electronic and optical properties of the molecules do not change.

Push-pull chromophores are among suitable candidates for introducing strong dipole moment into the fullerene derivatives. They consist of a strong electron donor and an acceptor groups connected via a $\pi$-conjugated spacer (D-$\pi$-A). D-$\pi$-A chromophores are traditionally used as dye in many applications [17–19].

2.2 Synthesis

We have synthesized four compounds. [6,6]-phenyl-C$_{61}$-butyric acid 2-dimethylamino-5-nitro-benzyl ester (PCBDN) with freely rotating push-pull group in the side chain of PCBM analogue, [6,6]-phenyl-C$_{61}$-butyric acid benzyl ester (PCBBz) the reference analogue without push-pull group, N-methyl-2-(2-dimethylamino-5-nitro-phenyl)fulleropyrrolidine (PPP) with a push-pull group close to the buckyball and N-methyl-2-phenylfulleropyrrolidine (PP) as the reference compound for PPP. The synthetic routes are shown in Scheme [21]. The substitution reaction of commercially available 2-chloro-5-nitrobenzaldehyde (1) with dimethylamine hydrochloride in pyridine afforded the corresponding benzaldehyde (2) in quantitative yield. The aldehyde (2) was efficiently reduced to 2-dimethylamino-5-nitro-benzyl alcohol (3) using sodium borohydride. The target methanofullerene PCBDN (5) was prepared by a transesterification reaction of PCBM with alcohol (3) in the presence of dibutyltin oxide (DBTO) in ODCB at 110 °C in 57% yield. Similarly, transesterification of PCBM with benzyl alcohol (6) afforded PCBBz (7) in 63% yield. According to Llauro et al. [20] and Otera [21], the initial step for the transesterification reaction, is formation of the alkoxy distannoxane, which then undergoes coordination with the ester (PCBM). Subsequent alcoholysis provides transesterified products (PCBDN and PCBBz).
and release of the alkoxydistannoxane. The main advantages of this transesterification method are simple and mild reaction conditions, inexpensive and commercially available catalyst and the compatibility with a variety of functional groups [22].

**Scheme 2.1**: The synthetic route for preparing PCBDN, PCBBz, PPP and PP.

The $^1$H-NMR spectrum of PCBDN is given in Figure 2.2. Beside the expected peaks for the protons in PCBX type methanofullerene, two singlet were observed at 2.9 ppm and 5.2 ppm,
which were related to the protons of the -N(Me)$_2$ moiety and the benzylic methylene group, respectively. In addition, the peaks related to the aromatic protons on the benzylic ring were seen at 7.0 ppm (doublet), 8.1 ppm (doublet of doublet) and 8.3 ppm (doublet).

![Figure 2.2: $^1$H-NMR spectrum of PCBDN.](image)

The target fulleropyrrolidine (PPP) (10) was prepared by Prato reaction of the 2-dimethylamino-5-nitro-benzaldehyde (2), $N$-methylglycine (sarcosine) (8) and $C_{60}$, in ODCB at 120 °C in 38% yield. For comparison, we also prepared PP (12), which lacks a dipole moiety, starting from benzaldehyde (11). The structures of the synthesized compounds were confirmed by analytical and spectroscopic data. The $^1$H-NMR spectrum of PPP is shown in Figure 2.3.

### 2.3 Characterization

#### 2.3.1 UV-vis absorption measurements

The UV-vis absorption spectra of compounds PCBDN, PCBBz and PCBM together with those of PPP and PP in $10^{-5}$ M CHCl$_3$ are shown in Figure 2.4. As it is clear from Figure 2.4(A), there is no significant difference in the UV absorption of PCBM, PCBBz and PCBDN in the range of 450 to 800 nm. The difference is in the range of 328 to 432 nm, which is related to the push-pull group absorption in the ester moiety. It should be noted that the same argument holds for UV-vis spectra for PPP and PP in the range of 328 to 432 nm. Hence, there seems to be very little interaction between the dipole and the fullerene moiety.
Figure 2.3: $^1$H-NMR spectrum of PCBDN.

