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Synthesis of a π-conjugated oligomer–fullerene dyad through a versatile [6,6]diphenylmethanofullerene carboxylic acid

Rafael Gómez *, José L. Segura *

Departamento de Química Orgánica, Facultad de Química, Universidad Complutense de Madrid, Avda. Complutense s/n, E-28040 Madrid, Spain

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ABSTRACT

In this article we describe the synthesis of an electron donor–acceptor dyad containing a [6,6]diphenylmethanofullerene moiety as the electron acceptor and a dialkylamino-substituted oligo-*p*-phenylenevinylene as the electron donor. The synthesis of this material has been successfully accomplished by an esterification reaction between a [6,6]diphenylmethanofullerene functionalized with a carboxylic acid and the corresponding oligomer substituted with a benzyl alcohol. Cyclic voltammetry and absorption spectroscopy show that both electroactive units preserve their nature in the ground state, whereas preliminary photophysical investigations show a strong fluorescence quenching.

1. Introduction

The exploration of organic semiconductors as active elements in electronic devices, such as light emitting diodes,[1] thin film transistors,[2] solid-state lasers[3] or organic solar cells[4] has experienced much progress in recent years. This progress has been possible due to the unique features that organic semiconductors offer, such as the tuning of the electronic properties, easy structural modifications, possibility of self-assembly or mechanical flexibility. All this enables the exploitation of organic semiconductors as materials for large-area and low-cost disposable electronic products. Since the discovery of ultrafast and efficient photoinduced electron transfer between π-conjugated oligomers (*electron donors*) and [60]fullerene derivatives (*electron acceptors*),[5] considerable interest for bulk heterojunction solar cells based on interpenetrating networks of conjugated systems and [60]fullerene derivatives has been generated.[6] However, the tendency of [60]fullerene to phase separate from the oligomer and crystallize is one of the prime limitations, as it imposes severe requisites for solubility in π-conjugated oligomeric matrices. A synthetic approach investigated during the last years to reduce clustering formation consists in the covalent linkage between the π-conjugated donor and the [60]fullerene. Conjugated oligomers are well defined in length, constitution and shape. They are also readily synthesized and processable from solution for film-formation. These properties have turned π-conjugated oligomers into one exciting class of electroactive materials, to be used as model compounds for the study of a variety of photophysical processes and as active materials in devices. The exploitation of these properties in dyads based on π-conjugated oligomers covalently linked to [60]fullerene has given rise to the synthesis of a large number of derivatives.[5a,7] Thus, we have prepared linear,[8] and branched[9] oligo-*p*-phenylenevinylenes covalently linked to [60]fullerene and carrying different electron donor groups. In this respect, we and others have shown that the properties of these dyads can be appropriately tailored by structural modifications and that the presence of dibutylamino groups greatly favours photoinduced electron transfer, disregarding the limited conjugation length of most conjugated backbones reported so far.[9,10]

Methanofullerenes are one of the most extensively studied [60]fullerene derivatives, because of their easiness in handling, synthetic availability, and striking resemblance to [60]fullerene in physical properties.[11] For the preparation of methanofullerenes, several methods have been developed to date, such as the Bingel reaction, the addition-thermal decomposition of diazo compounds or silylated nucleophiles, or the addition–elimination of stabilized onium ylides, among others.[12] However, most of these methods employ strongly basic conditions, which diminish their functionality tolerance. Taking this fact into account, a more general strategy has been followed: first, a soluble methano[60]fullerene possessing a protected functional group (**9**) has been prepared as a precursor, which has been converted into a reacting carboxylic acid group (**10**) later. Fulleroalkanoic acid **10** emerges as an interesting and versatile synthon in fullerene chemistry: simple monofunctionalized structure, synthetic accessibility and potential reactivity. The presence of alkyl chains provides synthon **10** a good solubility, making unnecessary to introduce the [60]fullerene

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* Corresponding authors. Tel.: +34 91 394 5142; fax: +34 91 394 4103.
E-mail addresses: rafaelgomez@quim.ucm.es (R. Gómez), segura@quim.ucm.es (J.L. Segura).

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moiety in the last synthetic step, as it is usually preferred to circumvent the inherent weak solubility of [60]fullerene.[8–10] In this respect, Nierengarten et al. have recently reported an interesting methanofullerene carboxylic acid prepared by a Bingel reaction from a soluble malonate.[13] On the other hand, it has been shown that particularly diphenylmethanofullerenes, structurally similar to the paradigmatic [6,6]-phenyl-C_{61} butyric acid methyl ester (PCBM), show remarkable photophysical properties[14] and good performance as acceptors in organic solar cells.[15] Therefore, we have developed a synthetic route for the synthesis of soluble diphenylmethanofullerenes endowed with a carboxylic acid, which will enable its further reactivity.

In this article we report the synthesis of an electron donor–acceptor dyad containing a [6,6]diphenylmethanofullerene moiety as the electron acceptor unit and a dialkylamino-substituted oligo-*p*-phenylenevinylene as the electron donor.

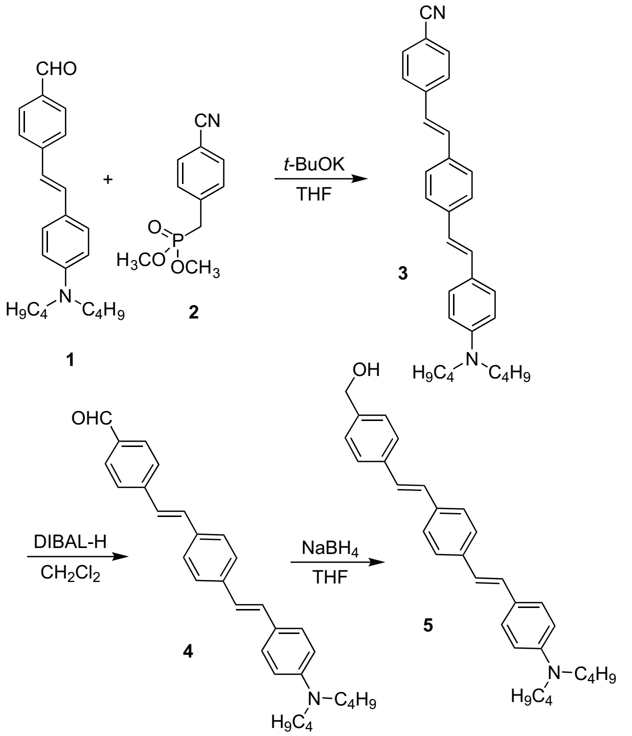
2. Synthesis

The synthesis of dyad **14** (Scheme 4) has been carried out by an esterification reaction between a [6,6]diphenylmethanofullerene derivative bearing a carboxylic acid group and the corresponding conjugated oligomer functionalized with a benzyl alcohol.

