Synthetic strategies for modifying dielectric properties and the electron mobility of fullerene derivatives
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Chapter 4

Designing High Dielectric Constant Fullerene Derivatives; Alternative Strategies

Abstract

Several new compounds were synthesized in order to study the effect of several parameters on the dielectric constant of fullerene derivatives. First, we investigated the effect of changing the length of ethylene glycol-type side chains; second we studied the effect of installing high dielectric constant side chains. Finally, the influence of inserting highly polarizable groups was investigated.
4.1 Introduction

So far we have looked at two different strategies for increasing dielectric constant of fullerene derivatives. These strategies include installing polar and flexible TEG side chains and incorporation of strong dipolar push-pull groups. Looking at the obtained results, one can conclude that tuning dielectric properties of complex molecules like fullerenes cannot be simply accomplished by conventional methods as suggested in Debye equation. More complex parameters like the intermolecular interactions or interaction of the incorporated groups with the fullerene cage may play a role as well in these materials. Therefore, studying the effect of numerous parameters by employing unconventional strategies can increase our understanding of dielectric response of fullerene derivatives and hence lead to new design rules for synthesizing high dielectric constant compounds. In this regard, several new parameter studies are proposed in this chapter.

4.2 The effect of ethylene glycol chain lengths

In the previous chapter, it was demonstrated that incorporating triethylene glycol monoethyl ether (TEG) chains in the molecular structure of the fullerene increases the dielectric constant of the compound. At this point, a rather obvious question is how the dielectric constant would change by increasing or decreasing the length of the ethylene glycol-type chains. Since the dielectric constant is directly related to the polarizability, the dependency of polarizability on chain length suggests that the dielectric constant would also be affected by changing the number of subunits along the chain. In this regard, we aim to study the effect of chain length on the dielectric constant of the compounds by studying fullerene derivatives bearing shorter or longer ethylene glycol side chains.

For this purpose, fulleropyrrolidines PDEG-1 and PDEG-2 bearing diethylene glycol methyl ether groups and PMEG-1 and PMEG-2 bearing ethylene glycol methyl ether groups were prepared via the Prato method. Similar to what we observed in TEG chains, we expected that the addition of DEG chain(s) to fullerenes would also improve their polarizability and hence their dielectric constant. This increase in the polarizability is attributed to the reorientation of the dipole moments of the ether moieties along the DEG chains.

The synthetic route to prepare fulleropyrrolidine PDEG-1, PDEG-2, PMEG-1 and PMEG-2 is depicted in Scheme. Treatment of diethylene glycol methyl ether (1) with toluene-p-sulfonyl
chloride (TsCl) and NaOH in THF obtained 2-[2-methoxyethoxy]ethyl $p$-tosylate (2). The etherification was performed by reaction of the resulting tosylated alcohol (2) and 4-hydroxybenzaldehyde together with $\text{K}_2\text{CO}_3$ in DMF afforded corresponding benzaldehyde (3) in good yield. The fulleropyrrolidine (PDEG-1) (4) was synthesized via the Prato method, by 1,3-dipolar cycloaddition of an azomethineylide (generated in-situ from the 4-(2-(2 methoxyethoxy) ethoxy) benzaldehyde (3) and $\text{N}$-methylglycine) and $\text{C}_6\text{O}_{60}$ in ODCB at 90 °C in 41% yield. PDEG-2 (6) was synthesized from 3,5-dihydroxybenzaldehyde by following a similar synthetic approach as described above in 46% yield. Similarly starting from ethylene glycol methyl ether (7) through the same synthetic approach PMEG-1 and PMEG-2 were obtained in 22% and 15% yield respectively.

Scheme 4.1: The synthetic route for preparing PDEG-1, PDEG-2, PMEG-1 and PMEG-2.

i) TsCl, NaOH, THF ii) 4-hydroxybenzaldehyde, $\text{K}_2\text{CO}_3$, DMF iii) $\text{C}_6\text{O}_{60}$, sarcosine, ODCB, 90 °C iv) 3,5-dihydroxybenzaldehyde, $\text{K}_2\text{CO}_3$, DMF
The structures of the synthesized compounds are confirmed by analytical and spectroscopic data. The $^1$H-NMR spectrum of PDEG-1 and PDEG-2 is given in Figure 4.1. Interestingly, the ortho H-atoms of the aryl group in PDEG-2 seemed to be broader than the corresponding ones in PDEG-1, which are shown by red stars in the Figure 4.1. This is most likely the result of the more hindered rotation of the phenyl group of PDEG-2 due to the presence of the two alkyl chains at the meta-positions. It is worth to mention that we have seen this behavior in almost all of the Prato adducts with 2 chains at the meta-position of the phenyl group.

The UV-vis absorption spectra of PDEG-1, PDEG-2, PMEG-1 and PMEG-2 are almost the same.
as that of PP. This similarity suggests that DEG and MEG chains have a minimal effect on UV-vis absorption, hence little or no electronic interaction with the fullerene cage, under these circumstances. In the next step, the electrochemical properties of PDEG-1, PDEG-2, PMEG-1 and PMEG-2 were investigated by cyclic voltammetry. We also studied PP (see section 2.3.2 of chapter 2) and PCBM as the reference compounds. The measured half-wave potentials of the reduction processes of all compounds are listed in Table 4.1. The first reduction potential, which approximates the LUMO energy level of these compounds, is almost the same for PDEG-1, PDEG-2, PMEG-1, PMEG-2 and the controls, PP and PCBM. This similarity implies that DEG and MEG chains do not affect the LUMO energy of these fullerene derivatives. In addition, there is no significant change in the potential of the second reduction.

Table 4.1: Electrochemical properties and $\varepsilon_r$ of PDEG-1, PDEG-2, PMEG-1, PMEG-2, PP and PCBM.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}$ 1, red</th>
<th>$E_{1/2}$ 2, red</th>
<th>$\varepsilon_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBGM</td>
<td>-1.092</td>
<td>-1.482</td>
<td>3.9 ± 0.1</td>
</tr>
<tr>
<td>PP</td>
<td>-1.114</td>
<td>-1.508</td>
<td>3.8 ± 0.4</td>
</tr>
<tr>
<td>PDEG-1</td>
<td>-1.101</td>
<td>-1.499</td>
<td>4.7 ± 0.4</td>
</tr>
<tr>
<td>PDEG-2</td>
<td>-1.107</td>
<td>-1.504</td>
<td>5.8 ± 0.8</td>
</tr>
<tr>
<td>PMEG-1</td>
<td>-1.110</td>
<td>-1.508</td>
<td>b</td>
</tr>
<tr>
<td>PMEG-2</td>
<td>-1.104</td>
<td>-1.501</td>
<td>b</td>
</tr>
</tbody>
</table>

*Experimental conditions: V vs Fc/Fc+, Bu$_4$NPF$_6$ (0.1 M) as the supporting electrolyte, ODCB/CH$_3$CN (4:1) as the solvent; scan rate, 10 mV/s

