

Synthesis and Excited-State Properties of an Oligophenylenevinylene Heptamer Substituted with Two Fullerene Moieties

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Dedicated to Prof. Heck in recognition of his pioneering work in the field of metal-catalyzed cross-coupling reactions

Abstract: An oligophenylenevinylene (OPV) derivative substituted with two fullerene subunits has been prepared starting from a fullerene carboxylic acid derivative and an OPV heptamer bearing two alcohol functions. Photophysical investigations have revealed the occurrence of intramolecular photoinduced energy- and electron-transfer processes in this hybrid compound.

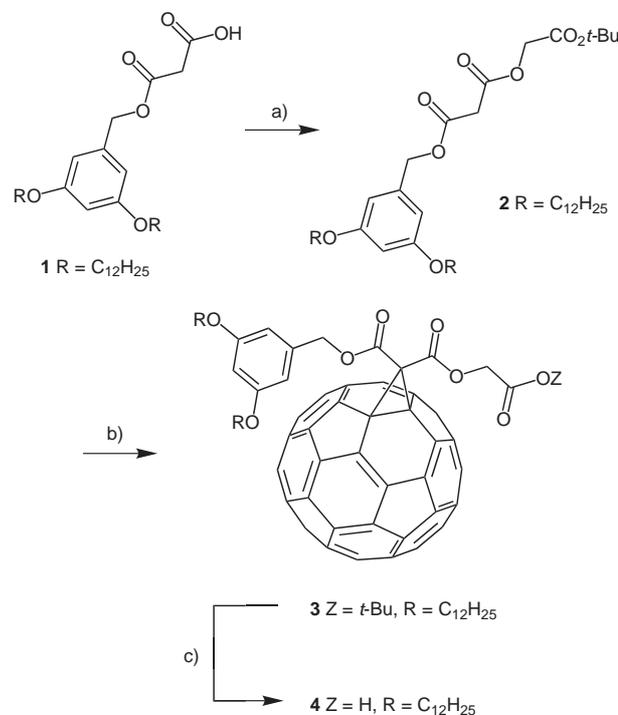
Key words: fullerene, conjugated system, energy transfer, electron transfer, singlet oxygen

The past several years have seen a considerable interest in the synthesis of new monodisperse π -conjugated oligomers with the aim of generating new advanced materials for optoelectronic applications.¹ If one important challenge of this research is to comprehensively investigate many physical properties relevant to materials science (charge transport, nonlinear optical effects, etc.), the characteristic features of these compounds make them also versatile photo- and/or electroactive components for the preparation of photochemical molecular devices.² Effectively, π -conjugated oligomers possess a broad range of attractive optical properties as well as the ability to accept or donate charges. In addition, their physical properties can be easily modulated by changing the length of the conjugated backbone or the nature of the substituents. Over the last few years, we have developed efficient synthetic procedures for the synthesis of oligophenylenevinylene (OPV) building blocks³ and shown that they can be used for the preparation of molecular devices which perform light-induced functions such as electron or energy transfer.⁴ In particular, the combination of OPV derivatives with fullerene subunits led to hybrid systems with interesting excited-state properties.⁵ Some of these compounds have also found applications in the field of solar energy conversion.^{5,6} Even if the energy conversion efficiency obtained with some of these organic photodiodes is quite promising,⁶ 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 materials with a stronger absorption in the visible range are needed.

In this paper, we report the synthesis and the excited-state properties of an OPV heptamer bearing two fullerene moieties. The C₆₀-OPV conjugates reported so far combine the fullerene accepting unit with relatively short OPV oligomers.⁵ By increasing the length of the OPV conjugated backbone, its absorption is extended to the red thus providing a new hybrid material with improved absorption properties for photovoltaic applications.

