Synthetic strategies for modifying dielectric properties and the electron mobility of fullerene derivatives
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Chapter 5

An effect of Acetylene Moieties on the Charge Carrier Mobility of Fullerene Derivatives?

Abstract

Developing conjugated organic materials that exhibit fast electron transport is of extreme importance for developing electronic devices based on organic materials. The electron transporting properties of three fullerene derivatives with different numbers of acetylene groups in the side chains were investigated using a space-charge limited current method. Our results first suggested dramatically improved electron mobility in thin films of fullerene derivatives with one or two acetylene moieties in each alkyl side chain (F2M and F2D) and even in a film of a similar fullerene derivative with simply saturated alkyl side chains (F2A), after mild thermal annealing. However, the mobility values showed a strong dependence on the contact material used for charge injection into the organic layer.
5.1 Introduction

Conjugated organic molecules yield materials that have interesting semiconductor properties therefore, they have gained widespread interest among scientific and industrial communities. The high potential for solution-based processing is a unique feature of these semiconductors, which opens up the possibility of developing low-cost, flexible and lightweight electronic devices. The charge-carrier mobility ($\mu$), which is an indication of the ability of a charge to move in the material, is considered as one of the main parameters that control the performance of organic devices such as light-emitting diodes (OLEDs), field-effect transistors (OFETs) and solar cells (OPVs). Therefore, developing new organic semiconducting materials with improved charge transport properties is essential for further advancement of organic electronic and optoelectronic devices with higher efficiencies and lower energy loss. In this respect, much effort in the organic electronics community is being placed in order to improve the charge transport capabilities of organic semiconductors through material design.

5.1.1 Charge transport in organic semiconductors

The charge carrier transport in organic semiconducting materials is usually described through a hopping mechanism \textsuperscript{[11]}. It is generally accepted that the disordered configuration of conjugated polymers and molecules leads to a Gaussian distribution of the energy states and the mean free path of the charge carriers is limited due to this distribution of localized states with different energy levels. Consequently, the charge carriers must hop from one energy state to another in order to participate in the charge transport through the organic device \textsuperscript{[2]}. The hopping charge transport in structurally disordered organic semiconductors is temperature, electric-field, and charge-density dependent and is usually slower than the transport via delocalized band states in crystalline inorganic semiconductors.

In a semiconductor, the key quantity that characterizes charge transport is the charge-carrier mobility. The charge carrier mobility, $\mu$, is defined as the amount of induced directional velocity of mobile charge carriers, $\langle \nu \rangle$, subjected to an external electric field, $E$, \textsuperscript{[3]} and is expressed as

$$\mu = \langle \nu \rangle / E.$$  \hspace{1cm} (5.1)

Charge mobility can be experimentally determined by various techniques such as time-of-flight (TOF) measurements \textsuperscript{[4]}, space-charge limited current (SCLC) measurements and from field
effect transistor (FET) characteristics [5]. The TOF and SCLC methods are the most commonly used techniques for measuring vertical bulk carrier mobility while the FET technique usually evaluates the charge carrier mobility parallel to the substrate. It is worth to mention that the FET mobility values can be about 2 orders of magnitude higher than the mobilities measured in diode configuration, which can be attributed to the enhanced carrier density in FETs [5].

We are particularly interested in the vertical bulk electron mobility, which is more relevant for diode-like devices such as solar cells and organic light emitting diodes [7]. In the TOF technique, the transient photocurrent is recorded as a function of time as the charge carriers drift to the charge-collecting electrode under an applied voltage. The photocurrent is usually generated by irradiating the material by a laser pulse in the proximity of one of the electrodes. In order to improve the signal to noise ratio in TOF measurement, the thickness of the organic layer must be around 2 to 8 \( \mu \text{m} \) which is much larger than the typical values of 50-100 nm in OLED devices. Since the mobility measured in a TOF experiment can be thickness-dependent, mobility values obtained from TOF measurements may not be directly applicable in performance estimations [8,9]. In this regard, SCLC techniques give more reliable mobility values for practical applications. In the SCLC technique the mobility is obtained by measuring the electrical characteristics of diodes, which are built by sandwiching an organic layer between two electrodes. The electrodes are usually chosen in such a way that only electrons or holes are injected at low voltage. In the absence of traps and at low electric fields, the current density \( J \) scales quadratically with applied bias potential \( V \). This behavior is a characteristic of a space-charge limited current and it corresponds to the situation where the number of injected charges reaches a maximum because their electrostatic potential prevents the injection of additional charges [10]. The space-charge limited current can be described by the following equation:

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

(5.2)

where \( \varepsilon_r \) is the dielectric constant of the medium, \( \varepsilon_0 \) is the dielectric constant of the vacuum, \( J \) is the current density, \( V \) is the applied electric field and \( L \) is the thickness of the device and \( \mu \) is the electron mobility [10,11]. The charge carrier mobility can be directly obtained using Eq. (5.2) and current density versus voltage \( (J - V) \) measurements on single carrier devices [12]. A large number of high mobility hole-transporting materials have been synthesized and characterized in recent years. As of the electron transporting materials, most of the works have been focused to improve FET mobilities [13,14]. However, there are limited reports regarding high bulk mobility electron-transporting semiconductors and devices. In this respect,
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Fullerenes and particularly C_{60} are amongst the best performing electron transporting molecular semiconductors known to date. However, the limited solubility of unsubstituted fullerenes in common organic solvents is a limiting factor for wide spread use of fullerenes in organic electronic devices. This problem is solved by introducing more soluble fullerene derivatives such as [60]PCBM, [70]PCBM and indene-C_{60} bis-adduct (ICBA) (see Figure 5.1). Despite these recent developments, fabrication of high performance electron transporting fullerene derivatives via solution processing still remains a significant challenge.

![Chemical structures of [60], [70]PCBM, and ICBA](image.png)

**Figure 5.1:** Chemical structures of [60], [70]PCBM, and ICBA (only one of many isomers shown here for ICBA).

### 5.1.2 Research goals

Previously, we reported a polymerizable fullerene derivative with two diacetylene groups (F2D) (see Figure 5.2). When annealing a F2D film at temperatures above 180°C, the fullerene derivative polymerizes, yielding an insoluble film. This allowed the fabrication of fullerene/polymer bilayers, which could be used for exciton diffusion length measurements [15]. Surprisingly, our recent mobility measurements of F2D showed excellent electron mobility before annealing, even surpassing the mobility of PCBM, while the electron mobility dropped to zero after annealing to the polymerization temperatures. Inspired by the appeared excellent mobilities of F2D before annealing, we decided to investigate the effect of (di)acetylene groups on bulk electron mobility of the fullerene derivatives. In this respect, two new fullerene derivatives, one with two acetylene moieties (F2M) and the other one without acetylene moieties (with only saturated alkyl chains) (F2A) were synthesized (see Figure 5.2) and their electrical and structural
features were characterized using SCLC measurements as well as by TEM imaging.

![Chemical structures of F2D, F2M and F2A.](image)

**Figure 5.2:** Chemical structures of F2D, F2M and F2A.

### 5.2 Synthesis

F2D was synthesized according to the previously published procedure [15]. The synthetic route to prepare F2M, and F2A is shown in Scheme 5.1. 1-bromo-4-undecyne (3) was obtained in the reaction of 1-octyne (1) with 1,3-dibromopropane (2) and n-BuLi in THF. A subsequent Williamsons-type reaction of compound (3) with 3,5-dihydroxybenzaldehyde in the presence of K₂CO₃ in DMF at 90°C led to the corresponding benzaldehyde (4). Finally, the target fulleropyrrolidine (F2M) (6) was prepared by a Prato reaction of the 3,5-bis(undeca-4-ynyloxy)benzaldehyde (4), N-methylglycine (sarcosine) (5) and C₆₀, in ODCB at 120°C in 39% yield. Sarcosine first forms an iminium ion with the aldehyde. After subsequent loss of CO₂, the resulting ylide can then react with a fullerene C=C bond via a 1,3-dipolar cycloaddition reaction. F2A (9) was synthesized from 1-bromo-undecane (7) following a similar synthetic approach in 32% yield.