2.1. Synthesis of functionalized oligo-*p*-phenylenevinylenes

The halogen-lithium exchange followed by quenching of the lithiated intermediate with *N*,*N*-dimethylformamide has been often claimed as an straight procedure leading to oligo-*p*-phenylenevinylene functionalized with aldehyde groups.[16] The presence of aldehyde groups is necessary for the elongation/functionalization of conjugated oligomers in conjunction with the Wittig–Horner protocol, one of the choice procedures in the chemistry of this type of systems as it usually yields exclusively *E* isomers.[17] However, in our hands it is much more convenient to introduce the aldehyde group masked as a nitrile, which can be further reduced.[8,9,17] Thus, Wittig–Horner reaction between 4-[2′-(4″-dibutylaminophenyl)vinyl]benzaldehyde (**1**)[18] and dimethyl 4-cyanobenzylphosphonate (**2**)[19] in tetrahydrofuran and using potassium *tert*-butoxyde as the base affords the corresponding cyano-substituted derivative **3** (Scheme 1). Further selective reduction of the cyano groups with diisobutylaluminium hydride affords aldehyde **4**. This procedure allows the convenient and straightforward obtention of **4** in a higher overall yield than the four-step procedure described in a short communication by Le Bozec et al. (21% vs. 65%).[20]

Finally, reduction of the aldehyde group in **4** with sodium borohydride in dichloromethane afforded the target hydroxymethyl-functionalized oligomer **5** in excellent yield.

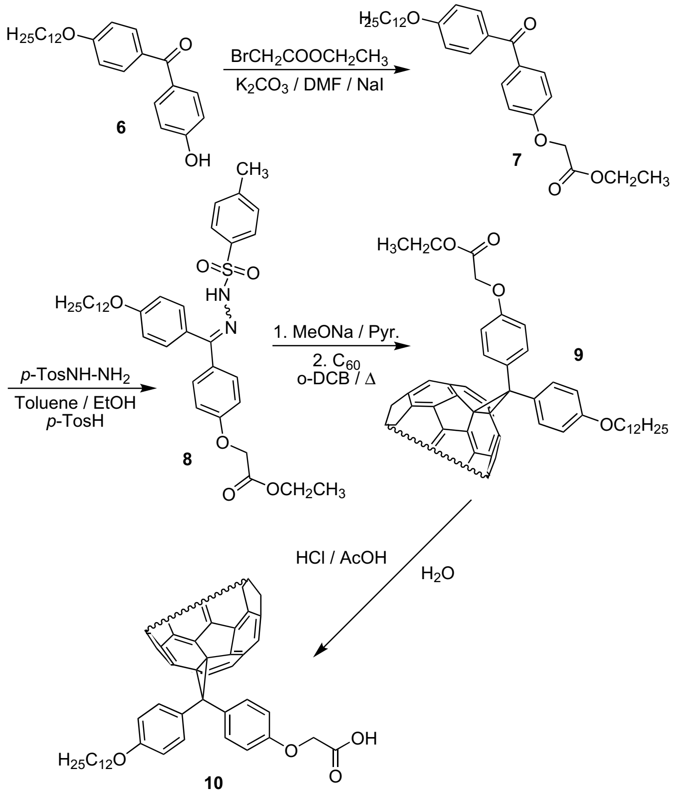


Scheme 1. Synthesis of benzyl alcohol functionalized oligo-*p*-phenylenevinylene **5**.

2.2. Synthesis of functionalized diphenylmethanofullerenes

Among the above-mentioned synthetic approaches to methanofullerenes, the 1,3-dipolar cycloaddition reaction of the diazo compounds generated in situ by a Bamford–Stevens reaction between *p*-tosylhydrazones and sodium methoxide is one of the most versatile. The synthesis of the target *p*-tosylhydrazone bearing one solubilizing alkoxy chain in one of the phenyl rings and a carboxylic acid on the other was designed starting from 4-hexyloxy-4′-hydroxybenzophenone (**6**),[21] readily prepared from the commercially available 4,4′-dihydroxybenzophenone by selective alkylation. Obviously, as the Bamford–Stevens reaction is carried out in a strong basic medium, the desired carboxylic acid group must be protected, advantageously as an ethyl ester. On the other hand, the presence of a long alkyl chain provides these diphenylmethanofullerene derivatives a good solubility, making unnecessary to introduce the [60]fullerene moiety in the last synthetic step, as it is usually preferred considering the reduction of solubility induced by this bulky unit.

Thus, Williamson etherification reaction between **6** and ethyl bromoacetate affords the unsymmetrically substituted



Scheme 2. Synthesis of functionalized diphenylmethanofullerenes.

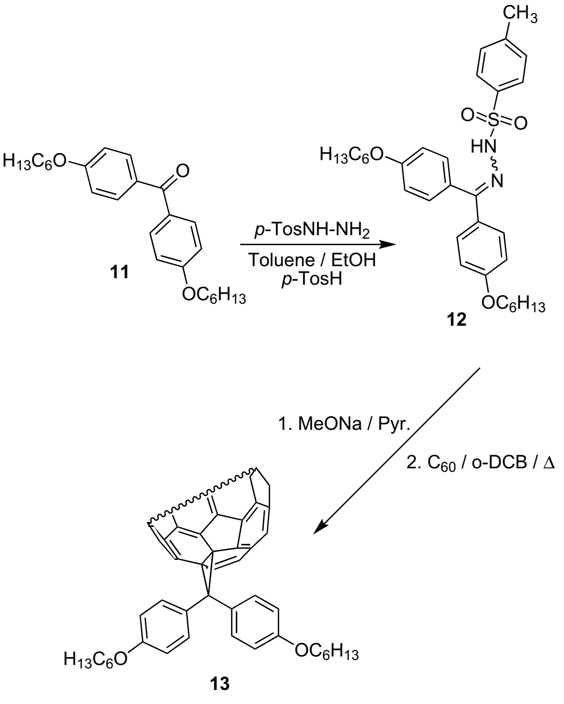
benzophenone **7** in good yield. Further condensation of **7** with *p*-tosylhydrazide in a mixture of toluene and ethanol affords *p*-tosylhydrazone **8**, which after sequential treatment with sodium methoxide in pyridine first and then with [60]fullerene in refluxing *o*-dichlorobenzene (*o*-DCB) affords **9** in 26% yield, comparable to similar reactions.[15,22] No methyl ester could be detected during this reaction, thus excluding ethyl–methyl interchange by an addition–elimination mechanism, in spite of the presence of methanolate. By following a similar synthetic procedure, the corresponding [6,6]-bis-(4-hexyloxyphenyl)-methanofullerene (**13**), used as a reference, was synthesized from 4,4′-dihexyloxybenzophenone (**11**) (Scheme 3). Although both [6,6]-closed and [5,6]-open isomers could be expected from the cycloaddition reaction, the high temperature at which the reaction proceeds allows the obtention of the thermodynamically more stable [6,6]-closed isomer solely. Thus, the ^{13}C NMR data for the series of diphenylmethanofullerenes **9**, **10** and **13** shows well resolved 22–28 resonances, which is in good agreement with the high symmetry of the proposed structure. In addition, the peaks assignable to the cyclopropane carbons (ca. 57 ppm for C_{60}-sp^3 and 79 ppm for C_{DPM} bridgehead) can be also clearly observed.