Figure 2.4: UV-vis spectra for (A) PCBDN, PCBBz compared with PCBM and (B) PPP and PP in $10^{-5}$M CHCl$_3$

2.3.2 Cyclic voltammetry measurements

The electrochemical properties of the synthesized compounds were investigated by cyclic voltammetry (CV) measurements. The half-wave potentials of the reduction processes of all compounds are listed in Table 2.1 and the voltage-current curves are presented in Figure 2.5. The
measured values indicate that the difference in the first reduction potential (6mV) of the various fullerene derivatives under the (polar; relatively high-ε) circumstances in the CV measurement is marginal. Therefore, any possible influence of the dipolar groups on the first reduction potential seems to be overwhelmed by the solvent, here.

Table 2.1: Electrochemical properties (V) and calculated HOMO and LUMO energies (eV) of PCBDN, PCBBz, PPP, PP and PCBM; experimental conditions: Bu$_4$NPF$_6$ (0.1 M) as the supporting electrolyte, ODCB/CH$_3$CN (4:1) as solvent; Pt, working electrode; Pt wire, counter electrode; Ag/AgCl, reference electrode; scan rate 10 mV/s, potentials are relative to Fc/Fc$^+$; Computational procedure: geometries of PCBDN, PCBBz and PCBM were optimised using DFT (B3LYP/6-31G**) with the program GAMESS-UK26. Subsequently, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of these molecules were calculated using DFT (BHandH/27/DZP) and the lowest 60 vertical excitation energies were calculated using time-dependent DFT (TD-DFT) (BHandH/DZP) with ADF [23, 24].

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}$ 1, red</th>
<th>$E_{1/2}$ 2, red</th>
<th>HOMO</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBDN</td>
<td>-1.089</td>
<td>-1.482</td>
<td>-7.92</td>
<td>-3.88</td>
</tr>
<tr>
<td>PCBBz</td>
<td>-1.095</td>
<td>-1.489</td>
<td>-7.90</td>
<td>-3.86</td>
</tr>
<tr>
<td>PCBM</td>
<td>-1.097</td>
<td>-1.487</td>
<td>-7.87</td>
<td>-3.83</td>
</tr>
<tr>
<td>PPP</td>
<td>-1.108</td>
<td>-1.505</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PP</td>
<td>-1.114</td>
<td>-1.508</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

2.4 Results and Discussions

Once that the fullerene derivatives bearing push-pull groups and their reference compounds were successfully synthesized and characterized, we focus on analyzing the properties of the synthesized compounds in the context of OPV technology.

2.4.1 Isotropic polarizabilities and dipole moment

The isotropic polarizabilities and dipole moments of PCBDN, PCBBz, PPP and PP were calculated using DFT (B3LYP/aug-ccpVDZ) with the program DALTON [10] and presented in
Table 2.2: Since the isotropic polarizability per electron for PCBDN (548 electrons), PCBBz (502 electrons), PPP (478 electrons) PP (432 electrons) are rather similar, we expect a similar optical dielectric constant (dielectric constant at optical frequencies, i.e., only electronic polarization defines \( \varepsilon_r \), here) for all four materials. However, when the additional screening from dipoles is also considered, a larger screening is expected for PPP and PCBDN embedding due to their larger dipole moments.

Table 2.2: Calculated isotropic polarizabilities (a.u.) and dipole moments (Debye) of PCBDN, PCBBz, PPP and PP.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Polarizability (a.u)</th>
<th>Polarizability per electron</th>
<th>Dipole moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBDN</td>
<td>838.79</td>
<td>1.53</td>
<td>5.97</td>
</tr>
<tr>
<td>PCBBz</td>
<td>784.54</td>
<td>1.56</td>
<td>2.35</td>
</tr>
<tr>
<td>PPP</td>
<td>744.40</td>
<td>1.56</td>
<td>6.46</td>
</tr>
<tr>
<td>PP</td>
<td>683.03</td>
<td>1.58</td>
<td>4.2</td>
</tr>
</tbody>
</table>

2.4.2 Dielectric constant of fullerene derivatives with push-pull side groups

Table 2.3 lists the dielectric constant values of all the synthesized materials, together with the values of their reference compounds, determined by spectral impedance measurements in the frequency range of 100 Hz to 1MHz. The dielectric constant of the synthesized compounds
does not show a considerable improvement and the observed values are constant within the measurement error. The $\varepsilon_r$ for PPP shows a slight increase compared to its reference compound PP and the measured dielectric constant for PCBDN is almost the same as that for PCBM ($\varepsilon_r \sim 3.9$). It should be noted that due to the low quality of the film, the dielectric constant of PCBBz as the reference compound for PCBDN could not be measured.