### 5.3 Characterization

The structures of the synthesized compounds were confirmed by analytical and spectroscopic data (¹H-NMR, ¹³C-NMR, FT-IR, and LCMS). The ¹H-NMR spectra of F2M recorded in CDCl₃ exhibited the expected signals of the hydrogen atoms in the chains, together with the characteristic peaks of the hydrogen atoms in the pyrrolidine ring. The signals of the ortho-hydrogen atoms of the phenyl group directly attached to the pyrrolidine ring appeared as broad singlet at room temperature due to restricted rotation of phenyl group [15, 16]. As it was mentioned
earlier in Chapter 3, the restricted rotation of the phenyl substituent on the pyrrolidine ring was observed for every Prato adduct that we synthesized with 2 chains at the meta-position of the phenyl group.

In addition, we have also investigated UV-vis absorption spectra of F2M and F2A. As expected, the optical properties of these molecules are similar, and show no significant difference with respect to the common Prato adducts like PP, which is mentioned in chapter 2.

It is noteworthy to mention that all of these compounds are very soluble in most of the common organic solvents, such as chloroform, toluene, and chlorobenzene.

Scheme 5.1: Synthetic route for fulleropyrrolidine compounds F2M and F2A.

[Scheme image with chemical structures and reaction steps]
5.4 Mobility measurements

The bulk electron mobility of the three synthesized fullerene derivatives was investigated by measuring the current-voltage characteristics of electron-only devices. In these electron-only devices, fullerene derivatives were sandwiched between an Au bottom contact and a LiF/Al top electrode. Based on the work functions, it is expected that LiF will form an Ohmic contact for electron injection into the organic layer. The work function of Au does not match the HOMO level of the fullerene derivatives (F2D, F2M, F2A), therefore, hole injection from Au into active layer can be neglected and only electrons are anticipated to flow under forward bias potential. The mobility values are obtained directly from the experimental \( J-V \) characteristics of electron-only devices of F2D, F2M, and F2A by using equation 5.2. The applied voltage was corrected for the built-in voltage, arising from the work-function difference of the electrodes. The obtained bulk electron mobilities of F2D, F2M and F2A at room temperature, measured in this way, are presented in Table 5.1. The results show that the electron mobilities for all of the synthesized compounds are higher than that of PCBM; F2D and F2M with two and one acetylene moieties in each chain show an increased electron mobility of 0.1 cm\(^2\)/Vs, which is a factor of 50 compared to PCBM (0.002 cm\(^2\)/Vs) and F2A (0.01 cm\(^2\)/Vs), with no acetylene moieties, shows a factor of 5 increase in electron mobility compared to PCBM.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \mu_e ) [cm(^2)/Vs] as cast</th>
<th>( \mu_e ) [cm(^2)/Vs] after annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBM</td>
<td>0.002</td>
<td>0.002 (^a)</td>
</tr>
<tr>
<td>F2D</td>
<td>0.1</td>
<td>0 (^b)</td>
</tr>
<tr>
<td>F2M</td>
<td>0.1</td>
<td>1.0-5.0 (^a)</td>
</tr>
<tr>
<td>F2A</td>
<td>0.01</td>
<td>0.5-1.0 (^c)</td>
</tr>
</tbody>
</table>

\(^a\) annealed 75 °C for 10 minutes  
\(^b\) annealed to 180 °C for 3 hours  
\(^c\) annealed 100 °C for 10 minutes

The effect of annealing on the electron mobility of the synthesized compounds was investigated (see Table 5.1). The measurements showed that while the electron mobility of PCBM did not change after and before annealing, the mobility of F2D strikingly dropped to zero after anneal-
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ing to 75°C. As reported earlier [15], F2D forms a highly cross-linked fullerene network (see Figure 5.4(d)), but it is not clear to us whether this plays a role regarding its strange transport behavior and it requires further investigations. In contrast, the electron mobility of fulleropyrrolidines with one (F2M) and no (F2A) acetylene moieties in each chain showed an increase of one order of magnitude after annealing to 1-5 cm²/Vs and 0.5-1 cm²/Vs respectively. At this point we would like to note that a bulk charge carrier mobility of > 1 cm²/Vs would be nothing less than spectacular: the observed values would be new record bulk charge carrier mobilities for organic semiconductors!

