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Synthesis of fullerene-substituted oligo(phenylenebutadiyndiyl)

Juan Luis Delgado de la Cruz, Uwe Hahn and Jean-François Nierengarten*

Groupe de Chimie des Fullerènes et des Systèmes Conjugués, Laboratoire de Chimie de Coordination du CNRS,
205 route de Narbonne, 31077 Toulouse Cedex 4, France

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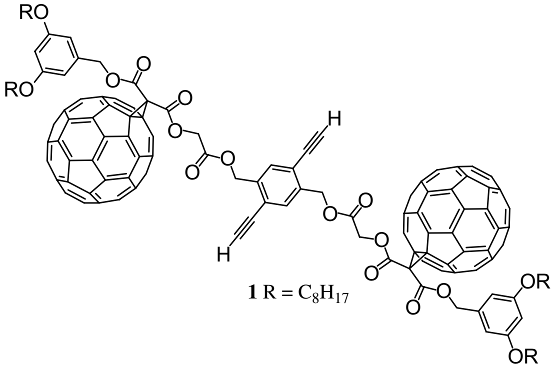
Abstract—A diethynylbenzene monomer substituted with two fullerene moieties has been prepared, and its oligomerization performed in the presence of phenylacetylene as end-capping reagent afforded the corresponding end-capped mono- and di-mer with an oligo(phenylenebutadiyndiyl) (OPB) conjugated backbone substituted with two and four fullerene subunits, respectively.

Following the preparation of the first photovoltaic devices from C_{60}-oligophenylenevinylene conjugates,[1] considerable research efforts have been devoted to the synthesis and the study of C_{60} derivatives substituted with π-conjugated oligomers.[2] The excited state properties of such hybrid systems have been extensively investigated, thus allowing a good understanding of the intramolecular photoinduced energy and electron transfer events occurring in these donor–acceptor dyads.[3] Several covalently linked fullerene-(π-conjugated oligomer) ensembles have also been tested as the active layer in solar cells.[4] Importantly, the behavior of a unique molecule in a photovoltaic device allows to establish easily structure/activity relationships for a better understanding of the photovoltaic system.[5] However, even if the energy conversion efficiency obtained with some of these organic photodiodes is quite promising,[4] it has to be improved dramatically for a commercial use. This is clearly an important challenge for materials scientists in general and for organic chemists in particular as new hybrid compounds with a stronger absorption in the visible range and a better stability toward light are needed.

As far as the synthesis of fullerene-(π-conjugated oligomer) conjugates is concerned, almost all of them have been prepared by the direct functionalization of C_{60} with already constructed conjugated oligomers.[2] In contrast, the preparation of fullerene-substituted monomers and their subsequent oligomerization has been considered to a lesser degree.[6] This is mainly associated with the chemical reactivity of fullerene derivatives limiting the range of reactions that can be used for the oligomerization of such monomers. In addition, due to the low solubility of C_{60} derivatives, only a few examples of conjugated backbones bearing multiple C_{60} units have been reported so far.[7] In this letter, we now report the preparation of diethynylbenzene derivative **1** substituted with two fullerene moieties. Oligomerization reactions of monomer **1** have been performed in the presence of an end-capping reagent in order to control the oligomer length. The end-capped mono- and di-mer thus obtained possess an oligo(phenylenebutadiyndiyl) (OPB) backbone and are substituted with two and four fullerene groups, respectively.



1 R = C_8H_{17}

The synthesis of fullerene-substituted monomer **1** is based on the use of the fullerene carboxylic acid building blocks developed in our group.[8] To this end, we have prepared a 1,4-diethynylbenzene derivative bearing two

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* Corresponding author. Tel.: +33 564 33 31 51; e-mail: jfnierengarten@lcc-toulouse.fr

