RECENT ADVANCES IN THE DESIGN, SYNTHESIS AND STUDY OF COVALENT CONJUGATED OLIGOMER–C_{60} ENSEMBLES

Raúl Blanco BAZACO[1], José L. SEGURA[2,*] and Carlos SEOANE[3,*]
Departamento de Química Orgánica, Facultad de Ciencias Químicas,
Universidad Complutense de Madrid, E-28040 Madrid, Spain;
e-mail: [1] raulblanco@quim.ucm.es, [2] segura@quim.ucm.es, [3] seoane@quim.ucm.es

Received December 19, 2008
Accepted April 1, 2009

At 85, as ever and forever, a bit of Alfred's soul pops out every time we open an Aldrich bottle. Thanks, Alfred.

This review presents an overview of the most recent results in the field of conjugated oligomer covalently attached to the C_{60} sphere focusing mainly on donor–conjugated oligomer–C_{60} triads and conjugated oligomer–multifullerene materials. Well-defined monodisperse oligomers as new materials that exhibit interesting optoelectronic properties have been the subject of intense study during the last decade. In this regard, a huge amount of work has been devoted to the development of new synthetic strategies toward the synthesis of conjugated oligomeric materials with precise length and constitution and to their chemical functionalization in order to incorporate them into more complex molecular and supramolecular architectures. An important area of research in the field of conjugated oligomers involves the design and synthesis of donor–acceptor ensembles by combination of monodisperse π-conjugated oligomeric systems with C_{60} fullerene. Such hybrid systems have shown excited-state interactions making them excellent candidates for fundamental photophysical studies. In addition, these materials have found applications in the field of photovoltaic devices. A review with 70 references.

Keywords: Fullerenes; Conjugated oligomers; Porphyrines; Oligothiophenes; Ferrocene; Alkynes; Functional molecules; Molecular electronics.

Polymeric and low-molecular-weight materials have been widely investigated during the last two decades due to their potential applications in the area of electronic and optoelectronic devices. A combination of optical and electronic properties of semiconductors with the processing advantages and mechanical properties of polymers makes conjugated polymers an especially important class of synthetic semiconductors[1]. Thus, many groups are engaged in the research and development of new light-emitting diodes,

Collect. Czech. Chem. Commun. 2009, Vol. 74, No. 6, pp. 857–886

doi:10.1135/cccc2008218

solid-state lasers, photoconductive and photovoltaic devices, nonlinear optics materials or field-effect transistors based on organic materials[2].

Among various applications, special attention has been devoted to the fabrication of photoelectric conversion devices due to a promise of low cost, low weight and flexible solar cells[3–5]. The first conjugated polymer-based single-layer devices showed power conversion efficiencies lower than 0.1%. However, since the observation of effective exciton generation by photoinduced electron transfer[6] from optically excited conjugated polymers to the [60]fullerene molecule and the observation of highly increased photoconductivities upon [60]fullerene addition to conjugated polymers, the development of polymer–[60]fullerene bilayer heterojunctions and bulk heterojunction devices[7] has made possible to achieve conversion efficiencies between 1.5 and 5% in only a few years.

In this kind of devices, the tendency to phase segregation of the donor and acceptor components has a crucial role in the efficiencies[8] so that much effort has been devoted to the optimization of the morphology of photoactive blend. One of the proposed approaches to attain the control of morphology of donor–acceptor phases is to design macromolecules where the donor and acceptor moieties are chemically linked. Thus, the covalent linking of electron acceptor moieties to a hole transporting conjugated polymer backbone has been proposed. With this aim, various types of conjugated polymers bearing side-chains containing [60]fullerene have been synthesized[9]. These macromolecules show in principle two different pathways for different signs of charges where a balanced transport of electrons and holes may be achieved[10].

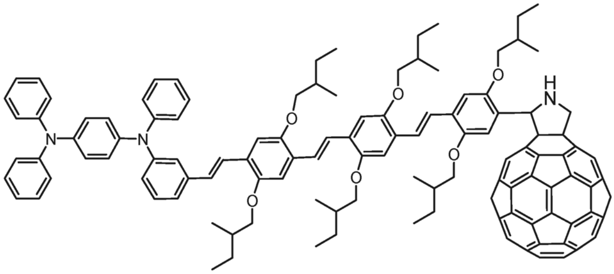
A characteristic of main-chain conjugated polymers is that they inevitably contain randomly distributed defects, i.e. non-conjugated segments, which lead to a statistical distribution of conjugated lengths. Thus, shortly after the publication of the first photovoltaic devices based on conjugated polymers, the study of monodisperse conjugated oligomers[11–13] started mainly to assess the role of the π-conjugation length of the donor[14] as well as the effect of the carbo- or heterocyclic nature of the monomers on the electron transfer process and morphology of the blends[15]. A recent review of Segura et al.[16] details the literature concerning conjugated oligomer–C_{60} ensembles until 2005 focusing mainly on the photophysical behavior of this kind of materials and their applicability to fabrication of photovoltaic devices. More recently, Nierengarten et al. have also reviewed this field but only considering systems which combine oligo(phenylenevinylene)s and C_{60} moieties[17]. In this review we will describe the most recent results on conjugated oligomer–C_{60} ensembles focusing mainly on (i) donor–conjugated oligomer–C_{60} triads and (ii) conjugated oligomer–multifullerene materials.

In the last few years, different strategies have been proposed in order to enhance the photovoltaic performance of devices based on conjugated oligomer–C_{60} ensembles. One approach involves an increase in the number of pendant fullerene units covalently linked to the conjugated oligomer. This increase in the linkage system strengthens intermolecular interactions among the fullerenes thus making a good path for electron transfer which is important in order to enhance the electron transport properties and hence the efficiency of devices. A second approach to enhance device performances involves the synthesis of C_{60}–conjugated oligomer–donor triads. This kind of systems has been synthesized in order to promote the photoinduced charge separation process. The introduction of a strong donor at the end of the conjugated oligomer chain is expected to induce long-distance charge separation thus contributing to some improvement in photovoltaic performance.

DONOR–CONJUGATED OLIGOMER–C_{60} TRIADS

Other more complex materials bearing C_{60} and conjugated oligomers have been synthesized for different purposes in the last few years. Especially relevant are some donor–conjugated oligomer–acceptor triads. The electron coupling along the spacer connecting electron donor and electron acceptor units allows to control the speed of the charge transfer between the groups at the end of the spacer[18]. The spacer plays a key role in many biological processes such as those in photosynthetic reaction center[19], redox proteins[20], membranes[21] or nucleic acids[22]. Especially interesting is the role of the spacer in donor–spacer–acceptor systems for molecular electronic devices[23]. In this regard, conjugated oligomers are suitable to act as spacers considering their rigidity and the possibility to tune their length by incorporating different numbers of monomeric units. Thus, in 1998, Ratner and Wasielewski performed a systematic study in a series of triads bearing tetracene moieties as donors, pyromellitimide as acceptor and oligo(phenylenevinylene) moieties of different lengths as spacers[24]. This investigation shows the importance of the appropriate relationship between the HOMO energy level of the donor and the LUMO energy level of the acceptor in order to achieve a molecular wire behavior.

In 2003 Janssen and coworkers carried out the synthesis of triad **1** bearing a *N*,*N*,*N*′,*N*′-tetraphenyl-1,4-phenylene-2-diamine (OAn) moiety as donor, oligo(phenylenevinylene) (OPV) as rigid spacer and [60]fullerene as acceptor (Fig. 1)[25].

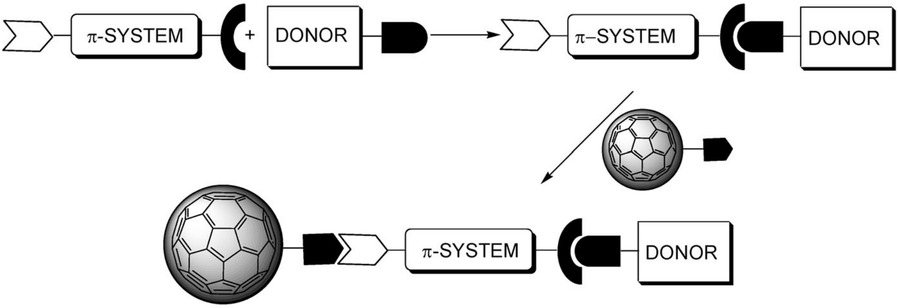


1

FIG. 1
OAn–OPV–fullerene ensemble **1**

In this material, a redox gradient is introduced considering that the oxidation potential increases from C_{60}, through OPV to diamine, simultaneously the reduction potential decreases and therefore the most favorable charge separated state corresponds to OAn^{+}–OPV–C_{60}^{-}. Interestingly, the OAn^{+}–OPV–C_{60}^{-} state exhibits a long lifetime (>1 ns) as a consequence of the weak electron coupling between the donor (OAn) and acceptor (C_{60}) redox sites in the excited state which produces stabilization of more than one order of magnitude.