Figure 5.3 shows the measured mobility versus the applied electric field for F2D, F2M and F2A devices under optimized annealing conditions, as indicated in Table 5.1. For F2D, best results were obtained without annealing. The mobilities in Figure 5.3 were evaluated at various temperatures (i.e., 215 to 295 K). As can be seen, electron mobility increases with temperature, which is in accordance to the theoretical models proposed by Gills and Bässler to describe the hopping charge transport in amorphous organic materials [17]. In agreement with decreasing disorder, the higher mobility compounds F2M and F2A show weaker temperature activation of the charge transport compared to F2D. Furthermore, F2A and F2M show a negative dependency of charge carrier mobility on the applied electric field in low voltages. This behavior is usually observed as a result of a hopping charge transport in disordered solids [18].

5.5 TEM measurements

It is well established that the formation of ordered regions in conjugated organic films results in better inter-chain electronic coupling and hence improving charge transport properties in these materials [10, 19]. This suggests that the possible higher electron mobility of F2M and F2A fullerene derivatives can be attributed to the improved morphology of the spin-coated films after annealing [20]. In order to test this hypothesis, we have performed transmission electron microscopy (TEM) studies on F2M and F2A films after annealing to 75 and 100°C, respectively. The TEM images show that F2A and F2M molecules form very well-ordered domains throughout the film while the PCBM films do not show such ordered regions. This can be due to the self-packing of the alkyl side chains with and without acetylene moieties in these fullerene derivatives (see Figure 5.4). Hence, one would be tempted to hypothesize that the measured record high bulk mobilities could result from this exceptionally strong and homoge-
Figure 5.3: Mobility versus applied electric field in different temperatures for a) F2D b) F2A and c) F2M.

neous ordering pattern. Equally tempting, the mobility values, derived from the measurements described above, coincide in a remarkable way with a theoretical upper limit for charge carrier mobility in fullerene-based solids of 5.6 cm$^2$/Vs, reported by Kwiatkowski et al [21].

5.5.1 The effect of electrodes on the mobility measurements

As was mentioned earlier, an Au/fullerene/LiF/Al device architecture was used to measure the current-voltage characteristics. In a recent investigation by our collaborators, the LiF/Al electrode was replaced by Ba/Al. Surprisingly, the measured electron mobility values for F2M and F2A showed a considerable drop to 0.01 cm$^2$/Vs upon exchange of the top electrode, while the electron mobility value for the reference compound PCBM did not show a tangible differ-
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Figure 5.4: The TEM images for (a) PCBM, (b) F2M and (c) F2A films. Schematic of possible packing of F2M molecules in the film.

ence. In order to understand the possible reasons for this behavior, the current-voltage characteristics of fullerene-based devices with Ba/Al as contact layer material was also investigated (see Figure 5.5). In the case of PCBM, the device with a LiF interlayer showed higher mobility compared with the one with Ba/Al (see Figure 5.5(a)). For the case of F2M, the device with Ba/Al interlayer showed an electron mobility similar to that of PCBM (see Figure 5.5(b)). The investigations suggest that one possible reason for observing high mobility in fullerene devices with LiF/Al contact could be the diffusion of Li$^+$ (and F$^-$) ions or LiF molecules into the fullerene based environment much deeper than just merely forming a thin n-doped layer adjacent to the cathode to facilitate charge injection/extraction. This behavior has been previously reported in $\pi$-conjugated organic devices with thin LiF/Al contacts [22]. Although, it is not understood why the effect of Li$^+$ or LiF ‘doping’ would be substantially greater in the case of the new compounds F2A and F2M, compared to PCBM, one possible reason would be that Li$^+$ ions can diffuse into the deeper parts of the film due to the more ordered structure in F2M and
F2A films. Even if the actual species that supposedly penetrate the fullerene layer were known, i.e. either individual ions or LiF molecules, it is for both cases difficult to understand how this would lead to ‘doping’ in the sense of classical chemical doping of semiconductors, leading to the presence (or an increase) of free carriers in either the valence or the conduction band, hence higher corresponding charge carrier mobility.