Eventually, the acid promoted hydrolysis of the ethyl ester group in **9** yields the target diphenylmethanofullerene carboxylic acid **10** (Scheme 2).

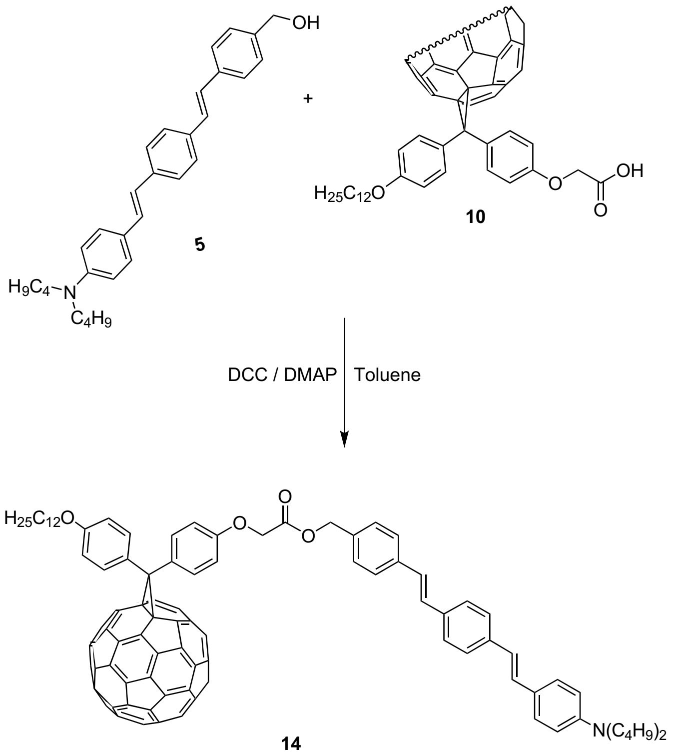
2.3. Synthesis of dyad 14

As it has been mentioned, the synthesis of dyad **14** was accomplished by a condensation reaction between **10** and benzyl alcohol **5**. The treatment of diphenylmethanofullerene carboxylic acid **10** with **5** in the presence of *N*,*N*-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)-pyridine (DMAP) affords dyad **14** as the main reaction product in a 64% yield (Scheme 4).

Dyad **14**, as well as all the synthetic intermediates, was characterized by the common analytical and spectroscopic techniques, all data being in good agreement with the proposed structures. Thus, the ^{1}H NMR spectra of dyad **14** show the correct ratio of aliphatic and aromatic protons, and most characteristic signals in the ^{1}H NMR spectra could be assigned. As in its precursors, dyad **14** shows in the aromatic region a series of AB doublets arising from the diphenylmethane and phenylene moieties, the protons located at the sp^2 carbons in alpha position respect to the dibutylamino substituents appearing at around 6.5 ppm, and at lower fields the three types of methylene groups directly linked to the oxygen (5.26, 4.71 and 3.99 ppm, for the Ar–CH_2–O, O–CH_2–CO and Alkyl–CH_2–O, respectively) and nitrogen (3.31 ppm) atoms. Besides, the rest of the signals corresponding to the alkyl chains can be observed at higher fields (1.50–0.89 ppm). Vinylenic protons are displayed at 7.07 and 6.88 ppm, with the characteristic $^3J_{trans}$ coupling of ca. 16 Hz and showing a clear AB pattern.



Scheme 3. Synthesis of reference diphenylmethanofullerene **13**.



Scheme 4. Synthesis of dyad **14**.

^{13}C NMR spectra show multiple peaks in the range 115–145 ppm, mostly arising from the methanofullerene moiety. As it was previously mentioned, resonances at ca. 57 for the C_{60}-sp^3 and 79 for the C_{DPM} bridgehead ensure the permanence of the [6,6]closed isomer. In the FTIR spectra of **14** the strong hydroxy bands around 3500 cm^{-1} of the precursor **5** disappear, and the most diagnostic bands are the one corresponding to the ester carbonyl group at 1763, the wagging vibration of the trans-configured double bonds, which is located at 959 cm^{-1}, and the typical band corresponding to the [60]fullerene moiety at 526 cm^{-1}. Finally, evidence concerning the purity of **14**, as in the case of all the intermediates used in their synthesis, is given by elemental analysis, that is in accordance with the expected values.

3. Electrochemistry

The electrochemical behaviour of dyad **14**, along with references **5** and **13**, has been investigated by cyclic voltammetry in *o*-dichlorobenzene/acetonitrile (4:1) mixtures. These experiments were carried out using tetrabutylammonium perchlorate as the supporting electrolyte, platinum as the working electrode and counter electrode, and Ag/Ag$^+$ as a quasi-reference electrode. The potentials were then referred to the ferrocene–ferrocenium couple. The cyclic voltammogram of **14** (Fig. 1) shows the amphoteric behaviour of this material. Thus, at negative values the first three

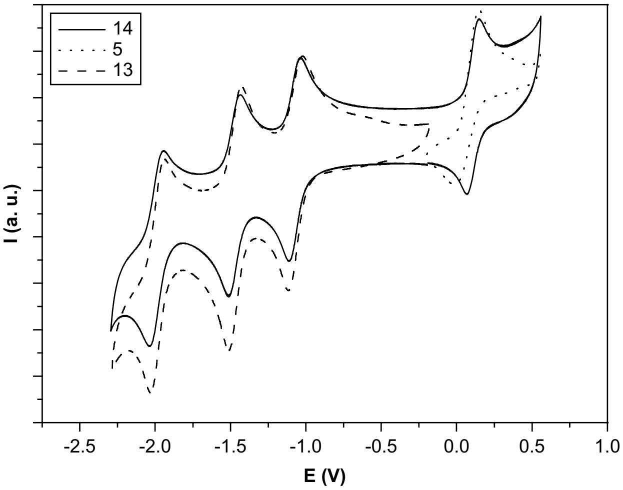


Figure 1. Cyclic voltammogram of dyad **14** along with references [6,6]-bis-(4-hexyloxyphenyl)methanofullerene (**13**) and **5** (10^{-2} M, Pt as working and counter electrode, $TBAClO_4$ (0.1 M) as supporting electrolyte and a scan rate of $200\ mV\ s^{-1}$ at room temperature. Ag/Ag^+ was used as quasi-reference electrode, values vs. Fc/Fc^+).

one-electron reduction waves arising from the stepwise reduction of the [6,6]methanofullerene moiety are clearly visible around $E^{red}_{1/2}=-1.07$, -1.48 and -2.00 V. These redox potentials are fully comparable to those of the reference [6,6]-bis-(4-hexyloxyphenyl)-methanofullerene (**13**) ($E^{red}_{1/2}=-1.07$, -1.47 and -1.98 V) under the same experimental conditions and are similar to those reported for other diphenylmethanofullerene derivatives showing very high values of open circuit voltages in photovoltaic devices.[15,23]

The positive scanning displays a reversible wave arising from the oxydation of the conjugated dibutylamino-substituted oligo-*p*-phenylenevinylene fragment at $E^{ox}_{1/2}=+0.10$ V. Compound **5**, used as a reference shows a similar peak at $E^{ox}_{1/2}=+0.08$ V. These values are in full agreement with the electrochemical data reported for other dialkylamino-substituted conjugated systems[17] and, although no coulombimetric experiments have been yet carried out, the comparison between the intensity of this wave and those arising from the monoelectronic reduction waves of the methanofullerene fragment suggests the also one-electron nature of this oxydation wave.