Conjugated oligomers have also been used to investigate the electronic communication through π-conjugated wires in covalently linked donor–C_{60} ensembles where the donors are tetrathiafulvalene (TTF)[26–28] and porphyrine[29] derivatives. The synthesis of the new materials was carried out by following the stepwise procedure of tail functionalization depicted in Scheme 1.



SCHEME 1
Synthesis of triads donor–conjugated oligomer–C_{60}

Synthesis of a homologous series of soluble oligomers bearing solubilizing alkoxy chains and aldehyde functionalities on the terminal positions was carried out. Afterwards, the donor moieties with triphenylphosphonium halide functionalities were reacted with the oligomers via Wittig olefination reactions under stoichiometry control. The last steps consist of the treatment of the donor–conjugated oligomer–aldehyde dyads with C_{60} and sarcosine (*N*-methylglycine) or *N*-octylglycine to afford the corresponding triads.

By using the synthetic strategy depicted in Scheme 1, a series of C_{60}–OPV–exTTF (**2**–**6**, Fig. 2) was synthesized and the electronic interactions between the three electroactive species were investigated by UV-Vis spectroscopy and cyclic voltammetry[26,27]. No significant interaction was observed in the ground state between the C_{60} and exTTF moieties although they are connected through the π-conjugated oligomer. Nevertheless, subsequent photoexcitation and efficient photoinduced electron transfer were observed leading to the radical pair C_{60}^{-}–OPV–exTTF^{+}. Interestingly, the measured lifetimes for the photogenerated charge-separated states have values between 465 and 557 ns thus indicating a very low influence of the oligomer length on the electron rate, which indicates a nanowire behavior.

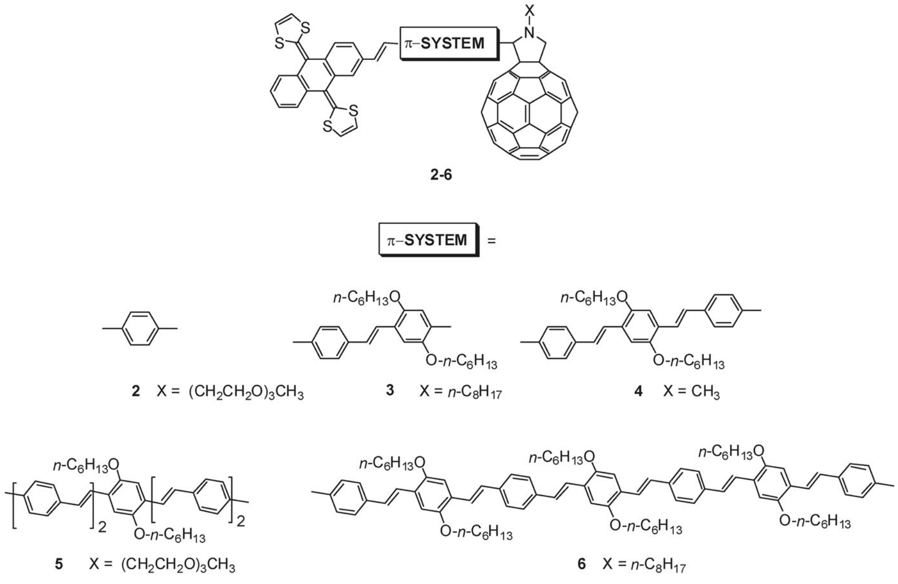


FIG. 2
exTTF–oligoPPV–fullerene triads

Following a similar strategy, a series of acceptor–bridge–donor triads with a pyrrolofullerene and a ferrocene (Fc) unit directly connected **7** or separated through oligo(phenylenevinylene) spacers **8**–**10** have been reported in 2008 (Fig. 3)[30]. UV-Vis spectra and cyclic voltammograms of these architectures indicate the presence of interactions between the C_{60} and the Fc moiety. These interactions decrease progressively when the length of the oligomer increases. On the other hand, the emission spectra in triads **8**–**10** show that the fluorescence of the C_{60} singlet excited states is completely quenched in dichloromethane. This is explained in terms of the ultrafast charge separation and recombination mediated by the OPV spacer. In less polar toluene, the dynamic process of singlet and triplet fullerene quenching shows a distance dependence along the OPV bridge. Nevertheless, the radical anion fingerprint of pyrrolofullerene could not be detected and the quenching mechanism between the fullerene and the ferrocene moieties is not clear.

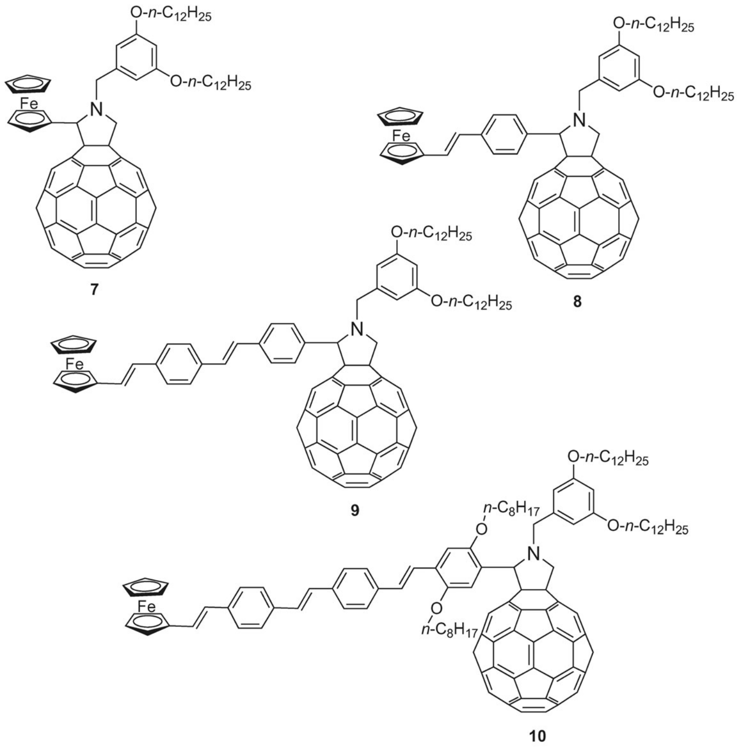
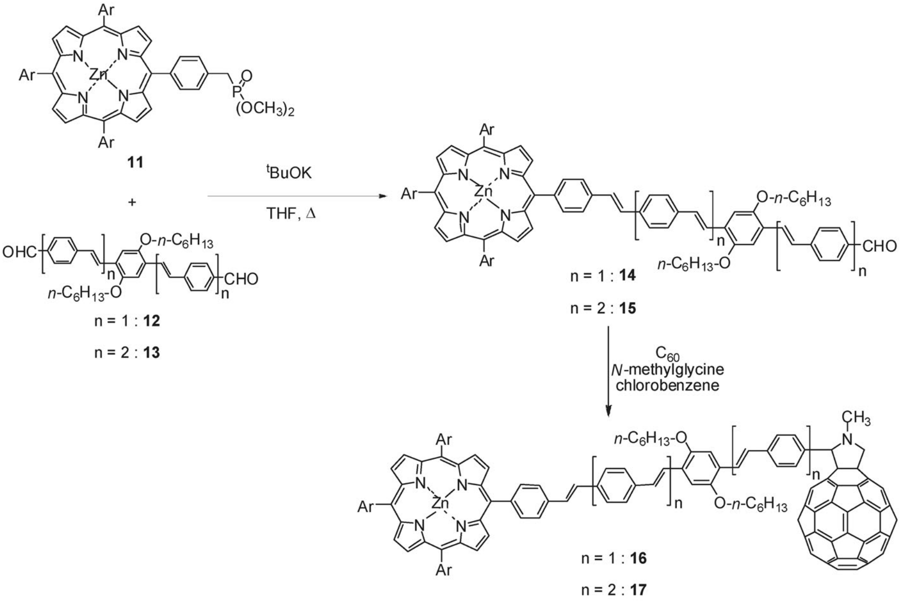


FIG. 3
Fc–fullerene dyad **7** and Fc–oligoPPV–fullerene triads **8**–**10**

By following a similar synthetic procedure, two donor–bridge–acceptor systems with C_{60} and zinc(II) tetraphenylporphyrin (ZnP) connected through oligo(phenylenevinylene) moieties have been synthesized (Scheme 2)[29].