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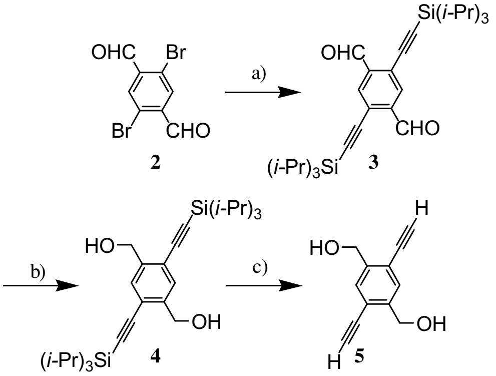
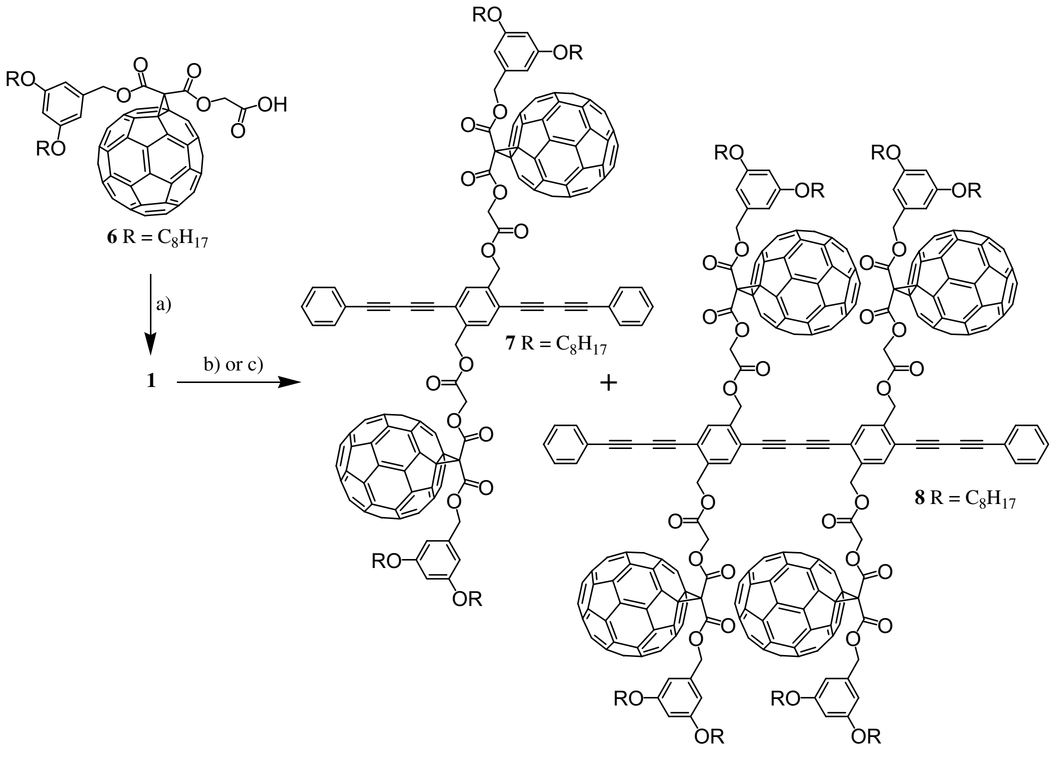
hydroxy groups allowing for the attachment of two fullerene carboxylic acid units via an esterification reaction. The preparation of this diol is depicted in Scheme 1. Reaction of **2** with triisopropylsilylacetylene under Sonogashira conditions afforded **3** in 60% yield. $LiAlH_4$ reduction followed by treatment of the resulting **4** with tetra-*n*-butylammonium fluoride (TBAF) yielded **5**.

Reaction of diol **5** with carboxylic acid **6** under esterification conditions using dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) afforded monomer **1** in 66% yield (Scheme 2). The oligomerization reactions of monomer **1** were performed under Cu-catalyzed conditions[9] with phenylacetylene as stopper. In a typical procedure, $Cu(OAc)_2$ (39 mg, 0.19 mmol), pyridine (0.06 ml, 0.74 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.01 ml, 0.066 mmol) were added to a solution of **1** (129 mg, 0.049 mmol) and phenylacetylene (50.52 mg, 0.49 mmol) in CH_2Cl_2 (100 mL). The resulting mixture was stirred for 4 h at room temperature and filtered over a pad of silica. Column chromatography (SiO_2, CH_2Cl_2/hexane 7:3) followed by gel permeation chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) gave **7** (54 mg, 39%) and **8** (18 mg, 7%). The yield of **7** and **8** was highly dependant of the monomer to end-capping reagent molar ratio. When a large excess of phenylacetylene (10 equiv) was used, end-capped monomer **7** and end-capped dimer **8** were obtained in reasonable yields. In contrast, when **1** and phenylacetylene were used in a 1:1 molar ratio, **7** and **8** were isolated in low yields (3% and 1%, respectively). It can also be noted that higher oligomers were formed during these reactions but they could not be separated into pure compounds nor properly characterized due to their poor solubility in common organic solvents.



Scheme 1. Reagents and conditions: (a) triisopropylsilylacetylene, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, 65 °C, 4 d (60%); (b) $LiAlH_4$, THF, 0 °C to room temperature, 3 h (91%); (c) TBAF, THF, room temperature, 3 h (82%).