*bInsufficient film quality

The dielectric constant of the synthesized fullerene derivatives was measured by spectral impedance measurements (for details regarding the dielectric constant measurement the reader is referred to section 2.6.2 of chapter 2). The average values obtained for the dielectric constant of PDEG-1, PDEG-2, PP and PCBM are shown in Table 4.1. The dielectric constant of PMEG-1 and PMEG-2 are not reported because the obtained values are unreliable due to insufficient film quality as resulting from the lower solubility of these compounds. As expected, the dielectric constant for both PDEG-1 and PDEG-2 increased to 4.7 and 5.8 respectively, in comparison to PCBM ($\varepsilon_r \sim 3.9$) and PP ($\varepsilon_r \sim 3.8$). It should be noted that, the measured dielectric constant for all these compounds is constant in the frequency range of 100 to $10^6$ Hz.
This enhancement of the dielectric properties with respect to the reference compounds PP and PCBM is most probably due to the increased polarizability afforded by DEG side chains. However, one should note that the measured dielectric constants for PDEG-1 and PDEG-2 differ only by the sum of their standard deviations. Hence, there is no clear difference. It is worth to mention that there is no significant difference in the measured values for PDEG-1 and PDEG-2 in comparison to fullerene derivatives PTEG-1 ($\varepsilon_r \sim 5.7\pm0.2$) and PTEG-2 ($\varepsilon_r \sim 5.3\pm0.2$) with longer side chain (TEG). We therefore conclude that the measured permittivity results from a complex interplay between the fullerene cages and their substituents and is not simply a result of increasing the volume fraction of glycol units in the film.

### 4.2.1 Increasing polarity of the chains

Hydrogen bonding can influence the dielectric constant of a material in several ways. First, hydrogen bond is necessarily considered as a polar bond which consequently results in a higher dipolar moment \[2, 3\]. Second, it can improve molecular orientational correlation in the material. Goldman and Joslin showed that hydrogen-bonded liquids tend to have high dielectric constants because the molecular orientational correlation is enhanced by intermolecular hydrogen bonds \[3\].

In connection to the previously mentioned points, we have altered the chemical structure of the fullerene derivatives by addition of ethylene glycol chains with a terminal OH group. This modification not only increases the polarity of the chains but also promotes hydrogen bonding as very polarizable units in the molecules. For this purpose, fullerene derivatives PCBTE-OH, PCBDE-OH and PCBE-OH with three, two and one ethylene glycol units have been synthesized. The synthetic routes for the proposed compounds are shown in Scheme 4.2.

It worth to mention that the first compound (15) (PCBE-OH) has been previously used by Subbiah et. al. as an interface layer at cathode in order to improve the power conversion efficiency of the OPV device \[4\].

The proposed fullerene derivatives are prepared according to the following method. Transesterification of PCBM (13) with ethylene glycol (14) in the presence of dibutyltin oxide (DBTO) in ODCB at 120 °C afforded PCBE-OH (15) in 38% yield. Transesterification of diethylene glycol (16) and triethylene glycol (18) with PCBM under the same condition afforded methanofullerene PCBDE-OH (17) and PCBTE-OH (19) in 30% and 42% yield, respectively. The structures of the synthesized compounds are confirmed by spectroscopic data. The $^1$H-NMR spectrum of
PCBDE-OH is given in Figure 4.2. The characteristic peaks of the protons on the methylene groups in PCBX type methanofullerenes were observed at 2.2 ppm, 2.5 ppm and 2.9 ppm. In addition, signals of the diethylene glycol protons appeared at 3.6 ppm, 3.7 ppm and 4.7 ppm. Interestingly, in the transesterification reaction of PCBM and diethylene glycol a side-product (PCB\textsubscript{2}DE) was obtained in 7% yield. The \textsuperscript{1}H-NMR and LCMS analysis suggested that this might be esterified product of the reaction of PCBDE-OH and PCBM. The possible structure and \textsuperscript{1}H-NMR of this side-product is shown in Figure 4.3.

**Scheme 4.2:** The synthetic route for preparing PCBE-OH, PCBDE-OH and PCBTE-OH.

The electrochemical properties of the compounds were investigated by cyclic volumetric (CV)
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Figure 4.2: $^1$H-NMR spectrum of PCBDE-OH

Figure 4.3: Structure and $^1$H-NMR spectrum of PCB$_2$DE.

measurements. The first and second half wave potentials are presented in Table 4.2. All of the compounds show a relatively similar half wave potential and hence LUMO energy level and there is no significant difference compared to PCBM.
Table 4.2: Electrochemical properties of PCBDE-OH, PCBTE-OH and PCBM.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}$ 1, red</th>
<th>$E_{1/2}$ 2, red</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBDE-OH</td>
<td>-1.111</td>
<td>-1.475</td>
</tr>
<tr>
<td>PCBTE-OH</td>
<td>-1.082</td>
<td>-1.476</td>
</tr>
</tbody>
</table>

$E_{1/2}$ values are referenced to V vs Fc/Fc$^+$, Bu$_4$NPF$_6$ (0.1 M) as the supporting electrolyte, ODCB/CH$_3$CN (4:1) as the solvent; scan rate, 10 mV/s.

The dielectric constant of the synthesized compounds has not been measured at the time of writing of this thesis by our collaborators. Therefore, it is not possible to draw any conclusion on the effect of addition of OH groups on the dielectric properties of fullerene derivatives, at this moment.

4.3 Installing high-$\varepsilon$ side chains

The next proposed strategy for synthetically tuning the dielectric constant of fullerene derivatives is to install side chains featuring an inherently high dielectric constant. Up to now, we have mainly studied fullerene derivatives bearing ethylene glycol chains with variable lengths and structures for tuning dielectric response. The inherent dielectric constant of these side chains ranges between $\sim$7 to 14. For example, triethylene glycol dimethyl ether (TEG) and ethylene glycol dimethyl ether chain have an apparent dielectric constant of 7.6 and 7.3 respectively while ethylene glycol monomethyl ether features a dielectric constant of 13.4 due to the presence OH group (see Figure 4.4).

Compared to ethylene glycol chains, cyclic carbonate groups due to their strong dipole-dipole interactions have an apparent dielectric constant ranging from $\sim$30 to 100 (see Figure 4.5).
Ethylene carbonate and methylene carbonate feature a dielectric constant of 89.6 ± 0.3 and 61.7 ± 0.3, respectively. Replacement of the hydrogen atom in ethylene carbonate by a (much larger!) chlorine atom decreases its dielectric constant. This might be due to reduction of the net dipole moment [6]. However, the change from a methylene carbonate to the monochloro-derivative leads to an increase in dielectric constant, despite the decreasing the dipole moment. It is thought that intermolecular hydrogen bonding may assist dipolar interactions in this case [6].

Figure 4.5: Molecular structure and dielectric constant of some cyclic carbonates.