Furthermore, the similarity of oxydation and reduction potentials between dyad **14** and their respective references **5** and **13** suggests that no significant interaction takes place between both electroactive moieties in the ground state.

4. Optical properties

The UV–vis absorption spectra of the donor–acceptor dyad **14** together with that of references [6,6]-bis-(4-hexyloxyphenyl)methanofullerene (**13**) and benzyl alcohol **5** in diluted (ca. $5\cdot10^{-6}$ M) dichloromethane solution are depicted in Figure 2.

The absorption spectrum of dyad **14** consists on the approximate superposition of the absorption features of its constitutive units. This confirms the minimal interaction between the chromophores in the ground state, and is in agreement with the electrochemical behaviour. No new intramolecular charge-transfer bands above 600 nm were detected in dyad **14**. The absorption spectrum of dyad **14** shows the characteristic bands arising from the fullerene units between 230 and 260 nm and at around 330 nm, the latter overlapping with a band arising from the conjugated fragment. Besides, it is worth mentioning that also the diagnostic weak band for dihydrofullerenes at around 430 nm (see inset in Fig. 2) is obscured by the HOMO–LUMO transition of the π-conjugated system.

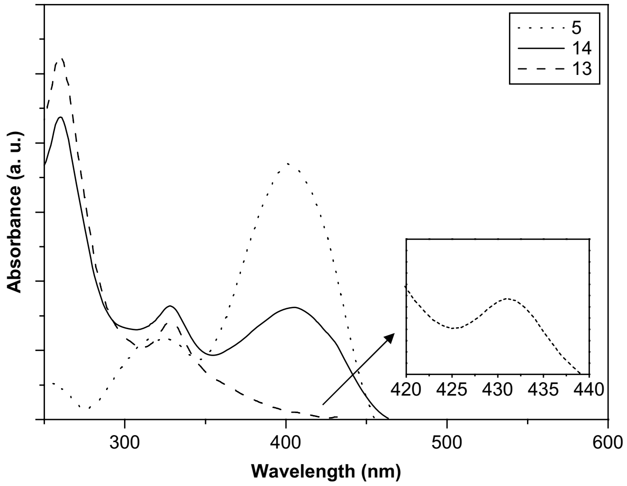


Figure 2. UV–vis spectra of dyad **14** along with references [6,6]-bis-(4-hexyloxyphenyl)methanofullerene (**13**) and **5**.

Fluorescence emission spectra of diphenylmethanofullerene-conjugated oligomer dyad **14** and oligobenzyl alcohol **5** were measured in diluted dichloromethane solutions at fixed optical density using an excitation wavelength of 405 nm. The fluorescence properties of the fluorescent chromophore in dyad **14**, i.e. the dibutylamino-substituted π-conjugated system, are greatly affected by the presence of the diphenylmethanofullerene moiety. Thus, a quantitative quenching (ca. 99%) of the oligomer fluorescent emission was observed in dyad **14** in comparison with the fluorescence spectrum of oligobenzyl alcohol reference (Fig. 3).

To explain this strong fluorescence quenching, energy transfer can be ruled out as the π-conjugated fragment has a smaller optical bandgap than the diphenylmethanofullerene moiety, i.e. there is little spectral overlap between the absorption spectrum of the π-conjugated system and the fluorescence spectrum of the diphenylmethanofullerene fragment. Quenching by the diphenylmethanofullerene→π-conjugated system energy transfer process due to the Förster mechanism will be prohibited, according to the energy level of both units (2.75 eV[24] for the π-conjugated oligomer and 1.76 eV for diphenylmethanofullerene[9b]).

Thus, we ascribe the complete fluorescence intensity quenching in dyad **14** to photoinduced electron transfer (PET) processes between the dibutylamino-substituted π-conjugated system and the

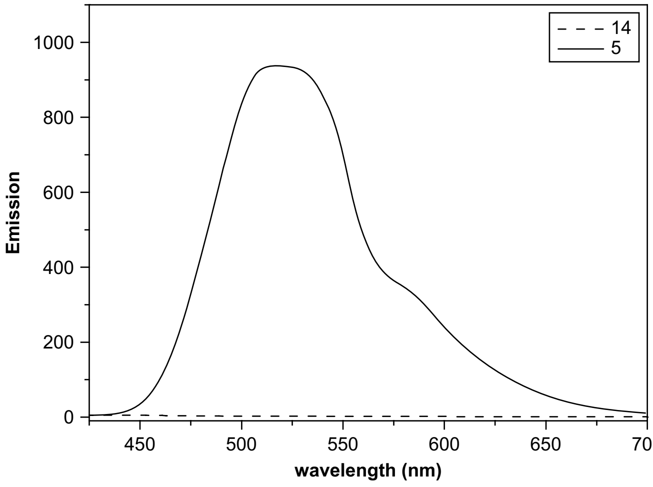


Figure 3. Fluorescence spectrum of dyad **14** along with oligobenzyl alcohol reference **5**.

diphenylmethanofullerene units. Indeed, a PET process is energetically favourable as the corresponding free energy ΔG_{PET} was estimated to be −2.54 eV using the Weller equation.[25] However, time-resolved absorption spectral studies (PIA) will be needed to provide further evidence for the above assumption.

5. Conclusions

In conclusion, we have described the synthesis of the electron donor–acceptor dyad **14**, which contains a diphenylmethanofullerene moiety as the electron acceptor fragment and a dialkylamino-substituted oligo-*p*-phenylenevinylene as the electron donor. Cyclic voltammetry and absorption spectroscopy show that both electroactive units preserve their nature in the ground state, whereas photoluminescence investigations show a strong fluorescence quenching, which makes this material a good candidate for the further investigation of the photophysical processes taking place after irradiation.

6. Experimental

6.1. General

Materials. Compounds **1**,[18] **2**,[19] **6**[21] and **11** were prepared by following previously reported synthetic procedures. All other chemicals were purchased from Aldrich and used as received without further purification. Column chromatography was performed on Merck Kieselgel 60 silica gel (230–240 mesh). Thin layer chromatography was carried out on Merck silica gel F_{254} flexible TLC plates. Solvents and reagents were dried by usual methods prior to use and typically used under inert gas atmosphere.