Oligomers **7** and **8** are well soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, or THF and complete spectroscopic characterization was easily achieved.[10] The ^1H NMR spectra of **1**, **7** and **8** recorded in $CDCl_3$ are depicted in Figure 1. The spectrum of **1** shows the characteristic features of the C_s symmetrical methanofullerene substituent as well as the signals of the central diethynylphenyl core. In particular, three sets of signals are observed at δ 5.0–5.5 ppm for the three different CH_2



Scheme 2. Reagents and conditions: (a) **5**, DCC, DMAP, CH_2Cl_2, room temperature, 5d (66%); (b) $Cu(OAc)_2$, pyridine, DBU, phenylacetylene (10 equiv), room temperature, 4 h (**7**: 39%; **8**: 7%); (c) $Cu(OAc)_2$, pyridine, DBU, phenylacetylene (1 equiv), room temperature, 4 h (**7**: 3%, **8**: 1%).

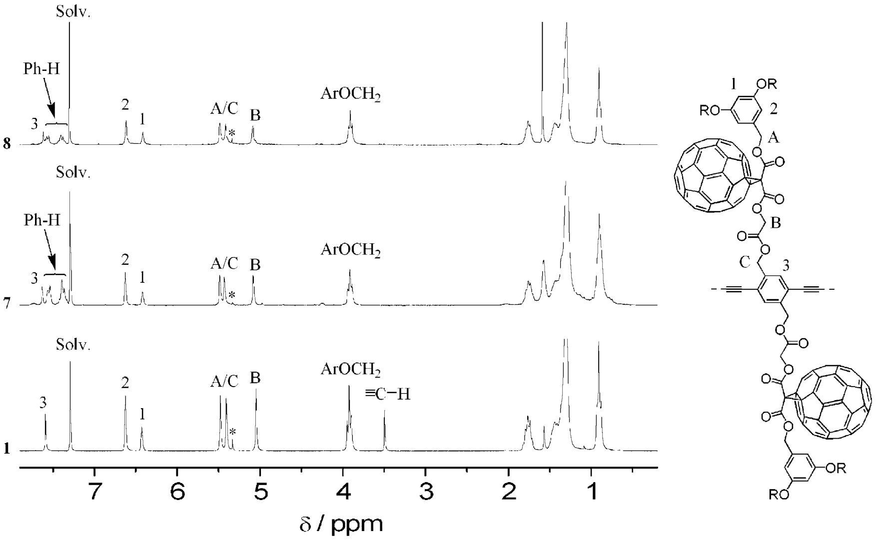


Figure 1. ^{1}H NMR spectra (CDCl$_3$, 300 MHz) of **1**, **7** and **8** (*: CH$_2$Cl$_2$ impurity).

groups (H$_A$, H$_B$ and H$_C$, see Figure 1) and a singlet is revealed at δ 3.47 ppm for the terminal alkyne protons. The ^{1}H NMR spectra of both end-capped oligomers **7** and **8** are in full agreement with their centrosymmetric structures and revealed no signals around δ 3.5 ppm corresponding to unreacted terminal alkyne functions. In both cases, the characteristic signals of the monomer units as well as those of the terminal phenyl groups are clearly distinguished. The number of monomer units in each oligomer is confirmed by the terminal phenyl to benzylic CH$_2$ proton ratio deduced from the integration of the ^{1}H NMR spectra.

The UV/vis spectra of CH$_2$Cl$_2$ solutions of **1**, **7** and **8** are shown in Figure 2. In the UV region, monomer **1** displays two intense bands typical of methanofullerene derivatives,[11] whereas in the visible region, the spectrum is much less intense with two bands at 426 and 689 nm. An analogous pattern is observed in UV/vis spectra of **7** and **8** with additional bands in the 350–420 nm region resulting from the OPB conjugated backbone. The latter absorption is clearly red-shifted when going from **7** to **8** as a result of the longer conjugated pathway in full agreement with the proposed structures. Finally, preliminary luminescence measurements reveal no emission from the OPB core in **7** or **8**, indicating a strong quenching of the OPB fluorescence by the fullerene moiety in both **7** and **8** suggesting the occurrence of intramolecular photo-induced processes. Detailed photophysical studies are currently under investigation and special emphasis is placed on the detection of long-lived charge-separated states.

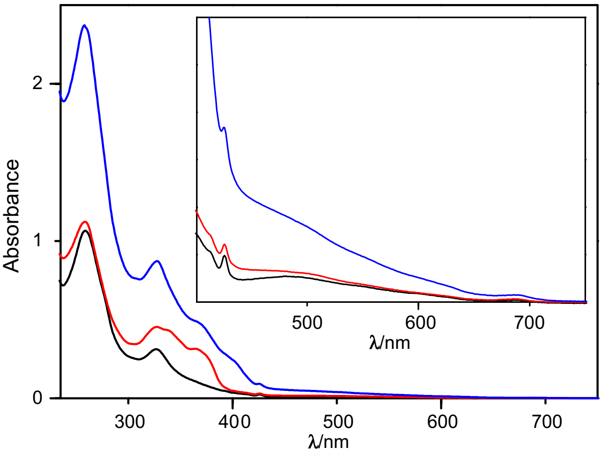


Figure 2. Absorption spectra of 5×10^{-6} M CH$_2$Cl$_2$ solutions **1** (black), **7** (red) and **8** (blue).