In this section we propose several new fullerene derivatives bearing carbonate groups. P1C5 and P2C5 (compound 22 and 24 in Scheme 4.3, respectively) contain one and two carbonate groups, respectively, which are attached to the fulleropyrrolidine through pentamethylene moieties. Furthermore, we have designed PCBC (compound 26 in Scheme 4.3) in which a carbonate group is close to directly attached to PCB moiety.

The synthetic routes for preparation of the proposed compounds are shown in Scheme 4.3. Treatment of 4-(bromopentyl)-1,3-dioxolan-2-one (20) with p-hydroxybenzaldehyde in the presence of K₂CO₃ in DMF afforded corresponding benzaldehyde (21) in good yield. The Prato reaction of C₆₀ with N-methylglycine and 4-[4-(pentoxy)-1,3-dioxolan-2-one]benzaldehyde (21) in ODCB led to target fulleropyrrolidine P1C5 (22) in 25% yield. P2C5 (24) was synthesized from 3,5-dihydroxybenzaldehyde by following a similar synthetic approach as described above.
in 44% yield. Transesterification of PCBM with 4-(hydroxymethyl)-1,3-dioxolan-2-one (25) in the presence of dibutyltin oxide (DBTO) in ODCB gave PCBC (26) in 30% yield. The structures of the synthesized compounds were confirmed by spectroscopic analysis. The $^1$H-NMR spectrum of PCBC is given in Figure 4.6. The characteristic peaks of the protons on the methylethyl carbonate moiety appeared at 4.3 ppm, 4.5 ppm and 4.8 ppm.

The reduction potentials of the synthesized compounds were investigated through CV measurements. Comparing the half wave potentials of these compounds with those of PCBM suggests that the addition of carbonate groups does not affect the reduction potentials of the first
and second reduction, compared to those of PCBM, under these circumstances (see Table 4.3).

**Table 4.3:** Electrochemical properties of P1C5, P2C5, PCBC and PCBM.

<table>
<thead>
<tr>
<th>Compound</th>
<th>E_{1/2} 1, red</th>
<th>E_{1/2} 2, red</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBM</td>
<td>-1.092</td>
<td>-1.482</td>
</tr>
<tr>
<td>P1C5</td>
<td>-1.110</td>
<td>-1.483</td>
</tr>
<tr>
<td>P2C5</td>
<td>-1.080</td>
<td>-1.485</td>
</tr>
<tr>
<td>PCBC</td>
<td>-1.079</td>
<td>-1.468</td>
</tr>
</tbody>
</table>

*Experimental conditions: V vs Fc/Fc\(^+\), Bu\(_4\)NPF\(_6\) (0.1 M) as the supporting electrolyte, ODCB/CH\(_3\)CN (4:1) as the solvent; scan rate, 10 mV/s

The dielectric constants of the synthesized compounds have not been measured by our collaborators at the time of writing of this thesis. Hence, it is not possible to discuss the effect of addition of incorporating high dielectric constant groups on the dielectric properties of fullerene derivatives, at this moment.

### 4.4 Incorporation of highly polarizable atoms

The presence of certain molecular structures and groups can provide a higher polarizability, which can subsequently lead to an increase in dielectric constant of the molecule. For example,
highly delocalized electron clouds in \( \pi \)-conjugated systems and electron clouds of large atomic orbitals heavy atoms like bromine and iodine are easily polarizable while the small size electron cloud of atoms like fluorine is tightly kept, resulting in lower polarizability. It is shown that generally the polarizabilities of fullerene halogenides are higher than a value of pristine \( C_{60} \) \[2\]. Since polarizability is a determining factor in the dielectric response of a material, inclusion of highly polarizable atoms in the molecular structure of fullerene could serve as a potential strategy for adjusting the dielectric constant.

**Scheme 4.4:** The synthetic route for preparing PCBTI and PCBPBr.

In this section, PCBM derivatives containing iodine and bromine atoms are synthesized in order to study the effect of highly polarizable atoms on the dielectric constant of a fullerene-based compound.

The synthetic routes for preparation of PCBTI and PCBPBr (compound 28 and compound 30 in Scheme 4.4, respectively) are shown in scheme 4.4. Transesterification of PCBM with 2,3,5-triiodobenzyl alcohol (27) and 2,3,4,5,6-pentabromobenzyl alcohol (29) following a similar
procedure as described in the previous section afforded the corresponding methanofullerenes PCBTI (28) and PCBPBr (30) in 10% and 18% yields, respectively. It should be mentioned that, due to the low solubility of these compounds in most organic solvents, the dielectric constants of the synthesized compounds have not been measured at the time of writing of these thesis by our collaborators. Therefore, it is not possible to draw any conclusion on the effect of bulky halogen atoms on the dielectric properties of PCBM, at this moment.

To conclude this Chapter, we have synthesized several series of fullerene derivatives with side groups of various types to start investigating their influence. The synthetized compounds are fully characterized and the spectroscopic data confirm the purity of the products. However, the dielectric constants of these compounds are not measured by the time of writing this thesis.

4.5 Experimental section

**General:** All reagents and solvents were used as received. All the solvents which were used for precipitation and washing the fullerene derivatives were HPLC grade. The C₆₀ 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). ¹H-NMR and ¹³C-NMR measurements were performed on a Varian Unity Plus (400 MHz) instrument, as indicated, at 25 °C; Chemical shift values are reported in ppm; Multiplicities are denoted as follows: s = singlet, m = multiplet, b = broad. 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); UV-vis absorption spectra were measured with a Perkin-Elmer Lambda 900 spectrometer.
4.5.1 Synthesis

2-[2-methoxyethoxy]ethyl p-tosylate (2): 

Sodium hydroxide (1.71 g, 42.8 mmol) dissolved in water (8 mL) and diethylene glycol methyl ether (3.6 g, 30 mmol) in dry THF (8 mL) was placed in a three-necked, 100 mL flask. The mixture was cooled on an ice bath. p-Toluenesulfonyl chloride (5.22 g, 27.8 mmol) in THF (8 mL) was added drop-wise to the mixture over 1 h. The solution was stirred at room temperature overnight, then poured into ice-water (150 mL) and the product was extracted with ethyl acetate. The organic layer was dried over Na₂SO₄. The solvent was evaporated in vacuo to give the NMR pure compound as colorless oil (6.95 g, 25.27 mmol, 90.8%).

1H-NMR (400 MHz, CDCl₃): δ = 7.76 (d, J = 8.0, 2H), 7.31 (d, J = 8.0, 2H), 4.13 (t, J = 4.8, 2H), 3.65 (t, J = 4.8, 2H), 3.55-3.53 (m, 2H), 3.45-3.43 (m, 2H), 3.31 (s, 3H), 2.41 (s, 3H).