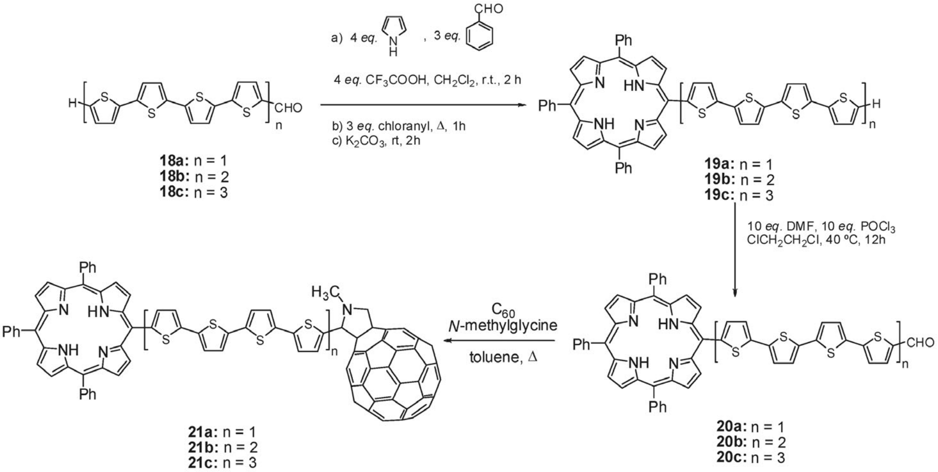


SCHEME 2
Synthesis of ZnP–oligoPPV–fullerene triads

The Wittig–Horner olefination reaction between phosphonatoporphyrin **11** and appropriately functionalized oligo(phenylenevinylene) derivatives **12** and **13** under stoichiometry control afforded the respective dyads **14** and **15** bearing an aldehyde functionality. Further reaction of these dyads with [60]fullerene and *N*-methylglycine in chlorobenzene gave the target C_{60}–oligoPPV–ZnP triads **16** and **17** [29].

Similar to the exTTF analogues **2**–**6**, the UV-Vis spectra of novel C_{60}–oligoPPV–ZnP triads **16** and **17** do not show significant interaction between the C_{60} and exTTF moieties although they are connected through a π-conjugated oligomer. In agreement with the lack of interaction between the donor and acceptor moieties in the ground state, the redox behavior of these systems exhibit an amphoteric behavior showing the characteristic waves corresponding to the three electroactive moieties. By performing a detailed physicochemical investigation it was also observed that the formation of charge separated states $ZnP^{\bullet+}/C_{60}^{\bullet-}$ is responsible for the fast deactivation of the photoexcited chromophore. By plotting the electron transfer rates as a function of donor–acceptor separation, attenuation factors β of 0.03 ± 0.005 $Å^{-1}$ were determined thus supporting the notion of wirelike behavior also in **16** and **17**.

Not only oligo(phenylenevinylene) derivatives have been used as rigid spacers. Different donor–conjugated oligomer–acceptor triads have been synthesized and investigated bearing oligothiophene moieties as spacers. In 2002, Aso, Otsubo, Ito and co-workers carried out the synthesis of porphyrin–oligothiophene–fullerene triads **21** as efficient intramolecular electron-transfer systems by using the synthetic strategy depicted in Scheme 3 [31].



SCHEME 3
Synthesis of porphyrin–oligothiophene–fullerene triads

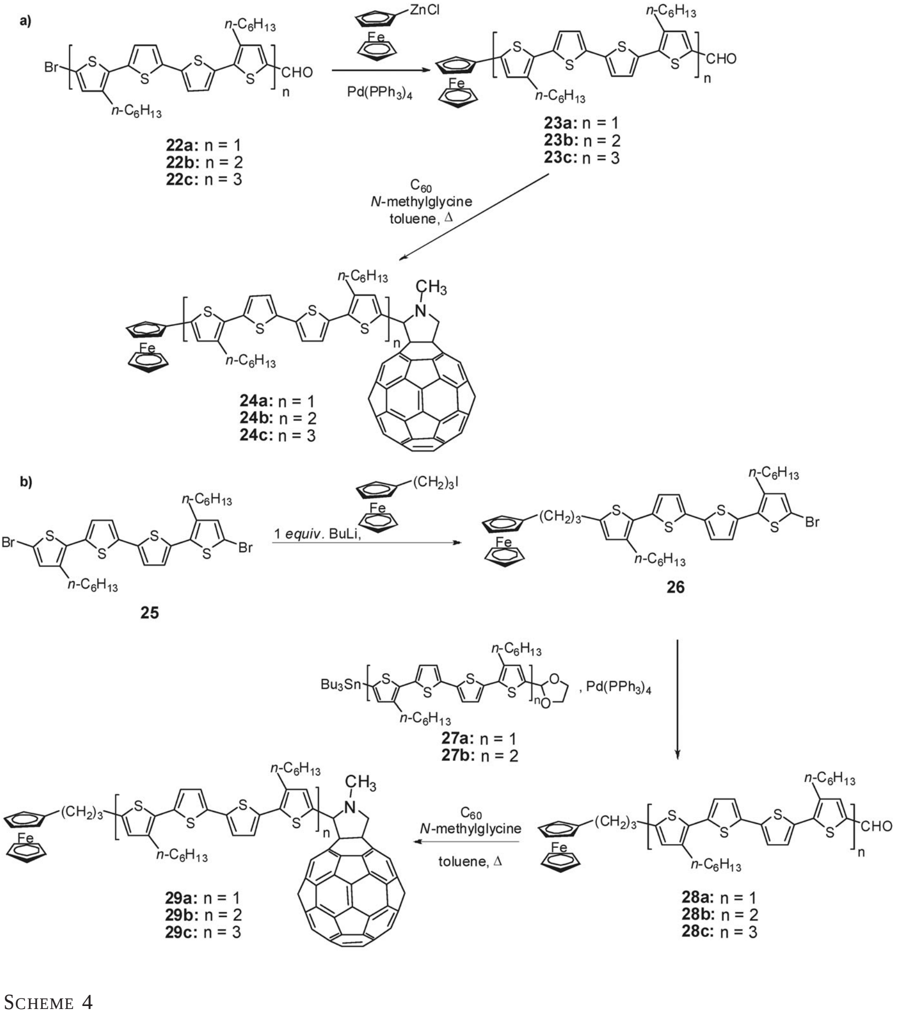
Formyloligothiophenes (**18a**–**18c**) were reacted with 3 molar equivalents of benzaldehyde and 4 molar equivalents of pyrrole in the presence of 4 molar equivalents of trifluoroacetic acid according to the Lindsay method[32]. The subsequent oxidation with *p*-chloranil afforded hybrid porphyrins which after chromatographic separation, allow to obtain the corresponding oligothiophene–porphyrin dyads **19a**–**19c**. Vilsmeier reaction of these dyads by treatment with $POCl_3$ in 1,2-dichloroethane afforded the formylated analogues **20a**–**20c**. Finally, treatment of these systems with fullerene in the presence of *N*-methylglycine in toluene according to Prato's method yielded the target C_{60}–oligothiophene–porphyrin triads **21a**–**21c** [31]. UV-Vis spectra of these triads indicate that there is no electronic interaction among the three chromophores in the ground state. On the contrary, the emission spectra are interactive showing significant quenching of the porphyrin fluorescence. Electron transfer takes place in these systems with rate constants (k_{ET}) of 5.7×10^9 s^{-1} for **21a**, 6.2×10^8 s^{-1} for **21b** and 2.0×10^8 s^{-1} for **21c**. From these values and the calculated center to center distance in the triads an attenuation factor $\beta = 0.11$ Å^{-1} could be obtained, which is smaller that that observed for saturated hydrocarbon bridges[33] or conjugated phenylenes[34] and comparable to that of polyenes[35] or polyynes[36]. It indicates a molecular wire behavior of the oligothiophene moieties which allow an efficient electronic coupling between donor and acceptor in these triads. Sun and coworkers further studied these systems by density functional theory (DFT) and obtained oscillator strengths and transition energies consistent with the experimental data[37]. The theoretical analysis with 2D and 3D real space analysis reveals that there are two intramolecular charge transfer mechanisms and that the experimental weak distance dependence of the oligothiophene spacer is benefiting from the superexchange mechanism.

Ito, Otsubo and co-workers also investigated the solvent dependence of photophysical processes in these systems. They observed that the lifetimes of the charge separated states were longer than 10 μs in *o*-dichlorobenzene (*o*-DCB) and in nonpolar solvents the energy transfer process competes with the charge separation process. In the energy transfer process, the oligothiophene moieties act as spacers. The lengths and the Gibbs energy changes of the oligothiophene moieties control the precedence of the paths[38].

The dramatic changes of the lifetimes of the charge-separated states with the solvent polarity were also confirmed in zinc porphyrin–oligothiophene–C_{60} triads[39]. Compared with analogues **21a**–**21c** containing free porphyrin, the lifetimes of the charge separated states of triads with zinc porphyrin are ~30 times longer. In this series, the role of the oligothiophene moieties varies much with the length, electronic factors and medium effects.