These results indicate that attaching a strong permanent dipole to the fullerene derivatives does not affect its dielectric properties. However, one should note, that we know very little about the details of the structures of the thin film of these materials, Complex intra- and inter molecular interactions should be accounted for in order to analyze the complete dielectric response of these materials. One possible reason for this behavior could be that the dipoles are not able to rotate and/or align fast enough with the applied field in the film due to interaction with the fullerene cage or with neighboring molecules. Another explanation could be the density of the film, which can play an important role in determining the dielectric constant.

**Table 2.3:** relative dielectric constant and electron mobility of fullerene derivatives.

<table>
<thead>
<tr>
<th>Fullerene derivatives</th>
<th>$\varepsilon_r$</th>
<th>$\mu_e$ [m$^2$/Vs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPP</td>
<td>4.2 ± 0.4</td>
<td>$2.0 \times 10^{-7}$</td>
</tr>
<tr>
<td>PP</td>
<td>3.8 ± 0.4</td>
<td>$2.0 \times 10^{-7}$</td>
</tr>
<tr>
<td>PCBDN</td>
<td>3.9 ± 0.2</td>
<td>$2.0 \times 10^{-7}$</td>
</tr>
<tr>
<td>PCBBz</td>
<td>$\bullet$</td>
<td>$\bullet$</td>
</tr>
<tr>
<td>PCBM</td>
<td>3.9 ± 0.2</td>
<td>$2.0 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

$a$Device structure for mobility measurements: Au/PEDOT:PSS/fullerene /LiF/Al
$b$Insufficient film quality

We have also studied the electron mobility in the PPP and PCBDN films by space charge limited current (SCLC) measurements in an electron-only device geometry (see Table 2.3). We found similar values for the electron mobility of the fullerenes with push-pull side group (PCBDN, PPP) and PCBM of $\sim 2 \times 10^{-7}$ m$^2$/Vs. Thus, in addition to the dielectric constant and electro-optical properties of the molecules being unaffected by addition of dipole side chains, their bulk electron mobility did not change with respect to the PCBM. The similarity between the electron mobility values of PCBDN and PPP with PCBM suggests that they have the same level of energetic disorder as PCBM, although they bear strong dipole moment groups.
2.4.3 Comparison With theory

The charge separation properties of PCBDN and its reference compound (PCBBz) were theoretically studied on the molecular scale by our collaborators [1]. A combination of molecular dynamics together with quantum chemical calculations was used to study the potential effect of reorientation of push-pull groups on the charge separation mechanism. The method was first used to predict the UV-vis spectra of PCBDN and PCBBz. The measured and calculated UV-vis absorption spectra of PCBDN, PCBBz and PCBM are very similar except for a blue shift of 0.6 eV for the calculated spectra due to the fact that stabilization effects from the environment are missing in the case of the calculated spectra.(see Figure 2.6). The optical properties of these molecules appear to be nearly similar. From this we conclude that installing a permanent dipole in the side chain of fullerene derivatives does not affect their optical properties.

![Experimental and theoretical UV-vis spectra for PCBDN, PCBBz and PCBM.](image)

**Figure 2.6:** Experimental and theoretical UV-vis spectra for PCBDN, PCBBz and PCBM.

Next, the electrochemical properties of PCBDN, PCBBz and PCBM were calculated and compared with cyclic voltammetry measurements. A summary of these electrochemical properties together with calculated HOMO and LUMO energies are presented in Table 2.1. The small differences between the first reduction potentials, which is an indication of the LUMO energy level of these compounds, suggests that the behavior of the reduction potential is not affected by these dipoles. Even though the absolute values are different, both theory and experiment show that the frontier molecular orbital energies and their differences are similar for these molecules. This suggests that installing a strong permanent dipole in the side chain of a fullerene derivative
does not interfere with the \(\pi\)-conjugated system of the cage. After benchmarking the proposed theoretical method with UV-vis and CV measurements, which were in close agreement with our experimental results, the method was used to study the charge separation properties of the synthesized compounds. These calculations suggests that a PCBDN environment around a central donor-acceptor complex facilitates charge separation due to the alignment of the embedding dipoles in response to charges present on the central donor-acceptor complex \([\text{II}]\).