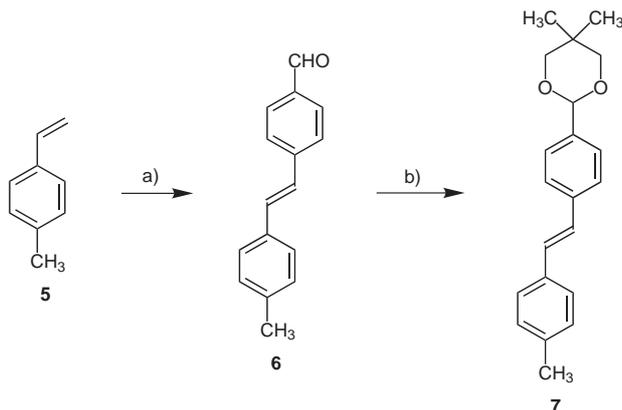
The synthesis of the C₆₀-OPV conjugate is based on the esterification reaction of fullerene carboxylic acid **4** with an OPV heptamer bearing two hydroxy groups. The preparation of methanofullerene derivative **4** is depicted in Scheme 1.

N,N'-dicyclohexylcarbodiimide (DCC)-mediated esterification of *tert*-butyl 2-hydroxyacetate with carboxylic acid **1**⁷ yielded malonate **2**. The reaction of C₆₀ with compound **2**, iodine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)



Scheme 1 Reagents and conditions: a) *tert*-butyl 2-hydroxyacetate, DCC, DMAP, CH₂Cl₂, 0 °C to r.t., 24 h (70%); b) C₆₀, DBU, I₂, PhMe, r.t., 3 h (70%); c) CF₃CO₂H, CH₂Cl₂, r.t., 4 h (94%).

under Bingel conditions⁸ then gave methanofullerene **3** in 70% yield. Subsequent hydrolysis of the *tert*-butyl ester group with CF₃CO₂H gave carboxylic acid **4** in 94% yield. The preparation of the OPV heptamer bearing two hydroxy groups was achieved in twelve steps from *p*-methylstyrene (Scheme 2, Scheme 3, and Scheme 4). The first step leading to stilbene **6** was based on Heck type chemistry.⁹ Thus, the reaction of *p*-methylstyrene (**5**) with *p*-iodobenzaldehyde in xylene–Et₃N in the presence of tri-*o*-tolylphosphine (POT) with a catalytic amount of Pd(OAc)₂ afforded **6** in 86% yield. Treatment of aldehyde **6** with 2,2-dimethylpropane-1,3-diol then gave **7** in 95% yield.

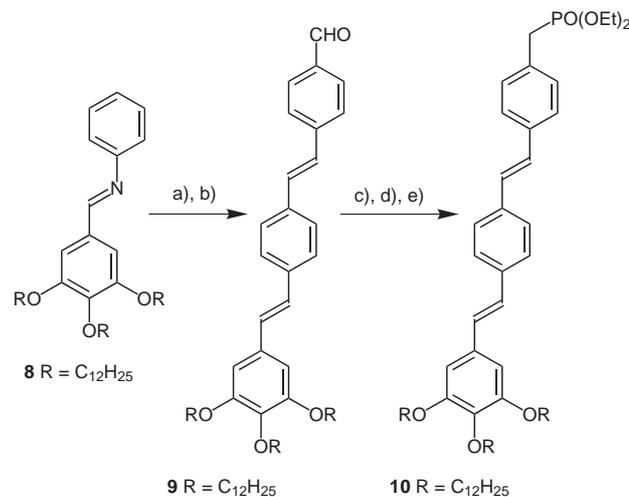


Scheme 2 Reagents and conditions: a) *p*-iodobenzaldehyde, Pd(OAc)₂, POT, Et₃N, xylene, 130 °C, 24 h (86%); b) 2,2-dimethylpropane-1,3-diol, *p*-TsOH, C₆H₆, reflux, Dean–Stark trap, 24 h (95%).