Otsubo, Ito and co-workers also investigated the synthesis and photophysical properties of ferrocene–oligothiophene–fullerene triads **24a**–**24c** and **29a**–**29c** (Scheme 4)[40]. A Negishi coupling of unsymmetrically functionalized oligothiophenes **22a**–**22c** with ferrocenylzinc chloride in the presence of catalytic tetrakis(triphenylphosphine)palladium in THF allows to obtain the ferrocenyl(oligothiophene)carbaldehydes **23a**–**23c**. Subsequent Prato reaction of **23a**–**23c** with [60]fullerene and *N*-methylglycine in refluxing toluene yielded the ferrocene–oligothiophene–fullerene triads

24a–**24c** (Scheme 4a). On the other hand, dibrominated quaterthiophene **25** was subjected to metal-halogen exchange with 1 equivalent of butyllithium in THF at –70 °C, followed by treatment with (3-iodopropyl)ferrocene at room temperature to afford the bromo(ferrocenylpropyl)quaterthiophene **26**. A subsequent Stille coupling of **26** with tributyltin derivatives **27a**, **27b** in the presence of catalytic tetrakis(triphenylphosphine)palladium in refluxing toluene yielded the ferrocenyl(oligothiophene)carbaldehydes **28a**–**28c**. Finally, Prato reaction of **28a**–**28c** with



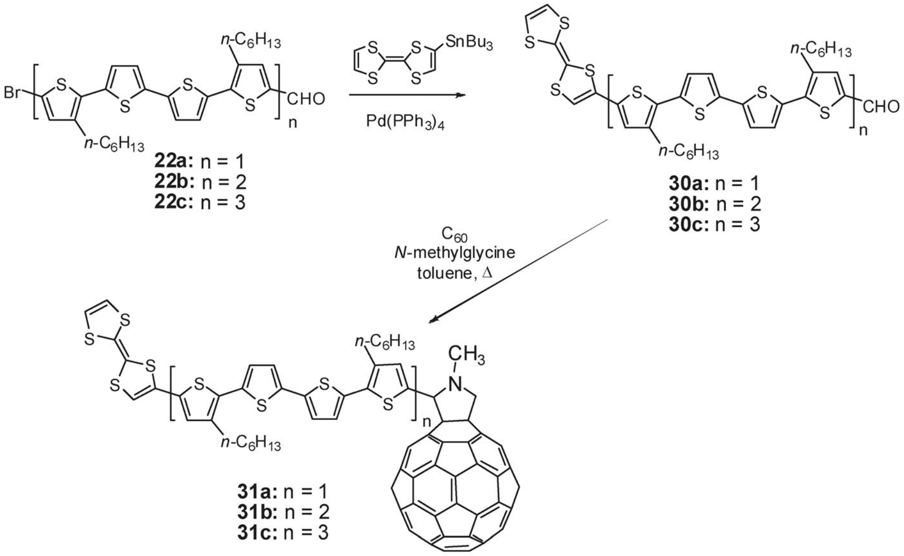
SCHEME 4
Synthesis of ferrocene–oligothiophene–fullerene triads

[60]fullerene and *N*-methylglycine in refluxing toluene yielded the ferrocene–oligothiophene–fullerene triads **29a**–**29c** (Scheme 4b).

The cyclic voltammograms and electronic absorption spectra of triads **24a**–**24c** and **29a**–**29c** indicate conjugation between the ferrocene and oligothiophene components. On the other hand, the emission spectra of triads **24a**–**24c** show that the fluorescence of the oligothiophene is significantly quenched when compared with similar oligothiophene–fullerene dyads without the ferrocene moieties. This is explained in terms of the stabilization of the charge-separated state by the presence of the additionally conjugated ferrocene. Thus, photoinduced electron transfer processes are promoted in those systems in which the ferrocene moieties are conjugated with the oligothiophene system. This is corroborated by the photophysical behavior of triads **29a**–**29c** in which the ferrocene moieties are not conjugated with the oligothiophenes. Thus, for these systems, the emission spectra are dominated by photoinduced energy transfer in the decay process. This behavior is similar to that observed for oligothiophene–fullerene dyads without the ferrocene moieties.

This effect of extension or prevention of π-conjugation on photoinduced electron transfer processes of ferrocene–oligothiophene–fullerene triads has been further investigated by Ito, Otsubo and coworkers[41]. In polar solvents, photoinduced electron transfer was observed for triads **24a**–**24c** as well as for **29a**–**29c**. Interestingly, it was observed that the prevention of π-conjugation between the ferrocene and oligothiophene moieties is more effective for maintaining the lifetime of the charge-separated state than the positive-charge delocalization between the ferrocene and oligothiophene moieties by extending π-conjugation. Additionally, it was also observed that the oxidation potentials of the oligothiophene moieties control the electron-transfer process, reflecting stabilization of the radical cations of the oligothiophene moieties.

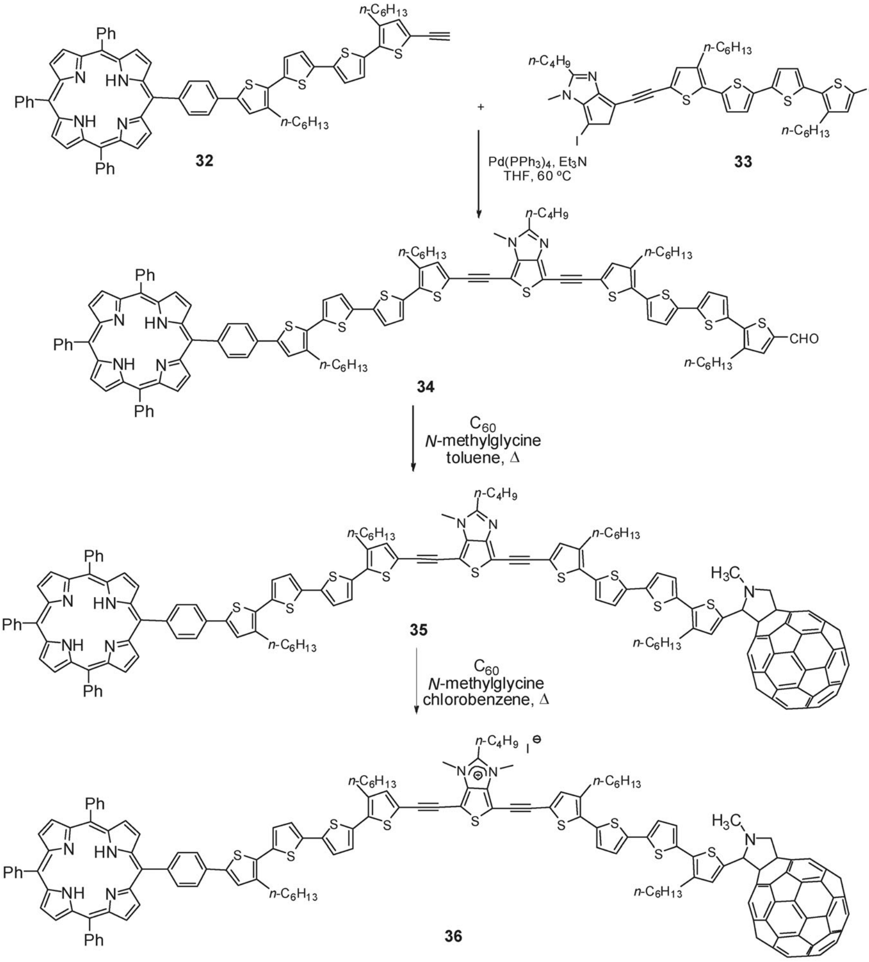
Otsubo and co-workers have also synthesized tetrathiafulvalene–oligothiophene–fullerene triads (**31a**–**31c**, Scheme 5) and explored their potential in photovoltaic devices[42]. The UV-Vis spectra of **31a**–**31c** indicate some electronic interaction between the oligothiophene and tetrathiafulvalene (TTF) moieties. Furthermore, investigation of the emission spectra suggests that efficient intramolecular electron transfer among the three chromophores may occur due to long range charge separation to $TTF^{\bullet+}$–oligothiophene–$C_{60}^{\bullet-}$. Triads **31a**–**31c** were investigated as single-components in photovoltaic devices with a configuration structure Al/TTF–oligothiophene–C_{60}/Au. When compared to the corresponding C_{60}–oligothiophene devices[43], the TTF–oligothiophene–C_{60} systems demonstrated somewhat higher photocurrents. Given that the TTF is a poor light harvester, it can be concluded that the attached TTF in the triads contributes to the enhancement of photoinduced charge separation and/or charge migration, resulting in an increase in the photocurrent.