2.5 Conclusions

In conclusion, we have synthesized fullerene derivatives with push-pull groups in order to study the influence of incorporating strong permanent dipole groups on polarizability and consequently the dielectric constant of fullerene derivatives. However, experimental measurements revealed that the dielectric response of the materials does not show a considerable improvement upon addition of push-pull groups. On the bright side, theoretical calculations suggest that installing polar groups and permanent dipoles in the molecular structure of the fullerene derivative is a viable approach to enhance charge separation at the donor-acceptor interface in OPV donor-acceptor blends.

2.6 Experimental

2.6.1 General

All reagents and solvents were used as received. PCBM used for the syntheses was 99.5% (purchased from Solenne BV, Groningen, The Netherlands). Column chromatography was performed using silica gel (Kieselgel Merck Type 9385, 230-400 mesh). \(^1\)H-NMR and \(^{13}\)C-NMR were performed on a Varian Unity Plus (400 MHz) instrument, as indicated, at 25 °C; Values are reported in ppm; Multiplicities are denoted as follows: s = singlet, m = multiplet, br = broad and J values are given in Hz. IR measurements were performed on a Nicolet Nexus FT-IR instrument. HPLC analyses were performed on an LC-MS system (Agilent/HP 1100 series) using an analytical Cosmosil Buckyprep@column (4.6 \(\times\) 250 mm); UV-vis absorption spectra were measured with a Perkin-Elmer Lambda 900 spectrometer.
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**2-dimethylamino-5-nitro-benzaldehyde [25]:**

A three-necked, 50 mL round-bottom flask was charged with 2-chloro-5-nitro-benzaldehyde (1.66 g, 9 mmol), NaHCO$_3$ (2.1 g, 24.7 mmol) and pyridine (10 mL). $N$, $N$-dimethylamine hydrochloride was dissolved in few drops of water was added to the reaction mixture, which was stirred under reflux condition for 4.5 hours. After cooling, the reaction mixture was filtered to remove inorganic salts. The solvent was evaporated in vacuo. The crude product was purified by recrystallization with CH$_2$Cl$_2$ and hexane to give the NMR pure compound as yellow solid (1.4 g, 7.8 mmol, 86%).

**2-dimethylamino-5-nitro-benzyl alcohol [26]:**

Sodium borohydride (80 mg, 2 mmol) was added to a 25 mL round-bottom flask, which was charged with 2-dimethylamino-5-nitro-benzaldehyde (390 mg, 2 mmol) and dry methanol (6 mL) at 0 °C with stirring. The reaction mixture was left at 0-5 °C for 1 h and then it was stirred for 2 h at r.t. After completion of the reaction the solvent was evaporated. Chloroform (20 mL) was added and the organic layer was washed with 5% sodium bicarbonate (10 mL) and water (20 mL), dried over anhydrous sodium sulfate, filtered, and concentrated under vacuo. The crude product was purified by recrystallization from CH$_2$Cl$_2$ and hexane to give the desired compound as yellow solid (310 mg, 1.6 mmol, 81%).
PCBDN:
An oven-dried three-necked, 250 mL round-bottom flask was charged with PCBM (546 mg, 0.6 mmol), 2-dimethylamino-5-nitro-benzyl alcohol (295 mg, 1.5 mmol), dibutyltin oxide (15 mg, 0.06 mmol) and dry o-dichlorobenzene (50 mL). The reaction mixture was stirred under N\textsubscript{2} at 120 °C for 96 h. The solvent was evaporated in vacuo, and the crude residue was dissolved in CHCl\textsubscript{3} and passed through a chromatography column (Silica gel; toluene) to afford the pure compound as a brown solid. The product was dissolved in 7 mL of chlorobenzene, precipitated with MeOH, washed repeatedly with MeOH and pentane, and dried in vacuo at 50 °C. This procedure gave 370 mg (0.34 mmol, 57%) of PCBDN.

\textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): δ 8.24 (d, J = 3 Hz, 1H), 8.11 (dd, J = 8.0 , 3.0 Hz, 1H), 7.93 (d, J = 8 Hz, 2H), 7.55 (t, J = 8.0 Hz, 2 H), 7.48 (m, 1H), 7.03 (d, J = 8 Hz, 1H), 5.20 (s, 2H), 2.94 (m, 2H), 2.86 (S, 6 H), 2.65 (t, J = 8Hz, 2 H), 2.24 (m, 2H).

\textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3}): 172.70, 157.53, 148.74, 147.71, 145.17, 144.69, 144.48, 144.00, 143.69, 142.96, 142.87, 142.12, 141.39, 140.72, 137.95, 137.56, 136.63, 132.02, 128.46, 128.27, 127.84, 125.44, 124.45, 117.50, 79.79, 62.22, 51.72, 43.97, 34.05, 33.54, 22.37.

IR (cm\textsuperscript{-1}): 2954, 2868, 2328, 1731, 1603, 1586, 1510, 1495, 1327, 1185, 1161, 1090, 958, 900, 825, 739, 713, 698.

Anal. Calcd. for C\textsubscript{80}H\textsubscript{23}N\textsubscript{2}O\textsubscript{4}: C, 89.30; H, 2.15; N, 2.60. Found: C, 88.67; H, 2.04; N, 2.85. Mass m/z: calcd: 1075.1, Found: 1074.8

PCBBz:
An oven-dried three-necked, 250 mL round-bottom flask was charged with PCBM (601 mg, 0.66 mmol), benzyl alcohol (495 mg, 4.6 mmol), dibutyltin oxide (23 mg, 0.09 mmol) and dry o-dichlorobenzene (50 mL). The reaction mixture was stirred under N\textsubscript{2} at 120 °C for 72 h. The solvent was evaporated in vacuo, and the crude
residue was resolved in CHCl$_3$ and passed through a chromatography column (Silica gel; toluene) to afford the pure compound as a brown solid. The product was dissolved in 7 mL of chlorobenzene, precipitated with MeOH, washed repeatedly with MeOH and pentane, and dried in vacuo at 50 °C. This procedure gave 415 mg (0.42 mmol, 63%) of PCBBz.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.92 (d, $J = 8$ Hz, 2H), 7.54-7.49 (m, 2H), 7.47-7.43 (m, 1H), 7.36-7.33 (m, 5 H), 5.12 (s, 2H), 2.91 (m, 2H), 2.57 (t, $J = 8$ Hz, 2H), 2.24-2.20 (m, 2 H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 172.85, 148.79, 147.76, 145.82, 145.17, 145.06, 145.02, 144.65, 144.40, 143.99, 143.74, 143.09, 143.01, 142.97, 142.91, 142.22, 142.16, 142.11, 140.98, 140.72, 138.02, 137.55, 136.70, 136.84, 132.09, 128.58, 128.42, 128.26, 79.85, 66.36, 51.83, 34.09, 33.64, 22.37.

IR (cm$^{-1}$): 2956, 2328, 2190, 1979, 1732, 1494, 1427, 1313, 1162, 1042, 964, 743, 697.

Anal. Calcd. for C$_{78}$H$_{18}$O$_2$: C, 94.92; H, 1.84. Found: C, 93.74; H, 1.81.


PPP:

An oven-dried three-necked, 250 mL round-bottom flask was charged with C$_{60}$ (1.44 g, 2 mmol), 2-dimethylamino-5-nitro-benzaldehyde (388 mg, 2 mmol), sarcosine (540 mg, 6 mmol) and o-dichlorobenzene (100 mL). The reaction mixture was stirred under N$_2$ at 110 °C for 72 h. The solvent was evaporated in vacuo. The crude residue was resolved in CHCl$_3$ and passed through a chromatography column (Silica gel; toluene) to afford the desired compound as a brown solid. The product was dissolved in chlorobenzene, precipitated with MeOH, washed repeatedly with MeOH and pentane, and dried in vacuo at 50 °C. This procedure gave 709 mg (0.75 mmol, 38%) of PPP.