Characterization. Melting points were measured with an Electrothermal melting point apparatus and are uncorrected. FTIR spectra were recorded as KBr pellets in a Shimadzu FTIR 8300 spectrometer. NMR were recorded on a Bruker AC-200, Avance 300 or AMX-400 apparatus as noted, and the chemical shifts were reported relative to tetramethylsilane (TMS) at 0.0 ppm (for ^{1}H NMR) and $CDCl_3$ at 77.16 ppm (for ^{13}C NMR). The splitting patterns are designated as follows: s (singlet), d (doublet), m (multiplet) and q (quadruplet). Mass spectra were recorded with a Varian Saturn 2000 GC–MS and with a MALDI-TOF MS Bruker Reflex 2 (dithranol as matrix). Elemental analyses were performed on a Perkin–Elmer EA 2400.

Electrochemistry. Cyclic voltammetry experiments were performed with a computer controlled EG & G PAR 273 potentiostat in a three-electrode single-compartment cell (5 ml). The platinum working electrode consisted of a platinum wire sealed in a soft glass tube with a surface of A=0.785 mm^2, which was polished down to 0.5 μm with Buehler polishing paste prior to use in order to obtain reproducible surfaces. The counter electrode consisted of a platinum wire and the reference electrode was a Ag/AgCl secondary electrode. All potentials were internally referenced to the ferrocene–ferrocenium couple. For the measurements, concentrations of 5.10^{-3} mol l^{-1} of the electroactive species were used in freshly distilled and deaerated dichloromethane (Lichrosolv, Merck) and 0.1 M tetrabutylammonium perchlorate ($TBAClO_4$, Fluka), which was twice recrystallized from ethanol and dried under vacuum prior to use.

6.2. 4-(2′-{4″-[2‴-(4⁗-Dibutylaminophenyl)ethenyl]phenyl}-ethenyl)benzonitrile (3)

To a refluxing and well-stirred suspension of 4-[2′-(4″-dibutylaminophenyl)ethenyl]benzaldehyde (**1**) (1.24 g, 3.70 mmol) and dimethyl 4-cyanobenzylphosphonate (**2**) (1.17 g, 5.20 mmol) in 60 ml of anhydrous tetrahydrofuran, potassium *tert*-butoxide (582 mg, 5.20 mmol) is added portionwise under argon atmosphere. After 24 h, the reaction crude is allowed to cool down to room temperature and methanol is added. The resulting precipitate is filtered, thoroughly washed with methanol and dried under vacuum to yield 4-(2′-{4″-[2‴-(4⁗-dibutylaminophenyl)ethenyl]phenyl}ethenyl)benzonitrile (**3**) as a bright orange solid in 90% yield. Mp: 117 °C (methanol); ^{1}H NMR ($CDCl_3$, 200 MHz) δ=7.71 (d, 2H, J=8.70 Hz), 7.64 (d, 2H, J=8.70 Hz), 7.45 (d, 2H, J=8.80 Hz), 7.33–7.24 (m, 4H), 7.15 (d, 1H, J_{trans}=16.23 Hz, –CH=CH–), 7.13 (d, 1H, J_{trans}=16.23 Hz, –CH=CH–), 6.93 (d, 2H, J_{trans}=16.23 Hz, –CH=CH–), 6.69 (d, 2H, J=8.90 Hz), 3.36 (t, 4H, J=7.26 Hz, –N–CH_2–), 1.69–1.58 (m, 4H, –CH_2–), 1.52–1.34 (m, 4H, –CH_2–), 0.93 (t, 6H, J=7.12 Hz, –CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ=148.15, 142.21, 139.09, 134.50, 132.59, 132.37, 129.78, 128.03, 127.36, 126.85, 126.41, 125.83, 124.34, 122.95, 111.75, 50.90 (–N–CH_2–), 29.61, 20.47, 14.12; FTIR (KBr, cm^{-1}) ν=2960, 2923, 2852, 2226, 1687, 1605, 1586, 1523, 1176, 967, 834; MS (FAB): 434 (M^+). Anal. Calcd for $C_{31}H_{34}N_2$: C: 85.67%; H: 7.88%; N: 6.44%. Found: C: 85.74%; H: 7.66%; N: 6.36%.

6.3. 4-(2′-{4″-[2‴-(4⁗-Dibutylaminophenyl)ethenyl]phenyl}-ethenyl)benzaldehyde (4)

To a refluxing solution of 4-(2′-{4″-[2‴-(4⁗-dibutylaminophenyl)ethenyl]phenyl}ethenyl)benzonitrile (**3**) (1.50 g, 3.60 mmol) in 50 of dry dichloromethane, a diisobutylaluminium hydride dichloromethane solution (1 M, 4.20 ml, 4.20 mmol) is added dropwise during a period of 1 h under argon atmosphere. The solution is allowed to react at reflux for 24 h and cooled to room temperature. Methanol is then carefully added until the reaction crude becomes a thick suspension. After water is added, the reaction crude is treated with concentrated hydrochloric acid until complete solution and extracted with chloroform. The combined organic extracts are then washed with water and dried over anhydrous magnesium sulfate. After vacuum evaporation of the solvent, the remaining residue is purified by column chromatography (silica gel, hexane/dichloromethane 3:7) to afford 4-(2′-{4″-[2‴-(4⁗-dibutylaminophenyl)ethenyl]phenyl}ethenyl)benzaldehyde (**4**) as an orange solid in 72% yield. Mp: 98 °C (hexane/dichloromethane); ^{1}H NMR ($CDCl_3$, 200 MHz) δ=9.92 (s, 1H, –CHO), 7.80 (d, 2H, J=8.30 Hz), 7.58 (d, 2H, J=8.30 Hz), 7.44 (d, 2H, J=9.35 Hz), 7.40 (d, 2H, J=9.35 Hz), 7.32 (d, 2H, J=8.80 Hz), 7.20 (d, 1H, J_{trans}=16.31 Hz, –CH=CH–), 7.05 (d, 1H, J_{trans}=16.31 Hz, –CH=CH–), 7.02 (d, 1H, J_{trans}=16.31 Hz, –CH=CH–), 6.80 (d, 1H, J_{trans}=16.31 Hz, –CH=CH–), 6.58 (d, 2H, J=8.86 Hz), 3.22 (t, 4H, J=7.25 Hz, –N–CH_2–), 1.59–1.49 (m, 4H, –CH_2–), 1.38–1.18 (m, 4H, –CH_2–), 0.89 (t, 6H, J=7.12 Hz, –CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ=191.56 (C=O), 147.98, 143.67, 138.81, 135.12, 134.64, 132.04, 130.23, 129.54, 127.88, 127.21, 126.76, 126.27, 124.25, 122.84, 111.61, 50.76 (–N–CH_2–), 29.47, 20.33, 13.98; FTIR (KBr, cm^{-1}) ν=2964, 2918, 2846, 1696, 1615, 1516, 1172, 834; MS (FABI): 437 (M^+). Anal. Calcd for $C_{31}H_{35}NO$: C: 85.08%; H: 8.06%; N: 3.20%. Found: C: 84.76%; H: 8.32%; N: 3.00%.