SCHEME 5
Synthesis of tetrathiafulvalene–oligothiophene–fullerene triads

In 2006, Aso and co-workers have reported the synthesis of a zinc porphyrin–oligothiophene–fullerene triad **36** (Scheme 6) where diethylthieno[3,4-*d*]imidazolium has been incorporated as a central unit of oligothiophene[44]. Palladium-catalyzed Sonogashira coupling of **32** and **33** furnished the formylated derivative **34**. Triad **35** was obtained from the azomethine ylide generated in situ from **34** and *N*-methylglycine by reaction with C_{60} in refluxing chlorobenzene. Treatment of **35** with methyl iodide gave the target triad **36**. The UV-Vis spectra of the triad indicate that there is no electronic interaction among the electroactive components in the ground state. In contrast, the fluorescence from the porphyrin chromophore in the triad **35** was quenched to 73% in comparison with that of the fullerene-free analogue **34**. Furthermore, the fluorescence intensity of **36** was further reduced to 35%, indicating a strong electronic perturbation of the imidazolium unit to accelerate the electron transfer. Addition of excess

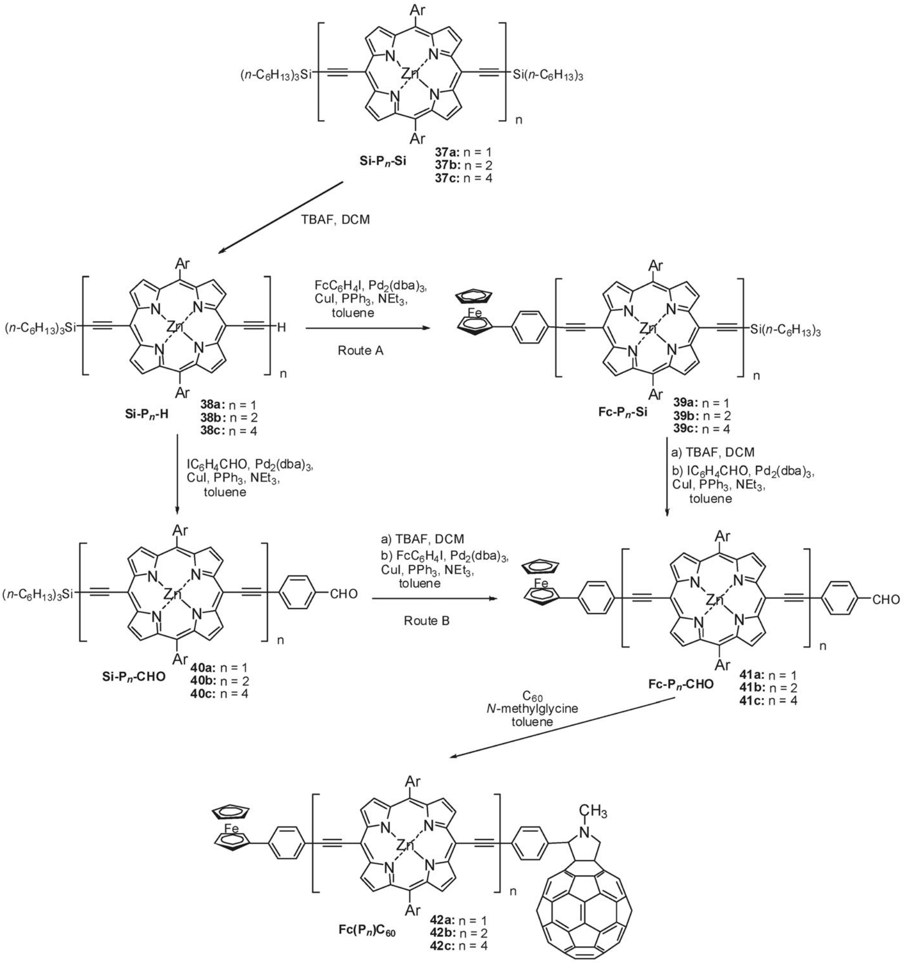
TBAF to benzonitrile solutions of **36** produced a marked enhancement of the fluorescence intensity, which contrasts with the almost negligible changes observed by addition of other ammonium salts ($TBA^+PF_6^-$, $TBA^+BF_4^-$ and $TBA^+ClO_4^-$).



SCHEME 6
Synthesis of zinc porphyrin–oligothiophene–fullerene triad **36** with diethylthieno[3,4-*d*]imidazolium as a central unit of oligothiophene

This behavior can be explained in terms of a strong coordination of fluoride anion to the imidazolium cation so that the cationic charge of the imidazolium is effectively neutralized to suppress its acceleration effect on the photoinduced electron transfer and thus represents a new type of chemical-gate system[45].

More recently, a series of ferrocene–porphyrin–fullerene triads **42a**–**42c** have been prepared with the aim of investigating the role of the spacer as an efficient molecular wire (Scheme 7)[46]. The structures Fc(P_n)CHO



SCHEME 7
Synthesis of ferrocene–porphyrin–fullerene triads

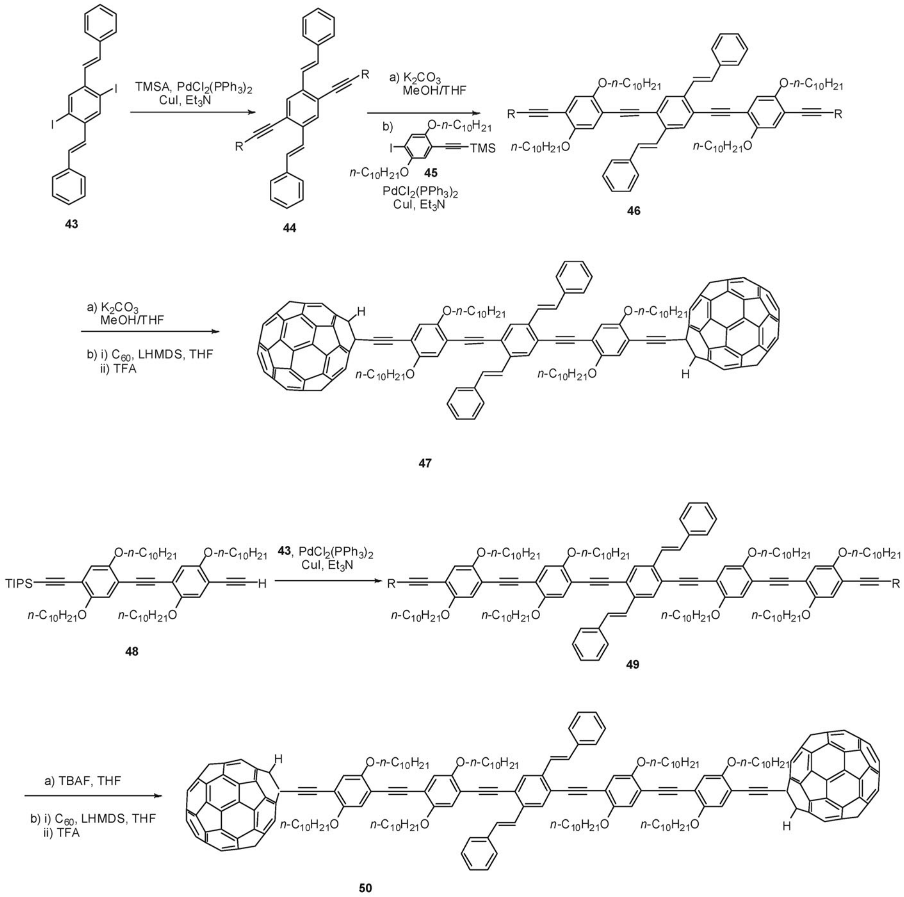
41a–**41c** were synthesized from the silicon terminated oligomers **37a**–**37c** through two different routes using palladium-catalyzed Sonogashira coupling. Finally, treatment of Fc(P_n)CHO **41a**–**41c** with [60]fullerene and *N*-methylglycine in refluxing toluene gave the ferrocene–porphyrin–C_{60} triads **42a**–**42c** (Scheme 7). UV-Vis spectra of these triads show little interaction among the three constitutive moieties in the ground state. Nevertheless, following photoexcitation of the porphyrin oligomer spacers, efficient photoinduced electron transfer was observed leading to long-range charge separated states. The measured rates of long-range charge recombination are between 1.3–15 × 10^8 s^{-1} and exhibit low dependence of the oligomer length. Interestingly, the porphyrin tetramer mediates fast long-range charge transfer over 65 Å, thus indicating potential applications of these structures as molecular wires.

Finally, it is worth mentioning that solid film versus solution-phase charge-recombination dynamics of TTF–oligo(phenylenethienylene)–C_{60} triads have been investigated[47]. Recombination dynamics measured in the solid films were tenfold slower than that observed in solution as a consequence of trapping the free carriers, formed after photoexcitation, at film defects. Thus, it is shown that the transient absorption studies of solid molecular films are important in order to develop organic solar cells based on molecular donor–acceptor structures.

CONJUGATED OLIGOMER–MULTIFULLERENE ENSEMBLES

A wide variety of C_{60} donor dyads in which the C_{60} core is covalently attached to an electron donor unit as promising candidates for the search of electron-transfer properties have been investigated. Following this approach, in order to provide access to the construction of two- and three-dimensional supramolecular architectures with defined geometries, a variety of C_{60}–linear conjugated oligomer–C_{60} triads have been synthesized based on oligothiophenes[48], oligo(phenylenevinylene)s[49], oligo(thienylenevinylene)s[50], oligo(phenyleneethynylene)s[51] and oligofluorenes[52]. The literature covering pioneering work in the field of the so-called fullerene dimers was reviewed by Segura et al.[53].