$^1$H-NMR (400 MHz, CS$_2$: D$_2$O): $\delta$ 9.03 (d, $J = 4$ Hz, 1H), 8.23-8.20 (dd, $J = 8$, 4Hz, 1H), 7.42 (d, $J = 8$Hz, 1H), 5.77 (s, 1H), 5.22 (d, $J = 8$Hz, 1H), 4.53(d, $J = 8$ Hz, 1H), 3.08 (s, 3H), 3.01 (s, 6H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 159.57, 156.11, 154.22, 153.40, 152.34, 147.36, 147.30, 146.57, 146.32, 146.16, 146.12, 146.02, 145.95, 145.73, 145.48, 145.37, 145.27, 145.25, 145.13, 145.02, 144.65, 144.54, 144.41, 144.12, 143.15, 143.07, 142.79, 142.75, 142.68, 142.34, 142.23, 142.13, 141.83, 141.78, 141.53, 140.40, 139.57, 139.28, 136.89, 136.52, 135.95, 134.24, 133.36, 126.33, 124.38, 120.85, 77.56,
Influence of Installing Permanent Dipole Groups on Dielectric Constant

76.39, 69.86, 69.16, 45.10, 39.87, 27.42.

IR (cm$^{-1}$): 2943, 2832, 2775, 1583, 1512, 1462, 1429, 1330, 1182, 1076, 1031, 835, 767, 727, 706, 599, 574.

Mass m/z : calcd for C$_{71}$H$_{15}$N$_3$O$_2$: 941.1, Found: 941.8.

2.6.2 Dielectric constant measurement

The dielectric constant was derived from spectral impedance measurements in the following device architecture: ITO/PEDOT:PSS /fullerene film/Al (see Figure 2.7a). The samples comprised glass substrates patterned with ITO in four different configurations (see Figure 2.7b).

![Figure 2.7: (a) General layout of the device (b) 9.5 mm$^2$, 16.16 mm$^2$, 35.7 mm$^2$, 99.5 mm$^2$ defined areas for four parallel plate capacitors on one substrate.](image)

The capacitance was determined from equivalent circuit (see Figure 2.8) fit over impedance response of fabricated capacitors. The dielectric constant was determined by:

$$ C = \varepsilon_0 \varepsilon_r A/D $$(2.1)

where $A$ is the capacitor’s area (m$^2$), $d$ is thickness of the fullerene film (m) and $\varepsilon_0$ is the permittivity of a vacuum ($8.85 \times 10^{-12}$ F/m).

2.6.3 Electron mobility measurements based on space-charge limited current

The experimental J-V curves show that the current density depends quadratically on the voltage in part of the voltage range, which is characteristic behavior for space-charge limited current.
Figure 2.8: Equivalent circuit to fit the measurement data, with capacitance \( C \), parallel resistance \( R_p \) and serial resistance \( R_s \).

(SCLC) and is described by

\[
J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_e \frac{V^2}{L^3}
\]

(2.2)

where \( \varepsilon_r \) is the dielectric constant of fullerene derivative obtained from impedance spectroscopy and \( L \) is the thickness of the film. We calculated mobility values from SCLC fits of the current density-voltage response of the devices determined.

2.6.4 Device fabrication

Commercially available glass substrates patterned with indium tin oxide (ITO) in four different dimensions were used to function as bottom electrode for capacitors. The cleaning of substrates was performed by scrubbing with soap/water solution, rinsing with de-ionized water, sonicication in acetone and isopropyl alcohol followed by oven drying and UV-ozone treatment. Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS; VP AI4083, H.C. Starck) was spin cast from an aqueous suspension in ambient condition and oven-dried at 140 \(^\circ\)C for 10 minutes. All films were spun from CHCl\(_3\) under an inert, nitrogen atmosphere. Metallic contacts and LiF were deposited at a pressure of \( \sim 10^{-6} \) mbar by thermal evaporation.

2.6.5 Device characterization

Impedance spectroscopy was performed in the range of 10 Hz to 10 MHz using a Solartron 1260 impedance gain-phase analyzer with an AC drive voltage of 10 mV. Current-voltage characterization was conducted with Keithley 2400 source meter. The stability of measurements was established by carrying the tests under inert, nitrogen atmosphere at a stable temperature (295 K) in the dark. Film thicknesses were obtained using a Dektak 6M Stylus Profiler and, in cases the films were too soft for the tip of the profiler, these thicknesses were verified by AFM profile
Bibliography