4-(2-(2 methoxyethoxy) ethoxy)benzaldehyde (3): 

A three-necked, 100 mL round-bottom flask was charged with p-hydroxybenzaldehyde (440 g, 3.63 mmol), 2-[2-methoxyethoxy]ethyl p-tosylate (1.17 g, 4.28 mmol), K₂CO₃ (800 mg, 5.8 mmol) and absolute DMF (15 mL). The reaction mixture was stirred overnight at 90 °C. After cooling, the crude reaction mixture was poured into water (50 mL, pH = 2) in a 100 mL Erlenmeyer flask and the product was extracted with ethyl acetate. The organic layer was washed subsequently with water (3 × 25 mL) and brine (1 × 25 mL) and dried over Na₂SO₄. The solvent was evaporated in vacuo to give NMR pure compound as light yellow oil (800 mg, 3.3 mmol, 90.9%).

1H-NMR (400 MHz, CDCl₃): δ = 9.87 (s, 1H), 7.81 (d, J = 8.0, 2H), 7.01 (d, J = 8.0, 2H), 4.21 (t, J = 4.0, 2H), 3.87 (t, J = 4.2, 2H), 3.74-3.68 (m, 2H), 3.58-3.53 (m, 2H), 3.42 (s, 3H).

13C-NMR (100 MHz, CDCl₃): δ = 190.74, 163.80, 131.92, 130.01, 114.84, 72.30, 70.83, 69.81, 67.71, 59.08.
PDEG-1 (4):
An oven-dried three-necked, 250 mL round-bottom flask was charged with \( \text{C}_{60} \) (720 mg, 1 mmol), 4-(2-(2 methoxyethoxy) ethoxy)benzaldehyde (240 mg, 1 mmol), sarcosine (270 mg, 3 mmol) and dry o-dichlorobenzene (100 mL). The reaction mixture was stirred under \( \text{N}_2 \) at 90° C for 72 h. The mixture was concentrated in vacuo to ~15 mL, and the crude residue was purified by column chromatography (Silica gel; toluene/ethyl acetate 4:1) to afford the pure compound as a brown solid. The product was dissolved in 10 mL of chloroform, precipitated with MeOH, washed repeatedly with MeOH (2 times) and pentane (2 times), and dried in vacuo at 50 °C. This procedure gave 400 mg (0.41 mmol, 41%) of PDEG-1.

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.70 \) (s, 2H), 6.96 (d, \( J = 8.0 \), 2H), 4.97 (d, \( J = 12.0 \), 1H), 4.87 (s, 1H), 4.25 (d, \( J = 12.0 \), 1H), 4.14 (t, \( J = 4.0 \), 2H), 3.85 (t, \( J = 4.0 \), 2H), 3.72-3.69 (m, 2H), 3.57-3.55 (m, 2H), 3.37 (s, 3H), 2.78 (s, 3H).

\(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \( \delta = 158.80, 156.37, 154.10, 153.64, 153.61, 147.29, 147.27, 146.77, 146.51, 146.32, 146.29, 146.24, 146.19, 146.13, 146.11, 146.07, 145.92, 145.90, 145.76, 145.53, 145.47, 145.44, 145.31, 145.29, 145.25, 145.21, 145.13, 144.68, 144.62, 144.38, 143.12, 142.96, 142.65, 142.56, 142.53, 142.52, 142.27, 142.24, 142.14, 142.10, 142.01, 141.94, 141.82, 141.66, 141.52, 140.13, 140.09, 139.88, 139.58, 136.75, 136.54, 135.77, 135.75, 130.41, 129.12, 114.67, 83.15, 77.20, 71.94, 70.75, 69.98, 69.77, 68.96, 67.33, 59.06, 39.97.

IR (cm\(^{-1}\)): 2846, 1609, 1509, 1312, 1259, 1225, 1174, 1128, 1103, 846, 600, 573, 551, 526.

Mass m/z : Calcd for C\(_{74}\)H\(_{21}\)NO\(_3\): 971.2. Found: 971.8

Anal. Calcd. For C\(_{74}\)H\(_{21}\)NO\(_3\): C, 91.45; H, 2.18; N, 1.44. Found: C, 91.35; H, 2.11; N, 1.60

3,5-bis(2-(2-methoxyethoxy)ethoxy) benzaldehyde (5):
A three-necked, 50 mL round-bottom flask was charged with 3,5-dihydroxybenzaldehyde (500 mg, 3.63 mmol), 2-[2-methoxyethoxy]ethyl p-tosylate (2.35 g, 8.58 mmol), K\(_2\)CO\(_3\) (1.6 g, 11.58 mmol), and dry DMF (25 mL). The reaction mixture was stirred over night at 90°C. After cooling, the crude reaction mixture was poured into water in a 100 mL Erlenmeyer flask and the product was extracted with
ethyl acetate. The organic layer was dried over Na$_2$SO$_4$. The solvent was evaporated in vacuo. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate 1:2) to give pure compound as light yellow oil (850 mg, 2.48 mmol, 68.5%).

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 9.84 (s, 1H), 6.98 (d, J = 2.3, 2H), 6.72 (t, J = 2.3, 1H), 4.13 (t, J = 4.0, 4H), 3.83 (t, J = 4, 4H), 3.69 3.67 (m, 4H), 3.55 3.53 (m, 4H), 3.35 (s, 6H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 190.83, 162.34, 135.64, 109.72, 107.61, 71.80, 70.87, 70.59, 69.78, 63.45, 16.14.

PDEG-2 (6):
An oven dried three-necked, 250 mL round-bottom flask was charged with C$_{60}$ (720 mg, 1.0 mmol), 3,5-bis(2-(2-methoxyethoxy)ethoxy) benzaldehyde (342 mg, 1mmol), sarcosine (270 mg, 3.0 mmol) and dry o-dichlorobenzene (100 mL). The reaction mixture was stirred under N$_2$ at 90°C for 72 h. The reaction mixture was concentrated in vacuo to ~15 mL, and the crude residue was purified by column chromatography (silica gel; toluene/ethyl acetate 2:1) to afford the pure compound as a brown solid. The product was dissolved in 7 mL of chloroform, precipitated with MeOH, washed repeatedly with MeOH (2 times) and pentane (2 times), and dried in vacuo at 50°C. This gave 500 mg (0.46 mmol, 46%) of PDEG-2.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 7.03 (br, 2H), 6.46 (s, 1H), 4.96 (d, J = 8.0, 1H), 4.81 (s, 1H), 4.23 (d, J = 8.0, 1H), 4.13- 4.11 (m, 4H), 3.82 (t, J = 4.0, 4H), 3.70 3.67 (m, 4H), 3.56 (t, J = 4.0, 4H), 3.37 (s, 6H), 2.80 (s, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 160.01, 156.91, 154.07, 153.41, 153.06, 147.28, 146.96, 146.42, 146.29, 146.25, 146.20, 146.09, 146.07, 146.06, 145.94, 145.91, 145.75, 145.53, 145.51, 145.46, 145.34, 145.28, 145.24, 145.13, 144.68, 144.60, 144.37, 144.35, 143.12, 142.95, 142.66, 142.55, 142.20, 142.14, 142.02, 141.92, 141.80, 141.66, 141.60, 140.15, 140.09, 139.86, 139.59, 139.23, 136.58, 136.47, 135.74, 135.70, 102.05, 83.60, 77.20, 76.91, 71.89, 70.75, 69.90, 69.61, 69.03, 67.50.