Benzaldimine **8**¹⁰ was subjected to the Siegrist reaction with stilbene **7** to give the protected OPV trimer. Subsequent deprotection with CF₃CO₂H in CH₂Cl₂–H₂O afforded aldehyde **9**. Reduction of aldehyde **9** with LiAlH₄, reaction of the resulting benzylic alcohol with trimethylsilyl bromide (TMSBr) in CHCl₃ and treatment of the benzylic bromide thus obtained with P(OEt)₃ under Arbuzov conditions gave phosphonate **10** in a 87% overall yield. It is worth noting that the choice of the appropriate conditions for the preparation of the benzylic bromide was the key to this synthesis.¹¹ Actually, this intermediate was found to be unstable. Under bromination conditions using TMSBr, the volatile by-products can be eliminated by simple evaporation and no purification step was required. Therefore, the product could be used in the next step as received.

Reduction of dialdehyde **11** with LiAlH₄ followed by treatment of the resulting **12** with triisopropylsilyl chloride (TIPSCl) in the presence of imidazole afforded protected derivative **13** (Scheme 4). Reaction of **13** with an excess of *t*-BuLi in THF followed by quenching with *N,N*-dimethylformamide (DMF) gave **14** in 83% yield. The protected OPV heptamer **15** was then prepared under Wadsworth–Emmons conditions from dialdehyde **14** and phosphonate **10**. Diol **16** was finally obtained in 48%

yield by treatment with tetra-*n*-butylammonium fluoride (TBAF) in THF at 0 °C. The moderate yields for the two last steps are mainly associated with difficulties encountered during the purification of the OPV heptamer derivatives **15** and **16**.



Scheme 3 Reagents and conditions: a) *t*-BuOK, DMF, 80 °C, 2 h (91%); b) TFA, CH₂Cl₂, H₂O, r.t., 4 h (96%); c) LiAlH₄, THF, 0 °C, 2 h (98%); d) TMSBr, CHCl₃, 0 °C, 3 h; e) P(OEt)₃, 150 °C, 12 h (88% from **9**).

Reaction of diol **16** with carboxylic acid **4** under esterification conditions using DCC and 4-dimethylaminopyridine (DMAP) afforded compound **17** in 71% yield. Both ¹H NMR and ¹³C NMR spectra were in full agreement with the centrosymmetric structure of compound **17**.¹² In addition, the molecular constitution of **17** was further confirmed by its MALDI-TOF mass spectrum which depicted the expected molecular ion peak at *m/z* = 4501 (MH⁺, calcd for C₃₂₀H₃₀₃O₂₂: 4500.82).

The electronic absorption spectra of the reference compounds **3** and **15**, and of the multicomponent system **17** in CH₂Cl₂ solution are reported in Figure 1. The spectrum of **17** is fairly similar to the profile obtained by summing the

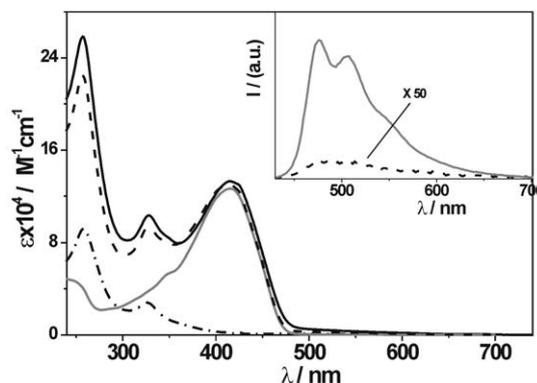


Figure 1 Electronic absorption spectra in CH₂Cl₂ solution of **3** (dashed-dotted line), **15** (grey full line), **17** (dashed line) and the sum of 2 × **3** + **15** (full line). Inset: Fluorescence spectra of **15** (grey full line) and **17** (dashed line) in the OPV emission region in CH₂Cl₂, λ_{exc} = 415 nm, O.D. = 0.07.