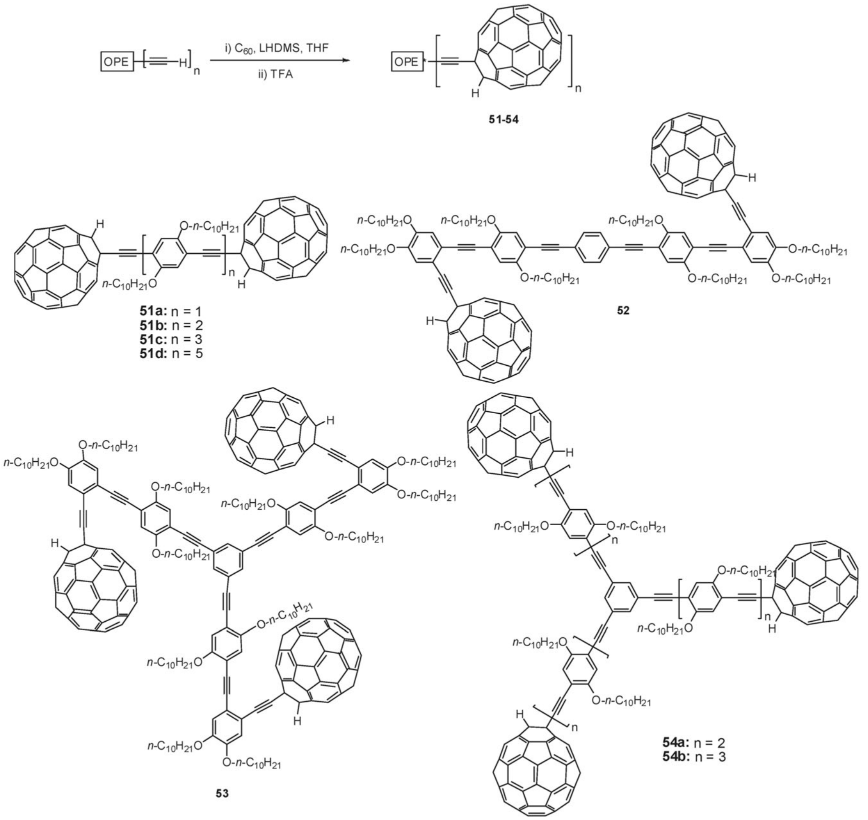
Zhao, Thompson and co-workers have reported the synthesis of C_{60}–conjugated oligomer–C_{60} triads **47** and **50**, in which cruciform OPE/OPV hybrid oligomers act as bridges between both fullerenes instead of the commonly used linear conjugated oligomers (Scheme 8)[54]. OPE/OPV hybrid oligomers with terminal alkynes **46** and **49** were obtained from (diiodophenylene)vinylene **43** using the palladium-catalyzed Sonogashira coupling. In order to obtain the target compounds, they used an in situ ethynylation methodology[55] based on the addition of a base (lithium hexamethyldisilazide, LHDMS) slowly into a well sonicated mixture of fullerene and suitable terminal alkyne precursors in THF. By using these conditions, LHMDS generates in situ the lithium acetylide species, which then quickly undergoes the fullerene addition reaction to afford the desired ethynylated fullerene derivatives **47** and **50** (Scheme 8).



SCHEME 8
Synthesis of C_{60}–cruciform oligomer–C_{60} triads **47** and **50**

The cyclic voltammograms indicate quite different electrochemical properties in comparison with the previously reported linear OPE bridged C_{60}–oligomer–C_{60} systems. The authors suggest that the electronic interactions between the oligomer bridge and both fullerenes are more significant in these cruciform oligomers. On the other hand, the strong quenching of the oligomer bridge emission was explained in terms of rapid photoinduced intramolecular energy/electron transfer, thus indicating that these structures are promising materials for applications in optoelectronic devices.

An intriguing and less studied approach consists of the synthesis of conjugated oligomer–multifullerene compounds. In 2005, Tour and coworkers reported the synthesis of multiple [60]fullerene–OPE hybrids **51**–**54** using in situ ethynylation methodology showed above (Scheme 9)[56]. The

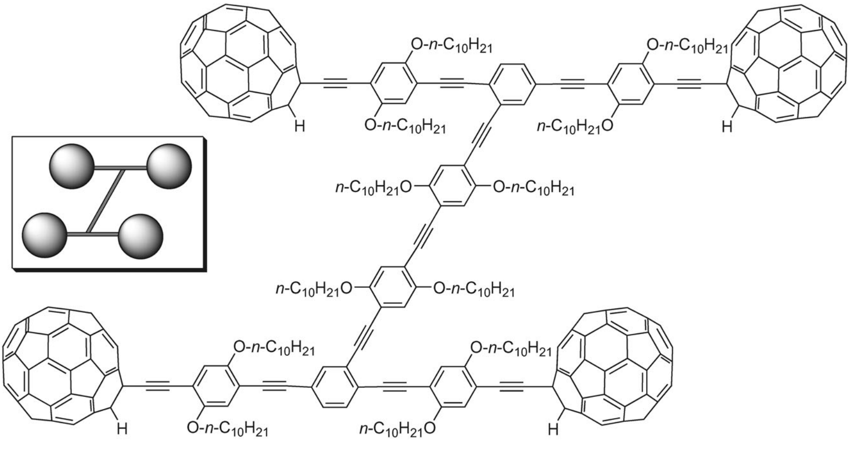


SCHEME 9
Synthesis of C_{60}–oligo(phenyleneethynylene) hybrids **51**–**54**

[60]fullerene–OPE hybrids **51**–**54** display only slight interactions between the electroactive components. The electronic behavior of the [60]fullerene cages is affected by the OPE backbones only through modest inductive effects as can be supported by their UV-Vis spectra and the electrochemical studies.

The third-order nonlinear optical (NLO) and nonlinear absorption properties of the [60]fullerene–OPE hybrid **51d** have also been investigated. It has been observed that by bonding the fullerenes to the conjugated OPE systems the electronic characteristics of both components are altered, thus modifying the overall NLO properties. For the third-order NLO measurements a differential optical Kerr effect (DOKE) detection technique[57] was used.

By following a similar synthetic procedure, Tour and co-workers carried out the synthesis of the conjugated oligomer–C_{60} ensemble **55** bearing four C_{60} moieties (Fig. 4)[58]. This systems was designed with the aim to study controlled molecular motion on surfaces by using surface-capable molecular structures called nanocars[59,60].