IR (cm$^{-1}$): 2861, 1591, 1443, 1347, 1330, 1293, 1103, 1066, 938, 848, 766, 746, 755, 726, 690, 597, 573, 552, 526.

Mass m/z : Calcd for C$_{79}$H$_{31}$NO$_6$: 1089.2. Found: 1089.8

Anal. Calcd. For C$_{79}$H$_{31}$NO$_6$: C, 87.05; H, 2.87; N, 1.28. Found: C, 86.49; H, 2.84; N, 1.43.
2-methoxyethyl p-tosylate (8): [8]
Sodium hydroxide (1.71 g, 42.8 mmol) dissolved in water (8 mL) and ethylene glycol monomethyl ether (2.28 g, 30 mmol) in dry THF (8 mL) were placed in a three-necked, 100 mL flask. The mixture was cooled on an ice bath. p-Toluenesulfonyl chloride (5.22 g, 27.8 mmol) in THF (8 mL) was added drop-wise to the mixture over 1 h. The solution was stirred at room temperature for overnight, then poured into ice-water (150 mL) and the product was extracted with ethyl acetate. The organic layer was dried over Na₂SO₄. The solvent was evaporated in vacuo to give the NMR pure compound as colorless oil (5.4 g, 23.48 mmol, 84.4%).

¹H-NMR (400 MHz, CDCl₃) δ = 7.76 (d, J = 8.0, 2H), 7.31 (d, J = 8.0, 2H), 4.12 (t, J = 4.0, 2H), 3.53 (t, J = 4.0, 2H), 3.26 (s, 3H), 2.40 (s, 3H).

4-(2-methoxyethoxy)benzaldehyde (9): [10]
A three-necked, 100 mL round-bottom flask was charged with p-hydroxybenzaldehyde (440 g, 3.63 mmol), 2-methoxyethyl p-tosylate (980 mg, 4.28 mmol), K₂CO₃ (800 mg, 5.8 mmol) and DMF (15 mL). The reaction mixture was stirred overnight at 100°C. After cooling, the crude reaction mixture was poured into water (50 mL) in a 100 mL Erlenmeyer flask and the product was extracted with ethyl acetate. The organic layer was washed subsequently with water (3×25 mL) and brine (1×25 mL) and dried over Na₂SO₄. The solvent was evaporated in vacuo. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate 2:1) to give pure compound as light yellow oil (510 mg, 2.8 mmol, 78%).

¹H-NMR (400 MHz, CDCl₃): δ = 9.84 (s, 1H), 7.78 (d, J = 8.0, 2H), 6.99 (d, J = 8.0, 2H), 4.17-4.15 (m, 2H), 3.75-3.73 (m, 2H), 3.42 (s, 3H).

¹³C-NMR (100 MHz, CDCl₃): δ = 190.76, 163.77, 131.91, 130.06, 114.82, 70.68, 67.59, 59.25.
PMEG-1 (10):
An oven-dried three-necked, 250 mL round-bottom flask was charged with C₆₀ (720 mg, 1 mmol), 4-(2-methoxyethoxy)benzaldehyde (180 mg, 1 mmol), sarcosine (270 mg, 3 mmol) and dry o-dichlorobenzene (100 mL). The reaction mixture was stirred under N₂ at 120°C for 72 h. The mixture was concentrated in vacuo to ~15 mL, and the crude residue was purified by column chromatography (Silica gel; toluene/chloroform 3:1) to afford the pure compound as a brown solid. The product was dissolved in 10 mL of chloroform, precipitated with MeOH, washed twice with MeOH and twice with pentane, and dried in vacuo at 50°C. This procedure gave 200 mg (0.22 mmol, 22%) of PMEG-1.

1H-NMR (400 MHz, CDCl₃): δ = 7.70 (s, 2H), 6.98 (d, J = 8.0, 2H), 4.97 (d, J = 8.0, 1H), 4.88 (s, 1H), 4.24 (d, J = 8.0, 1H), 4.14 - 4.11 (m, 2H), 3.75-3.72 (m, 2H), 3.47 (s, 3H), 2.68 (s, 3H).

13C-NMR (100 MHz, CDCl₃): δ = 158.80, 156.36, 154.09, 153.63, 153.61, 147.29, 147.27, 146.77, 146.51, 146.32, 146.29, 146.24, 146.19, 146.13, 146.11, 146.07, 145.92, 145.90, 145.76, 145.52, 145.47, 145.44, 145.31, 145.29, 145.25, 145.21, 145.12, 144.68, 144.61, 144.37, 143.12, 142.96, 142.65, 142.56, 142.53, 142.52, 142.27, 142.24, 142.14, 142.10, 142.06, 142.01, 142.00, 141.94, 141.82, 141.66, 141.52, 140.13, 140.09, 139.88, 139.58, 136.75, 136.54, 135.78, 135.76, 130.42, 129.09, 114.65, 83.14, 77.21, 71.94, 70.68, 69.83, 69.71, 68.86, 39.95.

IR (cm⁻¹): 2776, 1509, 1316, 1245, 1225, 1123, 103, 769, 576, 526.

Mass m/z: Calcd for C₇₂H₁₇NO₂: 927.2 Found: 927.8

Anal. Calcd. For C₇₂H₁₇NO₂: C, 93.2; H, 1.85; N, 1.51. Found: C, 92.69; H, 1.82; N, 1.62.

3,5-bis(2-(2-methoxyethoxy)ethoxy) benzaldehyde (11):
A three-necked, 50 mL round-bottom flask was charged with 3,5-dihydroxybenzaldehyde (500 mg, 3.63 mmol), 2-methoxyethyl p-tosylate (1.97 g, 8.58 mmol), K₂CO₃ (1.6 g, 11.58 mmol), and dry DMF (25 mL). The reaction mixture was stirred over night at 120°C. After cooling, the crude reaction mixture was poured into water in a 100 mL Erlenmeyer flask and the product was extracted with ethyl acetate. The organic layer was washed with water and dried over Na₂SO₄. The solvent was
evaporated in vacuo. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate 1:2) to give pure compound as light yellow oil (650 mg, 2.56 mmol, 70.5%).

$^1$H-NMR (400 MHz, CDCl$_3$) δ = 9.85 (s, 1H), 7.00 (d, J = 2.7, 2H), 6.77 (s, 1H), 4.12 (t, J = 4.0, 4H), 3.73 (t, J = 4, 4H), 3.43 (s, 6H).

PMEG-2 (12):

An oven-dried three-necked, 250 mL round-bottom flask was charged with C$_{60}$ (720 mg, 1.0 mmol), 3,5-bis(2-(2-methoxyethoxy)ethoxy) benzaldehyde (342 mg, 1mmol), sarcosine (270 mg, 3.0 mmol) and dry o-dichlorobenzene (100 mL). The reaction mixture was stirred under N$_2$ at 150°C for 72 h. The reaction mixture was concentrated in vacuo to ~10 mL, and the crude residue was purified by preparative layer chromatography (silica gel; chloroform) to afford the pure compound as a brown solid. The product was dissolved in 7 mL of chloroform, precipitated with MeOH, washed repeatedly with MeOH (2 times) and pentane (2 times), and dried in vacuo at 50°C. This gave 153 mg (0.15 mmol, 15%) of PMEG-2.