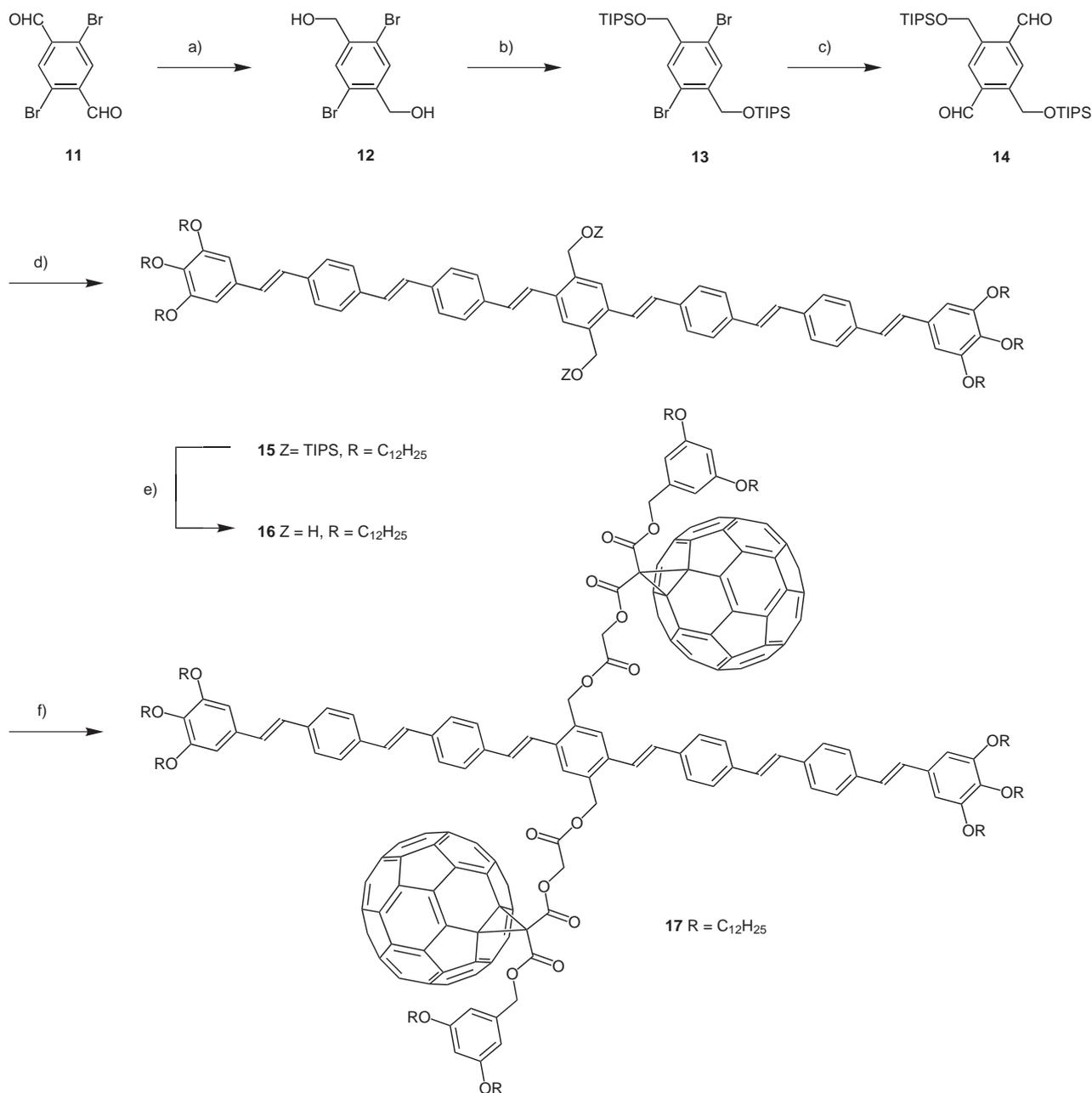
spectra of **3** and **15** suggesting no substantial ground state electronic interactions between the carbon spheres and the OPV-type rod.