Figure 5.5: $J - V$ curves for devices with LiF/Al and Ba/Al contacts for (a) PCBM and (b) F2M.
5.6 Conclusions

Charge carrier mobility of three fullerene derivatives which contain two (F2D), one (F2M) and no (F2A) acetylene moieties in each chain was investigated using a Au/fullerene/LiF/Al device architecture. The synthesized compounds did not show any significant difference in electro-optical and electro-chemical properties compared to PCBM but they exhibit better solubility. All of the synthesized compounds showed a dramatically improved charge carrier mobility compared to PCBM. The electron mobility of F2M and F2A improved after annealing to higher temperatures while the mobility of F2D drops down to virtually zero. ATEM analysis showed that both F2M and F2A form highly ordered domains throughout the whole film, after mild annealing. Such perfect order can potentially create favorable paths for charge transport in the ordered regions as compared to the amorphous regions. However, further investigations proved that the mobility values, calculated from the SCLC measurements, are dependent on the contact material. Replacement of the LiF/Al layer by a Ba/Al layer resulted in standard charge carrier mobilities. Hence, the high mobility is an artifact, a result of a process specific for the Al/LiF/fullerene interface. A high(er) charge carrier mobility is expected when the fullerene semiconductor layer is doped (in the classical semiconductor sense), leading to free charge carriers. However, at the moment we do not understand how such a doping could take place in this case, because it is not evident to us how penetrating Li\(^+\) (and F\(^-\)) ions or LiF molecules could dope the fullerene layer in this sense. This study does imply that in previously reported devices in which a LiF/Al/fullerene interface was present, the chemical composition of a substantial part of the fullerene layer might have been much more complicated than has been anticipated thus far.

5.7 Experimental

All reagents and solvents were used as received. The C\(_{60}\) used for the synthesis 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 (500MHz) or on a Varian Unity Plus (400 MHz) instrument, as indicated, at 25\(^\circ\)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 (4.6×250 mm).

**5.7.1 Device fabrication**

Electron-only devices were fabricated on glass substrates that were thoroughly cleaned by washing with detergent solution and ultrasonication in acetone and isopropyl alcohol, followed by UV-ozone treatment. Subsequently an Au (100 nm) electrode with a Cr (1 nm) adhesion layer was thermally evaporated. All fullerene-derivative films were spun from CHCl₃ under an inert, nitrogen atmosphere, yielding layers of around 300 nm. The devices were finished by evaporation of a LiF (1 nm)/ Al (100 nm) cathode. For TEM measurements, fullerene films were spin coated onto cleaned glass substrates, and annealed at their respective optimal temperatures. The films were floated off in deionized water and transferred onto a holey carbon TEM grid.

**5.7.2 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.

**5.7.3 Synthesis**

1-Bromoundec-4-yne (3): [23]

A solution of n-BuLi in hexane (1.6 M, 9.5 mL, 15.1 mmol) was added dropwise to a solution of 1-octyne (1.99 g, 18.1 mmol) in dry THF (20 mL) at -78 °C over a period of 20 min and the mixture was stirred for 1 h. After addition of DMPU (1,3-dimethyl-3,4,5,6-tetrahydro-2-pyrimidinone) (1.8 mL), the resulting mixture was transferred to a solution of 1,3-dibromopropane (3.0 g, 15.1 mmol) in dry THF (15 mL) and the mixture was allowed to warm to room temperature over 1 h. After stirring for 20 h saturated aqueous solution of NH₄Cl (30 mL, saturated aqueous solution) was added. The
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alkyne was extracted with ether three times (3×40 mL). The combined extracts were washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure. Purification was achieved by column chromatography (silica gel; hexane/ethyl acetate 9:1) to give 1-bromoundec-4-yne as colorless oil (69%, 2.4 g).

\[ ^1H-NMR \ (400 \text{ MHz, CDCl}_3): \delta = 3.50-3.53 \ (t, J = 6 \text{ Hz, 2H}), \ 2.30-2.35 \ (m, 2H), \ 2.15-2.11 \ (m, 2H), \ 2.01-1.98 \ (m, 2H), \ 1.50-1.45 \ (m, 2H), \ 1.30-1.22 \ (m, 6H), \ 0.88 \ (t, J = 6.0 \text{ Hz, 3H}). \]

3,5-Bis(undeca-4-ynyloxy)benzaldehyde (4):