$^1$H-NMR (400 MHz, CDCl$_3$): δ = 6.99 (br s, 2H), 6.49 (t, J = 2.6, 1H), 4.95 (d, J = 9.8, 1H), 4.82 (s, 1H), 4.23 (d, J = 9.8, 1H), 4.11- 4.09 (m, 4H), 3.72 - 3.70 (m, 4H), 3.42 (s, 6H), 2.80 (s, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): δ = 160.08, 156.86, 155.07, 153.47, 153.18, 147.39, 146.98, 146.46, 146.33, 146.25, 146.20, 146.09, 146.07, 146.06, 145.94, 145.91, 145.75, 145.53, 145.51, 145.46, 145.34, 145.28, 145.24, 145.13, 144.68, 144.60, 144.37, 144.35, 143.12, 142.95, 142.66, 142.55, 142.20, 142.14, 142.11, 142.02, 141.92, 141.80, 141.66, 141.60, 140.15, 140.09, 139.86, 139.59, 139.23, 136.58, 136.47, 135.74, 135.70, 102.12, 83.65, 77.20, 76.95, 72.79, 70.68, 68.90, 67.34.

IR (cm$^{-1}$): 2777, 1590, 1461, 1319, 1245, 1221, 1125, 1103, 769, 525

Mass m/z : Calcd for C$_{75}$H$_{23}$NO$_4$: 1001.2. Found: 1001.8

Anal. Calcd. For C$_{75}$H$_{23}$NO$_4$: C, 89.90; H, 2.31; N, 1.40. Found: C, 92.69; H, 2.27; N, 1.48.
**PCBE-OH (15):**

An oven-dried three-necked, 250 mL round-bottom flask was charged with PCBM (400 mg, 0.44 mmol), ethylene glycol (0.6 g, 10 mmol), dibutyltin oxide (47 mg, 0.19 mmol) and dry o-dichlorobenzene (50 mL). The reaction mixture was stirred under N\_2 at 120°C for 5 days. The solvent was evaporated in vacuo, and the crude residue was resolved in CHCl\_3 and passed through a chromatography column (Silica gel; toluene/CHCl\_3 1:1) 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 (2 times) and pentane (2 times), and dried in vacuo at 50°C. This procedure gave 160 mg (0.17 mmol, 38%) of PCBE-OH.

\^1\text{H}-NMR (400 MHz, CDCl\_3): \( \delta = 7.93 \) (d, J = 8 Hz, 2H), 7.57 - 7.48 (m, 3H), 4.28 (t, J = 8.0, 2H), 2.94 - 2.90 (m, 2H), 2.69 (t, J = 4.0, 2 H), 2.59 (t, J = 4.0, 2H), 2.22 2.18 (m, 2H).

Mass m/z : calcd for C\textsubscript{73}H\textsubscript{16}O\textsubscript{3}: 940.1, Found: 940.8.

**PCBDE-OH (17):**

An oven-dried three-necked, 250 mL round-bottom flask was charged with PCBM (500 mg, 0.55 mmol), diethylene glycol (1.06 g, 10 mmol), dibutyltin oxide (47 mg, 0.19 mmol) and dry o-dichlorobenzene (50 mL). The reaction mixture was stirred under N\_2 at 120°C for 5 days. The solvent was evaporated in vacuo, and the crude residue was resolved in CHCl\_3 and passed through a chromatography column (Silica gel; toluene/CHCl\_3 1:1) to afford the pure compound as a brown solid. The product was dissolved in 7 mL of chlorobenzene, precipitated with MeOH, washed twice with MeOH and twice with pentane, and dried in vacuo at 50°C. This procedure gave 164 mg (0.17 mmol, 30%) of PCBDE-OH.

\^1\text{H}-NMR (400 MHz, CDCl\_3): \( \delta = 7.95-7.92 \) (m, 2H), 7.57 - 7.53 (m, 2H), 7.50 7.43 (m, 1H), 4.27 4.25 (m, 2H), 3.75 - 3.69 (m, 4H), 3.61 - 3.59 (m, 2H), 2.94 - 2.90 (m, 2H), 2.57 (t, J = 8.0, 2H), 2.22 2.17 (m, 2H), 2.0 (br, 1H).

\(^{13}\text{C}-\text{NMR} (100 \text{ MHz, CDCl}\_3): \( \delta = 173.00, 148.78, 147.78, 145.84, 145.19, 145.15, 145.06, 145.03, \)
144.79, 144.76, 144.68, 144.65, 144.50, 144.42, 144.00, 143.75, 143.12, 143.03, 142.99, 142.93, 142.91, 142.22, 142.17, 142.13, 142.10, 140.98, 140.74, 138.03, 137.56, 136.72, 132.09, 128.44, 128.25, 79.87, 77.21 72.33, 69.08, 63.54, 61.74, 51.85, 33.98, 33.65, 22.35.

IR (cm\(^{-1}\)): 3420, 2867, 1731, 1426, 1243, 1201, 1125, 699, 525.

Mass m/z : calcd for C\(_{75}\)H\(_{20}\)O\(_4\): 984.1, Found: 984.9

Anal. Calcd. For C\(_{75}\)H\(_{20}\)O\(_4\): C, 91.46; H, 2.05. Found: C, 91.51; H, 2.08.

**PCBTE-OH (19):**

An oven-dried three-necked, 250 mL round-bottom flask was charged with PCBM (500 mg, 0.55 mmol), diethylene glycol (1.06 g, 10 mmol), dibutyltin oxide (35 mg, 0.14 mmol) and dry o-dichlorobenzene (50 mL). The reaction mixture was stirred under N\(_2\) at 120°C for 5 days. The solvent was evaporated in vacuo, and the crude residue was resolved in CHCl\(_3\) and passed through a chromatography column (Silica gel; ethyl acetate/ CHCl\(_3\) 1:5) 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 (2 times) and pentane (2 times), and dried in vacuo at 50°C. This procedure gave 240 mg (0.23 mmol, 42%) of PCBTE-OH.

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.97 - 7.94\) (m, 2H), 7.59 - 7.55 (m, 2H), 7.52 - 7.48 (m, 1H), 4.29 - 4.26 (m, 2H), 3.76 - 3.62 (m, 10H), 2.96 - 2.92 (m, 2H), 2.59 (t, J = 8.0, 2H), 2.25 - 2.18 (m, 2H), 1.4 (br, 1H).