On the contrary, **17** exhibits intercomponent excited-state interactions upon light excitation. Compound **15** is characterized by a very intense and short-lived ($\Phi_{\text{fluor}} = 0.36$; $\tau = 700$ ps) fluorescence spectrum peaked at $\lambda = 476$ nm, due to the deactivation of the lowest lying OPV singlet excited state^{4a,4b} (Figure 1). This level is dramatically quenched (>350 times) in **17**, owing to an OPV \rightarrow fullerene singlet energy transfer, as derived by excitation spectra at $\lambda_{\text{em}} = 705$ nm on the maximum of the fullerene fluorescence (see below) and in agreement with numerous

findings in dyads containing the same chromophores.^{5b,5c,5e} The rate constant of the process is estimated to be $5.0 \cdot 10^{11} \text{ s}^{-1}$ from fluorescence data.¹³

In Figure 2 are reported the fluorescence spectrum of the fullerene moiety of **17** and the corresponding spectrum band of the reference molecule **3** under the same experimental conditions. Such spectra are reported in three solvents of increasing polarity, namely toluene, CH₂Cl₂, and benzonitrile.

In any solvents **3** is characterized by a fluorescence band centered at $\lambda = 705$ nm with $\tau = 1.5 \pm 0.1$ ns, corresponding to the deactivation of the lowest-lying singlet level (¹C₆₀*). In apolar toluene medium ¹C₆₀* is quenched in



Scheme 4 Reagents and conditions: a) LiAlH₄, THF, 0 °C, 2 h (91%); b) TIPSCl, imidazole, DMF, 0 °C, 24 h (88%); c) *t*-BuLi, THF, -78 °C, 3 h then DMF, -78 to 0 °C, 3 h (83%); d) **10**, *t*-BuOK, THF, 0 °C to r.t., 3 h (46%); e) TBAF, THF, 0 °C, 2 h (48%); f) **4**, DCC, DMAP, CH₂Cl₂, 0 °C to r.t., 12 h (71%).

triad **17**, compared to reference **3**. By contrast, the same comparison shows a substantial quenching of the fluorescence band (ca. 70%) in more polar CH_2Cl_2 and benzonitrile. The fullerene singlet lifetime of **17** is shortened accordingly to 0.7 ± 0.1 ns in both solvents. This medium polarity dependent quenching is attributable to intramolecular photoinduced electron transfer from the OPV moiety to the carbon sphere.^{5c–5e} The experimental rate for charge separation, as determined with lifetime data, turns out to be $7.6 \cdot 10^8 \text{ s}^{-1}$. In an attempt to detect the charge recombination processes we carried out transient absorption measurements on the nanosecond timescale to detect fingerprints of the cationic (OPV^+) and anionic species (C_{60}^-) in the charge separated state.

Down to a scale of 10 ns no such signals were detected indicating that back electron transfer occurs on the subnanosecond timescale, as observed earlier for OPV- C_{60} arrays.^{5b,c,e,13} Nanosecond time resolved absorption spectra of **17** in the three solvents show only the features of the lowest fullerene triplet level ($^3\text{C}_{60}^*$). In air equilibrated solution the lifetimes of the excited states of **3** and **17** are identical in each solvent (670 ns in CH_2Cl_2). In oxygen free solution they turn out to be shorter for **17** compared to **3** (8 and 30 μs , respectively, in CH_2Cl_2), probably due to intramolecular excited-state interactions among the two fullerene subunits of **17**.¹⁴ $^3\text{C}_{60}^*$ is a potent singlet oxygen ($^1\text{O}_2^*$) sensitizer^{5c} and the sensitization process was monitored in air equilibrated solutions of **17** and **3** by recording the singlet oxygen luminescence spectra in the near infrared region (Figure 2). Notably, the ratio of $^1\text{O}_2^*$ luminescence intensity between **17** and **3** is pretty much the same as that measured for C_{60} fluorescence spectra. These findings show that the lower extent of triplet formation in **17** is only due to reduced intersystem crossing from the singlet level, which is depleted due to electron transfer (see above). It must be pointed out that the trend of emission spectra in Figure 2 is exactly the same either by excitation of the C_{60} ($\lambda = 520 \text{ nm}$) or of the OPV moiety ($\lambda = 415 \text{ nm}$), clearly indicating that the OPV rod of **17** simply

acts as a light harvesting antenna unit and electron transfer only takes place upon direct or indirect excitation of the fullerene fragment.