6.4. 4-(2′-{4″-[2‴-(4⁗-Dibutylaminophenyl)ethenyl]phenyl}-ethenyl)benzyl alcohol (5)

To a well-stirred suspension of 4-(2′-{4″-[2‴-(4⁗-dibutylaminophenyl)ethenyl]phenyl}ethenyl)benzaldehyde (**4**) (450 mg, 1.03 mmol) in 50 ml of anhydrous tetrahydrofurane, sodium borohydride (39 mg, 1.03 mmol) is added portionwise at reflux and under argon atmosphere. The reaction crude is allowed to react for 3 h and cooled down to room temperature. The resulting solution is treated with methanol and water and extracted with dichloromethane. The combined organic extracts are dried over magnesium sulfate and the solvent evaporated under vacuum. The remaining residue is purified by column chromatography (silica gel, dichloromethane) to afford benzyl alcohol **5** as a bright yellow solid in 92% yield. Mp: 164 °C (dichloromethane); ^{1}H NMR ($CDCl_3$, 200 MHz) δ=7.73–7.65 (m, 6H), 7.55 (d, 2H, J=8.01 Hz), 7.57 (d, 2H, J=8.66 Hz), 7.37 (d, 3H, J_{trans}=16.26 Hz, –CH=CH–), 6.80 (d, 1H, J_{trans}=16.26 Hz, –CH=CH–), 6.81 (d, 2H, J=8.81 Hz), 4.90 (s, 1H, –CH_2–OH), 4.87 (s, 1H, –CH_2–OH), 3.48 (t, 4H, J=7.31 Hz, –N–CH_2–), 1.83–1.75 (m, 4H, –CH_2–), 1.60–1.49 (m, 4H, –CH_2–), 1.14 (t, 6H, J=7.19 Hz, –CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ=147.99, 140.17, 138.01, 137.12, 135.56, 129.07, 128.71, 127.91, 127.48, 126.89, 126.71, 126.32, 124.57, 123.29, 111.77, 65.27 (–CH_2–OH), 50.89 (–N–CH_2–), 29.59, 20.45, 14.10; FTIR (KBr, cm^{-1}) ν=3575, 2957, 2931, 2871, 1606, 1590, 1520, 1369, 1220, 966, 827; MS (FAB): 439 (M^+). Anal. Calcd for $C_{31}H_{37}NO$: C: 84.69%; H: 8.48%; N: 3.19%. Found: C: 84.91%; H: 8.32 %; N: 3.26%.

6.5. Unsymmetrically substituted benzophenone 7

To a solution of 4-dodecyloxy-4′-hydroxybenzophenone (**6**) (2.00 g, 5.23 mmol) in 40 ml of anhydrous *N*,*N*-dimethylformamide, potassium carbonate (1.44 g, 10.5 mmol), ethyl bromoacetate (1.16 ml, 10.5 mmol) and a catalytic amount of sodium iodide were added under argon atmosphere. The mixture was heated at reflux for 72 h. The crude was allowed to reach the room temperature and treated with an 1 M HCl aqueous solution. The resulting mixture was extracted with dichloromethane and the combined organic fractions dried over $MgSO_4$ and evaporated under vacuum. The remaining residue was purified by column chromatography (silica gel, hexane/dichloromethane 1:1) to give **7** as a white solid in 76% yield. Mp: 77 °C (hexane/dichloromethane); ^{1}H NMR ($CDCl_3$, 200 MHz) δ=7.69 (d, 2H, J=8.87 Hz), 7.68 (d, 2H, J=8.87 Hz), 6.91–6.76 (m, 4H), 4.61 (s, 2H, –O–CH_2–COOR), 4.22 (q, 2H, J=7.15 Hz, –O–CH_2–CH_3), 3.94 (t, 2H, J=6.48 Hz, –O–CH_2–), 1.72 (m, 2H, –CH_2–), 1.36–1.17 (m, 18H, –CH_2–), 0.78 (t, 6H, J=6.74 Hz, –CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ=168.27 (C=O), 162.54 (C_{Ar}–O), 160.72 (C_{Ar}–O), 132.18, 132.05, 131.79, 114.00, 113.89, 68.20 (C–O), 65.21 (C–O), 61.48 (C–O), 31.82, 29.54, 29.49, 29.25, 29.04, 25.91, 22.59, 14.07, 14.01; FTIR (KBr, cm^{-1}) ν=2957, 2920, 2852, 1765, 1638, 1604, 1309, 1295, 1255, 1209, 1174, 765; MS (FAB): 468 (M^+). Anal. Calcd for $C_{29}H_{40}O_5$: C: 74.32%; H: 8.60%. Found: C: 74.72%; H: 8.64%.

6.6. Substituted benzophenone *p*-tosylhydrazone 8

Under argon atmosphere, a solution of **7** (700 mg, 1.5 mmol) and *p*-tosylhydrazide (556 mg, 3.0 mmol) in 60 ml of toluene and 8 ml of ethanol is refluxed for 72 h in the presence of a catalytic amount of *p*-toluensulphonic acid. After cooling to room temperature, the crude is concentrated under vacuum, cooled in an ice bath and the precipitate is collected by filtration, washed with cold toluene and diethyl ether to yield *p*-tosylhydrazone **8** in 53% yield as an off-white solid. Mp: 154 °C (diethyl ether); ^{1}H NMR ($CDCl_3$, 200 MHz) δ=7.85 (d, 2H, J=8.32 Hz), 7.53 (s, 1H), 7.42–7.32 (m, 3H), 7.05 (d, 2H, J=9.16 Hz), 6.99 (d, 2H, J=9.16 Hz), 6.81 (d, 1H, J=6.91 Hz), 6.81 (d, 1H, J=6.91 Hz), 4.62 (s, 2H, –O–CH_2–COOR), 4.32–4.11 (m, 2H, –O–CH_2–), 4.02 (t, 2H, J=6.46 Hz, –O–CH_2–), 2.44 (s, 3H, –CH_3), 2.05 (s, 1H, –NH–), 1.83 (m, 2H, –CH_2–), 1.58–1.23 (m, 18H, –CH_2–), 0.89 (t, 6H, J=6.74 Hz, –CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ=160.34 (C=O), 158.96 (C_{Ar}–O), 154.08 (C_{Ar}–O), 143.83, 135.48, 130.47, 129.71, 129.45, 129.13, 127.74, 122.48, 115.39, 114.05, 68.08 (C–O), 65.13 (C–O), 61.29 (C–O), 31.74, 29.42, 29.18, 28.99, 25.87, 22.51, 21.43, 13.93; FTIR (KBr, cm^{-1}) ν=2924, 2853, 1758, 1606, 1509, 1200, 1162, 813; MS (EI, %I): 636 (M^+, 3), 481 (M^+–Tos, 66), 454 (M^+–Tos–NH–N, 68), 286 (51), 199 (58), 91 (100). Anal. Calcd for $C_{36}H_{48}N_2SO_6$: C: 67.89%; H: 7.60%; N: 4.40%; S: 5.03%. Found: C: 67.62%; H: 7.42%; N: 4.67%; S: 5.34%.