A three-necked, 50 mL round-bottom flask was charged with 3,5-dihydroxybenzaldehyde (500 mg, 3.63 mmol), K₂CO₃ (1.6 g, 11.58 mmol), 1-bromoundec-4-yne (2.08 g, 9 mmol) and dry DMF (25 mL). The reaction mixture was stirred over night at 90℃ under N₂. The solution was cooled to room temperature, and water (15 mL) was added. The aqueous solution was extracted with EtOAc (3×40 mL). The combined organic phases were dried over Mg₂SO₄, concentrated in vacuo, and purified by column chromatography (silica gel; hexane/ethyl acetate 10:1) affording product as off-white solid (0.81 g, 51%).

\[ ^1H-NMR \ (400 \text{ MHz, CDCl}_3): \delta = 9.88 \ (s, 1H), \ 6.99 \ (d, J = 3 \text{ Hz, 2H}), \ 6.7 \ (t, J = 3 \text{ Hz, 1H}), \ 4.10-4.07 \ (t, J = 6 \text{ Hz, 4H}), \ 2.37-2.34 \ (m, 4H), \ 2.15-2.11 \ (m, 4H), \ 1.97-1.94 \ (m, 4H), \ 1.48-1.34 \ (m, 4H), \ 1.33-1.24 \ (m, 12H), \ 0.85 \ (t, J = 4.0 \text{ Hz, 6H}). \]

\[ ^{13}C-NMR \ (100 \text{ MHz, CDCl}_3): \delta = 191.88, \ 160.59, \ 138.32, \ 108.08, \ 107.65, \ 81.21, \ 78.59, \ 66.85, \ 31.33, \ 29.00, \ 28.60, \ 28.53, \ 18.71, \ 15.41, \ 14.09, \ 14.02. \]

F2M (6):

An oven-dried three-necked, 250 mL round-bottom flask was charged with C₆₀ (720 mg, 1 mmol), benzaldehyde from the previous reaction (4) (438 mg, 1 mmol), sarcosine (270 mg, 3 mmol) and dry o-dichlorobenzene (100 mL). The reaction mixture was stirred under N₂ at 110℃ for 72 h. The solvent was evaporated in vacuo. The crude residue was resolved in CHCl₃ and passed through a chromatography column (Silica gel; toluene).
to afford the desired compound as a brown solid. The product was redissolved in 7 mL of chloroform, precipitated with MeOH, washed repeatedly with MeOH and pentane, and dried in vacuo at 50°C. This procedure gave 600 mg (0.50 mmol, 50%) of F2M.

\[ \text{H-NMR (400 MHz, CDCl}_3\text{):} \delta = 6.99 \text{ (br s, 2H), 6.43 (s, 1H), 6.96 (d, J = 8 Hz, 1H), 4.82 (s, 1H), 4.23 (d, J = 8 Hz, 1H), 4.07-4.04 (m, 4 H), 2.82 (s, 3H), 2.33-2.29 (m, 4H), 2.13-2.09 (m, 4H), 1.93-1.86 (m, 4H), 1.49-1.41 (m, 4H), 1.36-1.23 (m, 12H), 0.87 (t, J = 8.0 Hz, 6H).} \]

\[ \text{C-NMR (100 MHz, CDCl}_3\text{):} \delta = 160.13, 156.09, 154.08, 153.62, 153.44, 147.28, 147.01, 146.44, 146.29, 146.23, 146.20, 146.13, 146.09, 146.06, 145.93, 145.92, 145.77, 145.53, 145.51, 145.46, 145.31, 145.26, 145.22, 145.12, 144.67, 144.62, 144.35, 143.10, 142.94, 142.66, 142.55, 142.20, 142.18, 142.14, 142.12, 142.10, 142.01, 141.99, 141.90, 141.79, 141.58, 140.15, 140.09, 139.78, 139.61, 139.14, 136.60, 136.43, 135.75, 135.73, 101.99, 83.70, 81.08, 78.87, 76.96, 76.69, 69.96, 69.03, 66.69, 40.09, 31.37, 29.08, 28.64, 28.61, 22.59, 18.80, 15.51, 14.11. \]

\[ \text{IR (cm}^{-1}\text{):} 2923, 2852, 2777, 2325, 2188, 1591, 1447, 1428, 1330, 1291, 1154, 1060, 849, 766, 689, 597, 573, 552. \]