\(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta = 173.08, 148.80, 147.80, 145.85, 145.18, 145.14, 145.07, 145.02, 144.78, 144.77, 144.68, 144.65, 144.49, 144.41, 143.99, 143.75, 143.11, 143.02, 142.98, 142.92, 142.91, 142.22, 142.17, 142.12, 142.10, 140.97, 140.73, 138.04, 137.55, 136.72, 132.11, 128.43, 128.24, 79.87, 77.21 76.70, 72.44, 70.55, 70.32, 69.12, 63.50, 61.76, 51.89, 33.93, 33.65, 22.31.

IR (cm\(^{-1}\)): 3422, 2865, 1733, 1428, 1243, 1201, 1125, 699, 526.

Mass m/z : calcd for C\(_{77}\)H\(_{24}\)O\(_5\): 1028.2, Found: 1028.9

4-[4-(pentoxy)-1,3-dioxolan-2-one]benzaldehyde (21):
A three-necked, 100 mL round-bottom flask was charged with p-hydroxybenzaldehyde (440 g, 3.63 mmol), 4-(bromopentyl)-1,3-dioxolan-2-one (1.01 g, 4.28 mmol), K$_2$CO$_3$ (800 mg, 5.8 mmol) and DMF (15 mL). The reaction mixture was stirred overnight at 90°C under N$_2$. After cooling, the crude reaction mixture was poured into water (30 mL) in a 100 mL Erlenmeyer flask and the product was extracted with ethyl acetate. The organic layer was dried over Na$_2$SO$_4$. The solvent was evaporated in vacuo. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate 1:1) to give NMR pure compound as light yellow oil (910 mg, 3.2 mmol, 89%).

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 9.85 (s, 1H), 7.80 (d, J = 8.0, 2H), 6.96 (d, J = 8.0, 2H), 4.74- 4.69 (m, 1H), 4.53- 4.49 (m, 1H), 4.11- 4.00 (m, 3H), 1.55- 1.35 (m, 8H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 190.81, 164.02, 154.99, 131.98, 129.82, 114.69, 76.74, 69.33, 67.92, 33.38, 28.81, 25.66, 24.27.

P1C5 (22):
An oven-dried three-necked, 250 mL round-bottom flask was charged with C$_{60}$ (720 mg, 1 mmol), 4-[4-(pentoxy)-1,3-dioxolan-2-one]benzaldehyde (280 mg, 1 mmol), sarcosine (270 mg, 3 mmol) and dry o-dichlorobenzene (100 mL). The reaction mixture was stirred under N$_2$ at 120°C for 72 h. The mixture was concentrated in vacuo to ~15 mL, and the crude residue was purified by preparative layer chromatography (silica gel; chloroform) to afford the NMR pure compound as a brown solid. The product was dissolved in 10 mL of chloroform, precipitated with MeOH, washed twice with MeOH and twice with pentane, and dried in vacuo at 50°C. This procedure gave 250 mg (25 mmol, 25%) of P1C5.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 7.70 (s, 2H), 6.93 (d, J = 8.0, 2H), 4.97 (d, J = 8.0, 1H), 4.88 (s, 1H), 4.75 4.66 (m, 1H), 4.52 (t, J = 8.0, 1H), 4.24 (d, J = 8.0, 1H), 4.06 (t, J = 8.0, 1H), 3.96 (t, J = 7.6, 2H), 2.79 (s, 3H), 1.79 1.48 (m, 8H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 158.98, 156.89, 154.90, 153.64, 153.56, 147.28, 146.79, 146.50,
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146.32, 146.37, 146.28, 146.27, 146.16, 146.11, 146.08, 145.93, 145.76, 145.53, 145.47, 145.44, 145.32, 145.30, 145.27, 145.22, 145.17, 145.12, 144.69, 144.57, 144.39, 144.36, 143.13, 142.97, 142.66, 142.64, 142.57, 142.55, 142.52, 142.24, 142.15, 142.08, 142.02, 141.95, 141.51, 140.15, 140.11, 139.87, 139.49, 136.78, 136.51, 135.78, 135.73, 130.51, 128.93, 127.68, 114.48, 83.17, 69.99, 69.29, 68.97, 67.45, 39.96, 33.86, 29.05, 25.78, 24.29.

IR (cm$^{-1}$): 2776, 1795, 1606, 1510, 1245, 1162, 1060, 766, 526.

Mass m/z: calcd for C$_{77}$H$_{23}$NO$_4$: 1025.2, Found: 1025.8

Anal. Calcd. For C$_{77}$H$_{23}$NO$_4$: C, 90.14; H, 2.26; N, 1.37. Found: C, 89.59; H, 2.25; N, 1.39.

3,5-bis(4-(pentoxy)-1,3-dioxolan-2-one) benzaldehyde (23):

A three-necked, 50 mL round-bottom flask was charged with 3,5-dihydroxybenzaldehyde (500 mg, 3.63 mmol), 4-(bromopentyl)-1,3-dioxolan-2-one (2.03 g, 8.58 mmol), K$_2$CO$_3$ (1.6 g, 11.58 mmol), and dry DMF (25 mL). The reaction mixture was stirred for 48 h at 120°C. After cooling, the crude reaction mixture was poured into water (50 mL) in a 100 mL Erlenmeyer flask and the product was extracted with ethyl acetate. The organic layer was dried over Na$_2$SO$_4$. The solvent was evaporated in vacuo. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate 1:4) to give pure compound as light yellow oil (1.2 g, 2.65 mmol, 73%).

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 9.87 (s, 1H), 6.96 (d, $J$ = 3.0, 2H), 6.66 (d, $J$ = 3.0, 1H), 4.73- 4.68 (m, 2H), 4.53- 4.49 (m, 2H), 4.11- 4.04 (m, 2H), 3.98 (t, $J$ = 8.0, 4H), 1.73- 1.45 (m, 16H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 191.99, 160.57, 155.01, 138.31, 107.90, 107.59, 76.75, 69.34, 67.95, 33.81, 28.82, 25.68, 24.22.
P2C5 (24):
An oven-dried three-necked, 250 mL round-bottom flask was charged with C$_{60}$ (720 mg, 1 mmol), 4-[4-(pentoxy)-1,3-dioxolan-2-one]benzaldehyde (452 mg, 1 mmol), sarcosine (270 mg, 3 mmol) and dry o-dichlorobenzene (100 mL). The reaction mixture was stirred under N$_2$ at 120°C for 72 h. The mixture was concentrated in vacuo. The crude residue was purified by column chromatography (silica gel; chloroform/ethyl acetate 7:1) to afford the NMR pure compound as a brown solid. The product was dissolved in 10 mL of chloroform, precipitated with MeOH, washed repeatedly with MeOH (2 times) and pentane (2 times), and dried in vacuo at 50°C. This procedure gave 500 mg (0.44 mmol, 44%) of P2C5.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 6.99 (br, 2H), 6.39 (s, 1H), 4.98 (d, $J = 9.2$, 1H), 4.74 4.63 (m, 2H), 4.50 (t, $J = 8.0$, 2H), 4.24 (d, $J = 8.0$, 1H), 4.04 (t, $J = 7.4$, 2H), 3.98 3.88 (m, 4H), 2.79 (s, 3H), 1.77 1.49 (m, 16H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ = 160.09, 156.15, 154.95, 154.07, 153.71, 153.37, 147.33, 147.28, 147.01, 146.42, 146.30, 146.22, 146.20, 146.11, 145.98, 145.96, 145.71, 145.55, 145.54, 145.47, 145.38, 145.30,145.25, 145.13, 144.73, 144.53, 144.40, 144.32, 143.18, 143.01, 142.72, 142.64, 142.63, 142.61, 142.21, 142.19, 142.15, 142.14, 142.06, 142.03, 141.95, 141.88, 141.71, 141.55, 140.22, 140.16, 139.73, 139.51, 139.29, 136.48, 136.44, 135.85, 135.71, 101.86, 83.65, 76.96, 76.87, 76.71, 69.93, 69.33, 69.04, 67.75, 40.12, 33.87, 28.88, 25.74, 24.29.