6.7. [6,6]Diphenylmethanofullerene ethoxycarbonyl derivative 9

To a solution of *p*-tosylhydrazone **8** (346 mg, 0.54 mmol) in 10 ml of anhydrous pyridine, sodium methoxyde (30 mg, 0.54 mmol) is added under argon atmosphere. After stirring at room temperature for 15 min, a solution of [60]fullerene (311 mg, 0.43 mmol) in 35 ml of *o*-dichlorobenzene is added at once and the resulting crude is heated at 180 °C for 18 h. After cooling to room temperature, the solvent is stripped away in a rotary evaporator and the remaining solid is purified by column chromatography (silica gel, toluene/dichloromethane 7:3) to yield **9** as a black solid in 26% yield after washing with methanol and diethyl ether. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=7.94 (d, 2H, J=8.72 Hz), 7.89 (d, 2H, J=8.72 Hz), 6.95–6.89 (m, 4H), 4.58 (s, 2H, –O–CH_2–COOR), 4.23 (q, 2H, J=7.15 Hz, –O–CH_2–CH_3), 3.91 (t, 2H, J=6.48 Hz, –O–CH_2–), 1.72 (m, 2H, –CH_2–), 1.48–1.19 (m, 18H, –CH_2–), 0.80 (t, 6H, J=6.68 Hz, –CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=169.20 (C=O), 159.20 (C_{Ar}–O), 157.81 (C_{Ar}–O), 148.87, 148.83, 145.76, 145.58, 145.49, 145.11, 145.02, 144.64, 144.25, 143.39, 143.32, 142.72, 142.69, 142.52, 141.23, 138.63, 138.56, 133.15, 132.40, 132.28, 131.44, 115.33, 115.06, 79.88 (C_{DPM}), 68.48 (C–O), 65.98 (C–O), 61.85 (C–O), 57.53 (C_{60}-sp^3), 32.33, 30.08, 30.05, 30.02, 30.00, 29.83, 29.76, 29.72, 26.52, 23.10, 14.62, 14.53; FTIR (KBr, cm^{-1}) ν=2957, 2920, 1766, 1627, 1323, 1250, 1217, 1174, 764, 526; MS (FAB): 1172 (M^+), 720 (C_{60}). Anal. calcd for $C_{89}H_{40}O_4$: C: 91.11%; H: 3.44%. Found: C: 92.00%; H: 3.42%.

6.8. [6,6]Diphenylmethanofullerene carboxylic acid 10

To a well-stirred solution of the [6,6]diphenylmethanofullerene derivative **9** (194 mg, 0.17 mmol) in 120 ml of toluene, concentrated hydrochloric acid (4 ml) and acetic acid (10 ml) are added and the mixture is heated at reflux for 48 h. The reaction crude is allowed to cool down to room temperature and vacuum evaporated. The remaining solid is then washed with methanol and diethyl ether, to afford carboxylic acid **10** in 92% yield as a brown solid. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=7.82 (d, 2H, J=8.68 Hz), 7.76 (d, 2H, J=8.68 Hz), 6.84 (d, 2H, J=8.75 Hz), 6.78 (d, 2H, J=8.75 Hz), 4.53 (s, 2H, -O–CH_2–COOH), 3.80 (t, 2H, J=6.39 Hz, –O–CH_2–), 1.63 (m, 2H, –CH_2–), 1.13–1.08 (m, 18H, –CH_2–), 0.72 (t, 3H, J=6.67 Hz, –CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=162.68 (C_{Ar}–O), 160.66 (C_{Ar}–O), 148.69, 148.65, 145.77, 145.74, 145.64, 145.56, 145.15, 145.11, 145.07, 144.99, 144.74, 144.29, 143.45, 143.40, 143.36, 143.35, 142.70, 142.67, 142.67, 142.56, 141.32, 138.74, 138.64, 133.65, 132.56, 132.31, 131.24, 115.37, 115.14, 79.74 (C_{DPM}), 68.52 (C–O), 65.31 (C–O), 57.39 (C_{60}-sp^3), 32.58, 30.35, 30.32, 30.30, 30.29, 30.11, 30.04, 29.97, 26.78, 23.43, 14.79; FTIR (KBr, cm^{-1}) ν=2920, 2850, 1741, 1703, 1611, 1234, 526; MS (FAB): 1144 (M^+), 720 (C_{60}). Anal. Calcd for $C_{87}H_{36}O_4$: C: 91.24%; H: 3.17%. Found: C: 90.00%; H: 3.32%.

6.9. 4,4′-Dihexyloxybenzophenone-*p*-tosylhydrazone (12)

Under argon atmosphere, a solution of 4,4′-dihexyloxybenzophenone (**11**) (382 mg, 1.0 mmol) and *p*-tosylhydrazide (186 mg, 1.0 mmol) in 25 ml of toluene is refluxed for 20 h in the presence of a catalytic amount of *p*-toluensulphonic acid. After cooling to room temperature, the crude is vacuum evaporated and the residue is purified by column chromatography (silica gel, hexane/ethyl acetate 9:1) to yield 4,4′-dihexyloxybenzophenone-*p*-tosylhydrazone (**12**) in 70% yield as a yellowish oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=7.85 (d, 2H, J=8.32 Hz), 7.53 (s, 1H), 7.42–7.32 (m, 3H), 7.05 (d, 2H, J=9.16 Hz), 6.99 (d, 2H, J=9.16 Hz), 6.81 (d, 1H, J=6.91 Hz), 6.81 (d, 1H, J=6.91 Hz), 4.32–4.11 (m, 2H, –O–CH_2–), 4.02 (t, 2H, J=6.46 Hz, –O–CH_2–), 2.44 (s, 3H, –CH_3), 2.05 (s, 1H, –NH–), 1.83 (m, 2H, –CH_2–), 1.58–1.23 (m, 14H, –CH_2–), 0.89 (t, 6H, J=6.74 Hz, –CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ=160.57, 160.22, 154.54 (C_{Ar}–O), 143.87, 135.62, 129.85, 129.53, 129.26, 129.19, 127.86, 122.79, 115.45, 114.00, 68.16 (C–O), 68.03 (C–O), 31.48, 29.07, 25.65, 25.60, 22.52, 21.55, 13.95; FTIR (KBr, cm^{-1}) ν=2931, 2859, 1607, 1510, 1248, 1171, 1161, 881, 664; MS (EI, %I): 550 (M^+, 8), 395 (M^+–Tos, 100), 366 (M^+–Tos–NH–N, 39), 311 (23), 197 (25). Anal. Calcd for $C_{32}H_{42}N_2SO_4$: C: 69.78%; H: 7.69%; N: 5.09%; S: 5.82%. Found: C: 69.42%; H: 5.13%; S: 5.47%.