Mass: m/z calcd. for C_{91}H_{47}NO_{2}: 1186.4, Found : 1187.0

Anal. Calcd. For C_{91}H_{47}NO_{2}: C, 92.13; H, 3.99; N, 1.18. Found : C, 92.32; H, 3.93; N, 1.33

3,5-Bis-(undecanoxy)benzaldehyde (8): \[ \text{[24]} \]

A three-necked, 50 mL round-bottom flask was charged with 3,5-dihydroxybenzaldehyde (500 mg, 3.63 mmol), K_{2}CO_{3} (1.6 g, 11.58 mmol), 1-bromoundecane (2.11 g, 9 mmol) and DMF (25 mL). The reaction mixture was stirred over-night at 90°C under N_{2}. The solution was cooled to room temperature, and water (20 mL) was added. The aqueous solution was extracted with CH2Cl2 (3×40 mL). The combined organic phases were dried over Na_{2}SO_{4}. The solvent was removed under reduced pressure. Purification was achieved by column chromatography (silica gel; hexane/ethyl acetate 5:3) to afford product (8) as light yellow solid (0.9 g, 85%).

\[ \text{H-NMR (400 MHz, CDCl}_3\text{):} \delta = 9.89 \text{ (s, 1H), 6.98 (s, 2H), 6.69 (s, 1H), 3.98 (t, J = 6 Hz, 4H), 1.82-1.76 (m, 4H), 1.33-1.27 (m, 32H), 0.88 (t, J = 8.0 Hz, 6H).} \]
F2A (9):
An oven-dried three-necked, 250 mL round-bottom flask was charged with C60 (720 mg, 1 mmol), 3,5-Bis-(undecanoxy)benzaldehyde (8) (291 mg, 1 mmol), sarcosine (270 mg, 3 mmol) and o-dichlorobenzene (100 mL). The reaction mixture was stirred under N2 at 110 °C for 72 h. The solvent was evaporated in vacuo. The crude residue was resolved in CHCl3 and passed through a chromatography column (Silica gel; toluene) to afford the desired compound as a brown solid. The product was redissolved in 7 mL of chloroform, precipitated with MeOH, washed repeatedly with MeOH and pentane, and dried in vacuo at 50 °C. This procedure gave 410 mg (34 mmol, 34%) of F2A.

1H-NMR (500 MHz, CDCl3): δ = 6.98 (br s, 2H), 6.41 (s, 1H), 6.98 (d, J = 8 Hz, 1H), 4.83 (s, 1H), 4.26 (d, J = 8 Hz, 1H), 3.97-3.94 (m, 4 H), 2.84 (s, 3H), 1.75-1.69 (m, 4H), 1.45-1.42 (m, 4H), 1.34-1.27 (m, 26H), 0.87 (t, J = 8.0 Hz, 6H).

13C-NMR (125 MHz, CDCl3): δ = 149.99, 148.99, 148.95, 148.90, 148.83, 148.80, 148.77, 148.64, 148.61, 148.47, 148.22, 148.02, 147.95, 147.93, 147.91, 147.90, 147.83, 147.81, 147.74, 147.72, 147.58, 147.47, 147.37, 147.31, 147.26, 147.06, 147.04, 145.82, 145.64, 145.36, 145.26, 144.88, 144.84, 144.80, 144.71, 144.60, 144.50, 144.36, 144.27, 142.85, 142.79, 142.48, 142.29, 138.42, 86.44, 79.90, 70.92, 42.80, 34.60, 32.33, 32.32, 32.29, 32.11, 32.05, 31.84, 28.71, 25.39, 16.84.

IR (cm⁻¹) : 2918, 2849, 2777, 2326, 1591, 1449, 1429, 1355, 1330, 1292, 1155, 1054, 1028, 940, 897, 830, 766, 689, 557.

MS:mass: m/z calcd. for C91H55NO2 : 1194.4, Found : 1195.0
Anal. Calcd. For C91H55NO2: C, 91.51; H, 4.64; N, 1.17. Found : C, 91.20; H, 4.62; N, 1.28

Bibliography


An effect of Acetylene Moieties on the Charge Carrier Mobility of Fullerene