In conclusion, a new approach for the synthesis of fullerene-(π-conjugated oligomer) conjugates has been developed. This enables us to prepare fullerene-rich OPB derivatives, which present all the characteristic features required for photovoltaic applications. Further efforts are currently under way to prepare related derivatives with longer OPB backbones.

Acknowledgement

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10. Compound **1**: ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 0.87$ (t, $J = 7$ Hz, 12H), 1.19–1.44 (m, 40H), 1.74 (m, 8H), 3.47 (s, 2H), 3.89 (t, $J = 7$ Hz, 8H), 5.02 (s, 4H), 5.37 (s, 4H), 5.45 (s, 4H), 6.39 (t, $J = 2$ Hz, 2H), 6.59 (d, $J = 2$ Hz, 4H), 7.56 (s, 2H); ^{13}C NMR (CDCl$_3$, 75 MHz): $\delta = 14.2$, 22.7, 26.2, 29.3, 29.4, 31.85, 51.24, 62.5, 64.7, 68.1, 69.14, 71.2, 79.8, 85.2, 101.65, 107.3, 122.2, 132.5, 136.6,137.4, 138.5, 139.7, 140.8, 140.9, 141.8, 141.9, 142.15, 142.2, 142.9, 143.0, 143.8, 143.85, 144.4, 144.5, 144.6, 144.65, 144.9, 145.0, 145.1, 145.15, 145.2, 145.26, 163.0, 166.2; IR (KBr): $\nu = 3296$ (≡C–H), 2197 (C≡C), 1748 (C=O) cm^{-1}; UV/vis (CH$_2$Cl$_2$): λ_{max} (ε) = 259 (213,000), 327 (62,000), 426 (5100), 686 (200). Compound **7**: ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 0.87$ (t, $J = 7$ Hz, 12 H), 1.19–1.44 (m, 40H), 1.73 (m, 8H), 3.88 (t, $J = 7$ Hz, 8H), 5.02 (s, 4H), 5.39 (s, 4H), 5.45 (s, 4H), 6.39 (t, $J = 2$ Hz, 2H), 6.59 (d, $J = 2$ Hz, 4H), 7.30–7.38 (m, 6H), 7.50–7.53 (m, 4H), 7.60 (s, 2H); ^{13}C NMR (CDCl$_3$, 75 MHz): $\delta = 14.2$, 22.7, 26.15, 29.3, 29.4, 31.85, 51.2, 62.6, 64.6, 68.2, 69.1, 71.1, 73.6, 81.9, 85.0, 101.6, 107.3, 128.5, 128.8, 131.0, 132.7, 136.6, 138.6, 139.7, 140.8, 140.9, 141.6, 141.8, 141.85, 142.1, 142.2, 142.9, 143.0, 143.8, 144.4, 144.5, 145.0, 145.1, 145.2, 160.5, 163.0, 166.0; IR (KBr): $\nu = 2208$ (C≡C), 1750 (C=O); UV/vis (CH$_2$Cl$_2$): λ_{max} (ε) = 258 (224,000), 327 (91,000), 340 (sh) (85,500), 364 (sh) (63,000), 426 (6000), 686 (300). Compound **8**: ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 0.87$ (t, $J = 7$ Hz, 24H), 1.26–1.41 (m, 40H), 1.73 (m, 16H), 3.88 (t, $J = 7$ Hz, 16H), 5.05 (s, 8H) 5.38 (s, 8H), 5.45 (s, 8H), 6.38 (br s, 4H), 6.58 (br s, 8H), 7.32–7.40 (m, 6H), 7.50–7.56 (m, 4H), 7.59 (s, 4H); ^{13}C NMR (CDCl$_3$, 75 MHz): $\delta = 14.2$, 22.7, 26.2, 29.3, 29.4, 29.7, 31.9, 62.5, 64.8, 68.2, 69.2, 71.1, 79.8, 85.2, 101.6, 107.3, 128.54, 128.84, 131.0, 132.7, 136.6, 138.6, 139.7, 140.8, 140.9, 141.6, 141.8, 141.85, 142.1, 142.2, 142.9, 143.0, 143.8, 144.4, 144.5, 144.6, 144.9, 145.0, 145.1, 145.2, 160.5, 163.0, 166.2; IR (KBr): $\nu = 2208$ (C≡C), 1748 (C=O); UV/vis (CH$_2$Cl$_2$): λ_{max}(ε) = 258 (474,000), 327 (174,000), 368 (sh) (95,900), 401 (sh) (48,100), 425 (18,400), 686 (750).
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