6.10. [6,6]-Bis-(4-hexyloxyphenyl)methanofullerene (13)

To a solution of 4,4′-dihexyloxybenzophenone-*p*-tosylhydrazone (**12**) (200 mg, 0.36 mmol) in 8 ml of anhydrous pyridine, sodium methoxyde (19 mg, 0.36 mmol) is added under argon atmosphere. After stirring at room temperature for 15 min, a solution of [60]fullerene (276 mg, 0.36 mmol) in 30 ml of *o*-dichlorobenzene is added at once and the resulting crude is heated at 180 °C for 24 h. After cooling to room temperature, the solvent is stripped away in a rotary evaporator and the remaining solid is purified by column chromatography (silica gel, toluene/dichloromethane 1:1) to yield [6,6]-bis-(4-hexyloxyphenyl)methanofullerene (**13**) as a black solid in 32% yield after washing with methanol and diethyl ether. ^{1}H NMR ($CDCl_3$, 200 MHz) δ=7.97 (d, 4H, J=8.80 Hz), 6.98 (d, 4H, J=8.80 Hz), 3.98 (t, 4H, J=6.62 Hz, $-O-CH_2-$), 1.79 (m, 4H, $-CH_2-$), 1.50–1.26 (m, 12H, $-CH_2-$), 0.91 (t, 6H, J=6.68 Hz, $-CH_3$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ=158.70 ($C_{Ar}-O$), 148.59, 145.40, 145.15, 145.06, 144.68, 144.57, 144.19, 143.83, 142.97, 142.90, 142.31, 142.09, 140.78, 138.18, 131.80, 131.32, 114.63, 79.66 (C_{DPM}), 68.05 (C–O), 57.38 (C_{60}-sp^3), 31.58, 29.27, 25.76, 22.59, 14.02; FTIR (KBr, cm^{-1}) ν=2922, 2851, 1608, 1508, 1484, 1246, 1182, 526; MS (FAB): 1086 (M^+), 720 (C_{60}). Anal. Calcd for $C_{85}H_{34}O_2$: C: 91.22%; H: 3.06%. Found: C: 91.04%; H: 3.72%.

6.11. [6,6]Diphenylmethanofullerene-conjugated oligomer dyad 14

To a solution of [6,6]diphenylmethanofullerene carboxylic acid **10** (70 mg, 0.06 mmol), *N*,*N*-dicyclohexylcarbodiimide (25 mg, 0.12 mmol) and 4-(dimethylamino)-pyridine (15 mg, 0.12 mmol) in 40 ml of anhydrous toluene and under argon atmosphere, a solution of benzyl alcohol **5** (80 mg, 0.18 mmol) in 10 ml of anhydrous toluene is added. After 3 days, the reaction crude is vacuum evaporated and the remaining residue purified by column chromatography (silica gel, dichloromethane) and washed with methanol and diethyl ether to yield **14** in 66% yield as a black solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ=8.00 (d, 2H, J=8.48 Hz), 7.98 (d, 2H, J=8.48 Hz), 7.50–7.41 (m, 6H), 7.39 (d, 2H, J=8.74 Hz), 7.33 (d, 2H, J=8.74 Hz), 7.07 (d, 2H, J_{trans}=16.00 Hz, $-CH{=}CH-$), 7.00 (d, 2H, J=8.70 Hz), 6.98 (d, 2H, J=8.70 Hz), 6.88 (d, 2H, J_{trans}=16.00 Hz, $-CH{=}CH-$), 6.64 (d, 2H, J=8.70 Hz), 5.26 (s, 2H, $Ar-CH_2-O-$), 4.71 (s, 2H, $-O-CH_2-CO$), 3.99 (t, 2H, J=6.42 Hz, $-O-CH_2-$), 3.31 (t, 4H, J=7.54 Hz, $-CH_2-N-$), 1.82 (q, 2H, J=6.93 Hz, $-CH_2-$), 1.46–1.27 (m, 26H, $-CH_2-$), 0.98 (t, 6H, J=7.20 Hz, $-CH_3$), 0.89 (t, 3H, J=6.60 Hz, $-CH_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ=169.20 (C=O), 159.18 ($C_{Ar}-O$), 157.69 ($C_{Ar}-O$), 148.84, 148.80, 148.28, 145.77, 145.75, 145.57, 145.48, 145.10, 145.04, 145.00, 144.63, 144.23, 143.38, 143.32, 142.68, 142.50, 141.22, 138.61, 138.55, 138.51, 135.63, 134.44, 133.18, 132.39, 132.29, 131.44, 129.67, 129.50, 129.41, 128.24, 127.43, 127.28, 127.01, 126.64, 124.76, 123.47, 115.29, 115.03, 112.00, 79.86 (C_{DPM}), 68.48 (C–O), 67.37 (C–O), 65.91 (C–O), 57.49 (C_{60}-sp^3), 51.20 (C–N), 32.34, 30.09, 30.06, 30.03, 29.89, 29.84, 29.77, 29.72, 26.52, 23.11, 20.77, 14.56, 14.44; FTIR (KBr, cm^{-1}) ν=2952, 2923, 2852, 1763, 1607, 1591, 1519, 1509, 1285, 1174, 959, 821, 742, 526; MS (FAB): 1565 (M^+), 720 (C_{60}). Anal. Calcd for $C_{118}H_{71}NO_4$: C: 90.45%; H: 4.57%; N: 0.89%. Found: C: 90.89%; H: 4.42%; N: 0.63%.

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24. Value corresponding to the band onset featured in the emission spectra.
25. Weller, A. *Z. Phys. Chem. (Muenchen, Ger.)* **1982**, *133*, 93–98 $\Delta G_{PET}=e[E_{ox}(\mathrm{oligomer})-E_{red}(\mathrm{DPM})]-E(S_1)-e^2/4\pi\varepsilon_0\varepsilon_s R_{cc}-e^2/8\pi\varepsilon_0(1/r^+ + 1/r^-)(1/\varepsilon_{ref}-1/\varepsilon_s)$. In this equation, E_{ox}(oligomer) and E_{red}(DPM) are the oxidation and reduction potentials of the donor and acceptor in a solvent with relative permittivity ε_{ref}; $E(S_1)$ the energy of the excited state from which electron transfer occurs; R_{cc} the center-to-center distance of the positive and negative charges in the charge separated state; r^+ and r^- are the radii of the positive and negative ions; ε_s is the relative permittivity of the solvent; and e and ε_0 are the electron charge and the vacuum permittivity, respectively. The radius of the DPM unit (4.4 Å), the oligomeric system (9.5 Å) and R_{cc} (12.8 Å) was estimated by semiempirical PM3 calculations, assuming a conformation with both electroactive units as separated as possible.