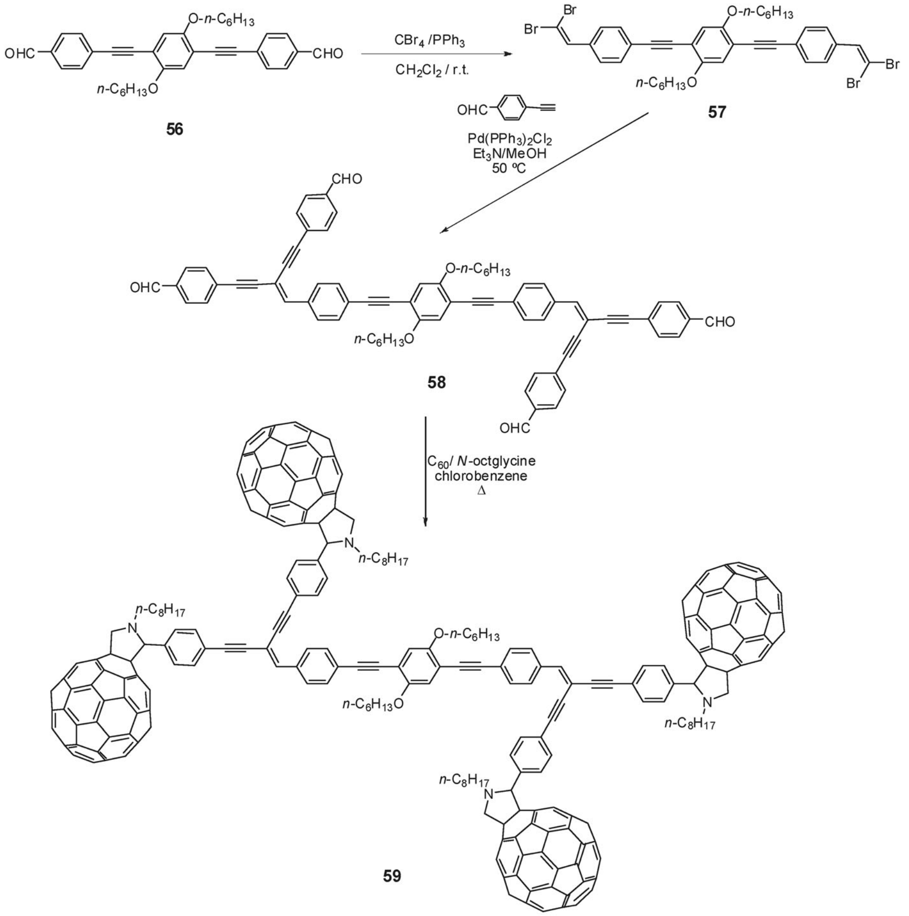


55

FIG. 4
Nanocar based on a conjugated oligomer–C_{60} ensemble

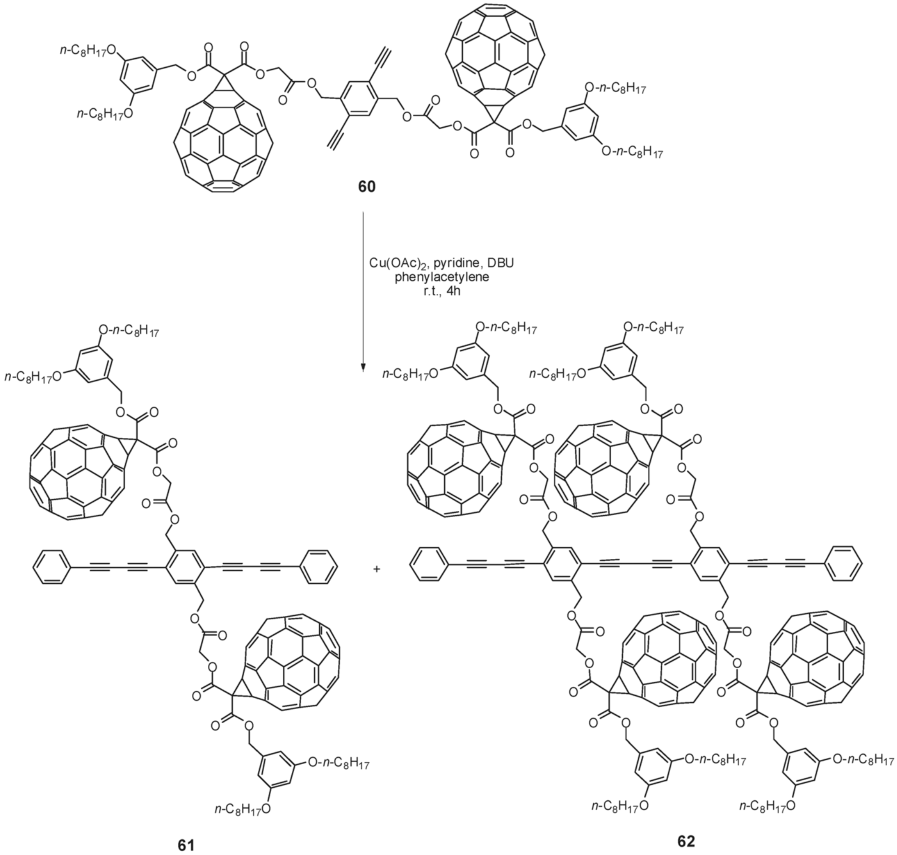
This molecule has been investigated by using scanning tunneling microscopy (STM) on Au(111) on mica. The use of spherical wheels based on [60]fullerene and freely rotating axles based on oligo(phenylene-ethynylenes) permits directed nanoscale rolling of the molecular structure by direct manipulation with the STM tip.

Another tetrafullerene-conjugated oligomer nanoarray **59** (Scheme 10) was synthesized to be used in the fabrication of photovoltaic devices[61]. This new material can be obtained from the diformylated oligo(phenylene-ethynylene) **56** by following the three-step reaction sequence depicted in Scheme 10. Reaction of **56** with tetrabromomethane and triphenylphosphine in dichloromethane afforded trimer **57** with 2,2-dibromovinyl functionalities. Subsequent Sonogashira cross coupling reaction between **57** and 4-ethynylbenzaldehyde yielded the tetraformyl derivative **58** which after the Prato reaction with [60]fullerene and *N*-octylglycine in refluxing chlorobenzene yielded the tetrafullerene–conjugated oligomer nanoarray **59**.



SCHEME 10
Synthesis of the light harvesting conjugated oligomer–multifullerene ensemble **59**

Cyclic voltammetry measurements performed with **59** show eight redox processes and an amphoteric redox behavior corresponding to the presence of the electron donor (π-conjugated oligomer) and C_{60} moieties. The system shows an appreciable absorption over the entire visible region up to ~700 nm and was tested in photovoltaic devices. Pure **59** gave no significant photovoltaic effect given that energy transfer processes between C_{60} and the central π-conjugated oligomer prevent an efficient photoconversion. Nevertheless, external quantum efficiencies of 15% were obtained in photovoltaic devices using blends of **59** and poly(3-hexylthiophene) (P3HT) as active layer.



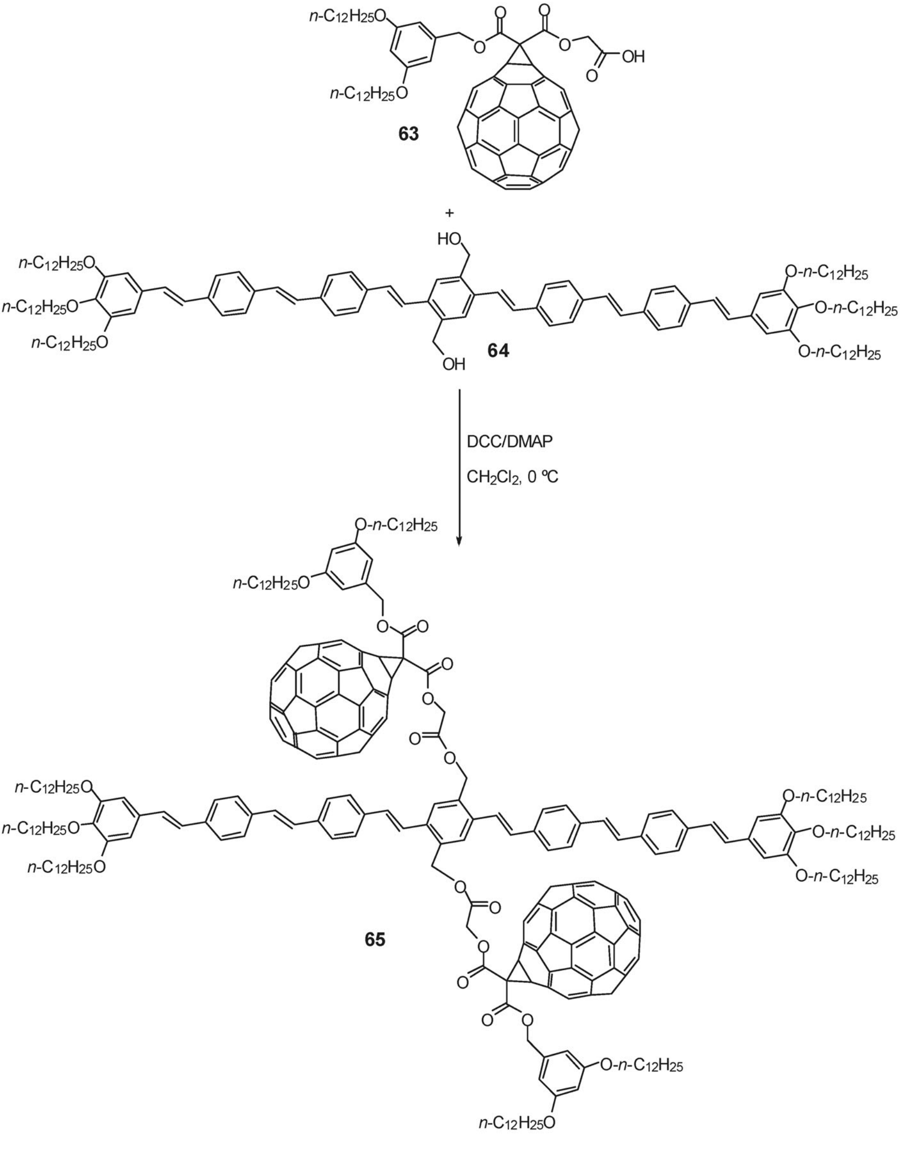
SCHEME 11
Synthesis of multifullerene oligo(phenyleneethynediyl)s **61** and **62**

Nierengarten and co-workers have carried out the synthesis of a diethynylbenzene derivative **60** containing two [60]fullerene moieties which can be used to generate the multifullerene-substituted oligo(phenylene-ethynylene)s **61** and **62** by reaction with phenylacetylene as end-capping reagent (Scheme 11)[62]. Luminescence measurements reveal no emission from the conjugated oligomer moiety suggesting the presence of intramolecular photo-induced processes.