In conclusion we have synthesized a novel OPV derivative substituted with two fullerene subunits, which exhibit light induced energy and electron transfer processes from the OPV central unit to the appended C_{60} fragments. The charge separation process shows a strong solvent-polarity dependence.

Acknowledgment

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- (12) Compound **17**: $^1\text{H NMR}$ (300 MHz, CDCl_3): $\delta = 7.69$ (s, 2 H), 7.48 (m, 16 H), 7.32 (d, $^3J = 16.0 \text{ Hz}$, 2 H), 7.15 (d, $^3J = 16.0 \text{ Hz}$, 2 H), 7.08 (s, 4 H), 7.04 (d, $^3J = 16.0 \text{ Hz}$, 2 H), 6.94 (d, $^3J = 16.0 \text{ Hz}$, 2 H), 6.72 (s, 4 H), 6.57 (d, $^4J = 1.5 \text{ Hz}$,

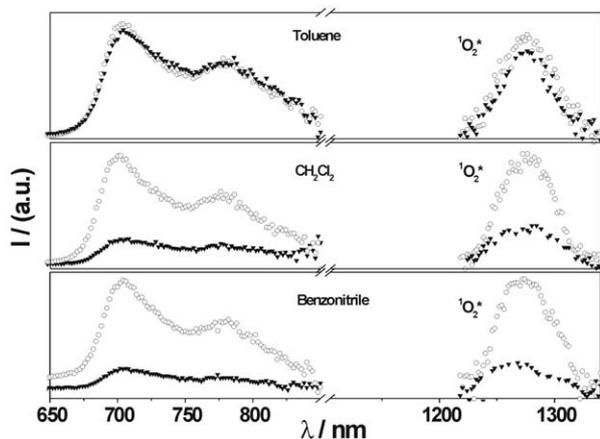


Figure 2 Fluorescence spectra (left) and sensitized singlet oxygen luminescence (right) of **17** (triangles) and **3** (empty circles) in three different solvents. From top to bottom toluene, CH_2Cl_2 and benzonitrile; in all cases $\lambda_{\text{exc}} = 520 \text{ nm}$, 298 K.

4 H), 6.38 (t, ⁴J = 1.5 Hz, 2 H), 5.44 (s, 4 H), 5.39 (s, 4 H), 5.02 (s, 4 H), 4.03 (t, ³J = 6.5 Hz, 8 H), 3.98 (t, ³J = 6.5 Hz, 4 H), 3.85 (t, ³J = 6.5 Hz, 8 H), 1.80 (m, 20 H), 1.32 (m, 180 H), 0.87 (2t, ³J = 6.0 Hz, 30 H). ¹³C NMR (75 MHz, CDCl₃): δ = 166.9, 163.4, 163.3, 160.9, 153.7, 145.6, 145.55, 145.5, 145.4, 145.35, 145.3, 145.0, 144.9, 144.85, 144.2, 143.4, 143.3, 142.5, 141.25, 141.2, 127.8, 127.4, 127.3, 127.1, 107.7, 105.7, 102.0, 73.9, 71.6, 69.6, 69.5, 68.6, 63.1, 51.7, 32.4, 30.8, 30.15, 30.1, 29.9, 29.8, 29.7, 26.6, 23.1, 14.6,

14.5. IR (ATR): 1702 (C=O). MS (MALDI-TOF): 4501 [MH⁺]. Anal. Calcd for C₃₂₀H₃₀₂O₂₂: C, 85.41; H, 6.76. Found: C, 85.68; H, 6.73.

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