IR (cm$^{-1}$): 2779, 1786, 1589, 1453, 1331, 1154, 1055, 764.

Mass m/z : calcd for C$_{85}$H$_{35}$NO$_8$: 1197.2, Found: 1197.8

Anal. Calcd. For C$_{85}$H$_{35}$NO$_8$: C, 85.20; H, 2.94; N, 1.17. Found: C, 85.66; H, 2.90; N, 1.26.
PCBC (26):
An oven-dried three-necked, 250 mL round-bottom flask was charged with PCBM (455 mg, 0.5 mmol), 4-(Hydroxymethyl)-1,3-dioxolan-2-one (1.18 g, 10 mmol), dibutyltin oxide (23 mg, 0.09 mmol) and dry o-dichlorobenzene (50 mL). The reaction mixture was stirred under N₂ at 120°C for 72 h. The solvent was evaporated in vacuo, and the crude residue was resolved in CHCl₃ and passed through a chromatography column (Silica gel; CHCl₃) to afford the pure compound as a brown solid. The product was dissolved in 6 mL of CHCl₃, precipitated with MeOH, washed twice with MeOH and twice with pentane, and dried in vacuo at 50°C. This procedure gave 150 mg (0.15 mmol, 30%) of PCBC.

1H-NMR (400 MHz, CDCl₃): δ = 7.95- 7.92 (m, 2H), 7.57- 7.53 (m, 2H), 7.50 - 7.43 (m, 1H), 4.93- 4.89 (m, 1H), 4.54 (t, J = 8.0, 1H), 4.40- 4.37 (m, 1H), 4.36- 4.24 (m, 2H), 2.93 - 2.89 (m, 2H), 2.60 (t, J = 8.0, 2H), 2.25 - 2.19 (m, 2H).

13C-NMR (100 MHz, CDCl₃): δ = 172.41, 154.20, 148.72, 148.70, 147.71, 145.86, 145.84, 145.20, 145.16, 145.06, 144.80, 144.73, 144.68, 144.66, 144.51, 144.45, 144.02, 143.76, 143.14, 143.05, 143.00, 142.94, 142.91, 142.19, 142.17, 142.14, 142.10, 141.01, 141.00, 140.77, 137.99, 137.58, 136.61, 132.08, 128.51, 128.33, 79.79, 79.77, 73.64, 65.94, 63.13, 51.66, 33.64, 33.55, 22.17.

IR (cm⁻¹): 2935, 1769, 1736, 1145, 1047, 698, 556.


PCBTI (28):
An oven-dried three-necked, 250 mL round-bottom flask was charged with PCBM (600 mg, 0.66 mmol), 2,3,5-triiodobenzyl alcohol (1.26 g, 2.6 mmol), dibutyltin oxide (43 mg, 0.2 mmol) and dry o-dichlorobenzene (50 mL). The reaction mixture was stirred under N₂ at 140°C for 10 days. The mixture was concentrated in vacuo to ~7 mL, and the crude residue was purified and was passed through a chromatography column (Silica gel; toluene)
to afford the pure compound as a brown solid. The product was dissolved in dry chlorobenzene, precipitated with MeOH, washed repeatedly with MeOH (2 times) and pentane (2 times), and dried in vacuo at 50°C. This procedure gave 90 mg (0.07 mmol, 10%) of PCBTI.

$^{1}$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 8.18 (d, $J = 1.9$, 1H), 7.92 (d, $J = 7.7$, 2H), 7.58 (s, 1H), 7.54 (t, $J = 7.4$, 2H), 7.47 (t, $J = 7.3$, 1H), 5.08 (s, 2H), 2.96 - 2.92 (m, 2H), 2.64 (t, $J = 5.9$, 2H), 2.29 - 2.22 (m, 2H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): 171.50, 148.55, 147.57, 146.57, 145.77, 145.23, 145.19, 145.09, 145.04, 144.81, 144.76, 144.70, 144.53, 144.47, 144.13, 143.79, 143.76, 143.13, 143.09, 143.04, 142.97, 142.16, 142.11, 141.08, 140.82, 138.04, 137.71, 136.62, 136.30, 132.09, 128.62, 128.41, 112.68, 111.45, 95.26, 79.70, 72.17, 51.72, 34.01, 33.71, 22.70.

Anal. Calcd. for C$_{78}$H$_{15}$O$_2$I$_3$: C, 68.65; H, 1.11. Found: C, 67.93; H, 1.14.
Mass m/z: calcd for C$_{78}$H$_{15}$O$_2$I$_3$: 1363.8, Found: 1364.4.

**PCBPBr (30):**

An oven-dried three-necked, 250 mL round-bottom flask was charged with PCBM (180 mg, 0.2 mmol), 2,3,4,5,6-pentabromobenzyl alcohol (1.6 g, 3.2 mmol), dibutyltin oxide (78 mg, 0.32 mmol) and dry o-dichlorobenzene (50 mL). The reaction mixture was stirred under $N_2$ at 140°C for 3 days. The mixture was concentrated in vacuo to ~7 mL, and the crude residue was purified and was passed through a chromatography column (Silica gel; toluene) to afford the pure compound as a brown solid. The product was dissolved in chlorobenzene, precipitated with MeOH, washed twice with MeOH and twice with pentane, and dried in vacuo at 50°C. This procedure gave 50 mg (0.04 mmol, 18%) of PCBTI.

$^{1}$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 7.89 (d, $J = 7.3$, 2H), 7.52 (t, $J = 7.4$, 2H), 7.46 (t, $J = 6.8$, 1H), 5.58 (s, 2H), 3.09 - 2.76 (m, 2H), 2.56 (t, $J = 7.2$, 2H), 2.32 - 2.03 (m, 2H).

Anal. Calcd. for C$_{78}$H$_{13}$O$_2$Br$_5$: C, 67.82; H, 0.95. Found: C, 66.90; H, 1.03.
Mass m/z: calcd for C$_{78}$H$_{13}$O$_2$Br$_5$: 1381.5, Found: 1381.4.
Bibliography