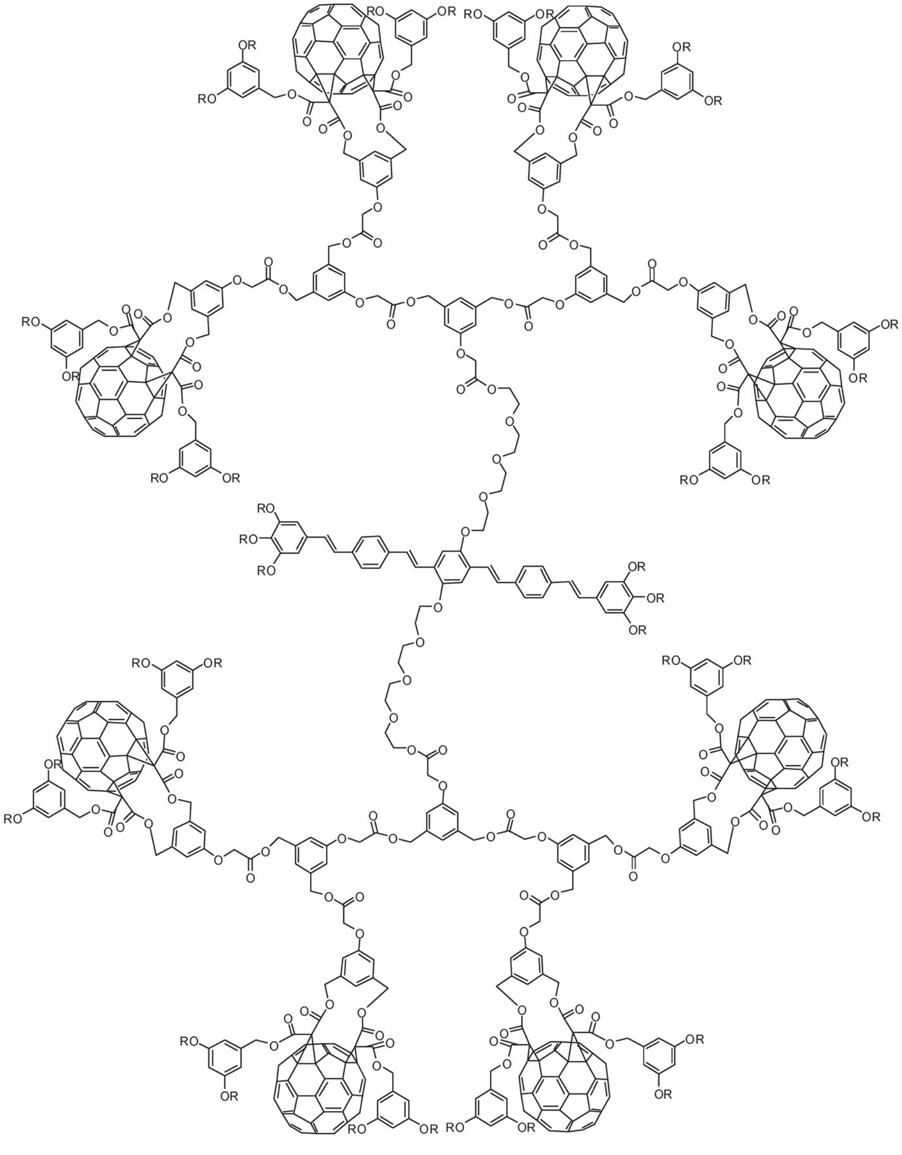
More recently, Nierengarten and coworkers have also reported the synthesis of an oligo(phenylenevinylene) heptamer substituted with two fullerene moieties **65** (Scheme 12)[63]. The target compound **65** was prepared from methanofullerene carboxylic acid derivative **63** and diol **64** under esterification conditions by using dicyclohexyl carbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP). The electrochemical measurements indicated an amphoteric behavior of the material, thus showing the characteristic electrochemical features of its constitutive units, methanofullerene and OPV heptamer. Preliminary luminiscence mesaurements reveal a strong quenching of the conjugated oligomer fluorescence suggesting the presence of intramolecular photo-induced processes.

Nierengarten and co-workers have also developed synthetic strategies towards soluble dendritic branches with fullerene subunits at the periphery and a carboxylate functionality at the focal point. By the variation of the nature of the core, a series of dendrimers based on oligo(phenylene-vinylene)[64], stannoxane[65] or hexaphenylbenzene[66] have been synthesized. The highest generation dendrimer **66** with an oligo(phenylenevinylene) core (Fig. 5) contains eight peripheral fullerene units. The photophysical properties of this series of dendrimers have been investigated in solvents of increasing polarity. It has been observed that ultrafast singlet energy transfer takes place for the whole series of dendrimers, whatever the solvent. On the other hand, electron transfer has also been observed in this series of dendrimers but in this case the electron transfer is thermodynamically allowed only in polar solvents (dichloromethane and benzonitrile) and not in toluene. Furthermore, despite the fact that identical electron transfer partners are present, the extent of the electron transfer is not the same along the series. Thus, with increasing size of the dendrimer, electron transfer is progressively more difficult as a consequence of the isolation of the oligo(phenylenevinylene) core by the dendritic branches.

Gan, Pei, Li and co-workers have synthesized a family of donor–acceptor derivatives with three chromophores (truxene moieties in the core, conjugated oligothiophene in the branch bridges and [60]fullerene as the end-capped groups (Scheme 13)[67].

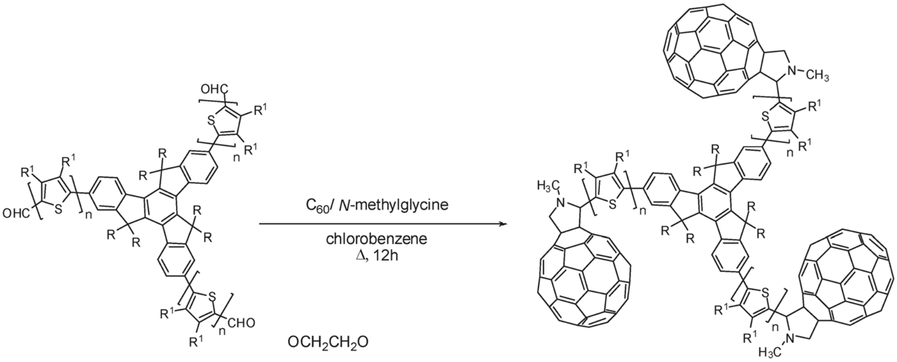


SCHEME 12
Synthesis of multifullerene oligo(phenylenevinylene) **65**



66: R = *n*-$C_{12}H_{25}$

FIG. 5
Dendrimer **66** with an oligo(phenylenevinylene) core and eight peripheral fullerene units



Comps.	R^1	n
67a	H	1
67b	H	2
67c	H	3
67d	H	4
67e	OCH_2CH_2O	1
67f	OCH_2CH_2O	2

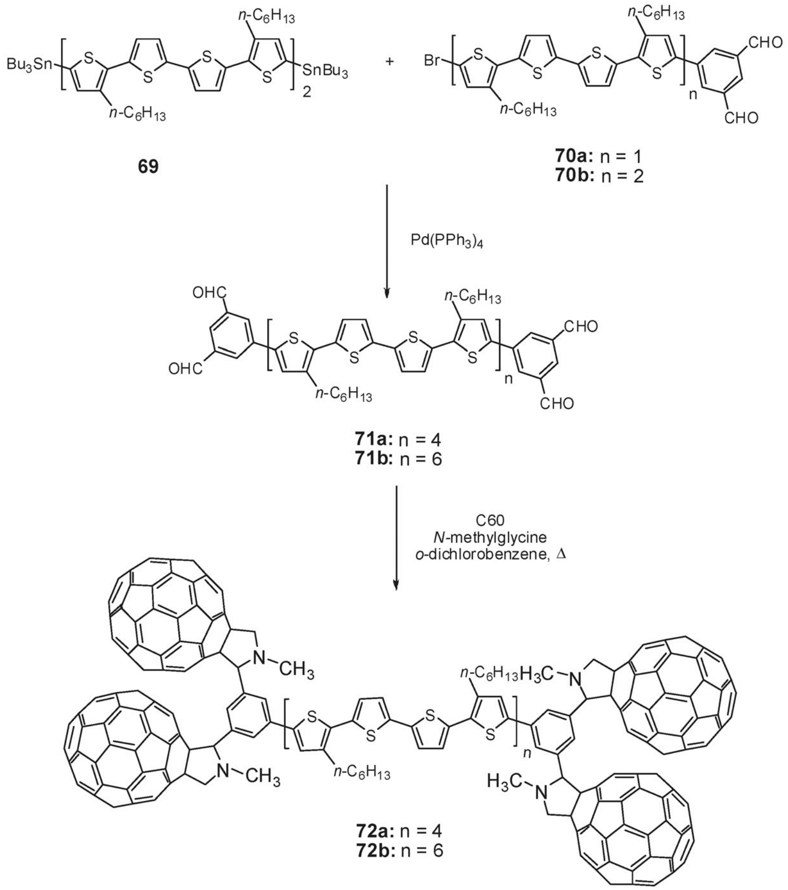
R = *n*-C_6H_{13}

Comps.	R^1	n
68a	H	1
68b	H	2
68c	H	3
68d	H	4
68e	OCH_2CH_2O	1
68f	OCH_2CH_2O	2

SCHEME 13
Synthesis of nanosized rigid multi[60]fullerenes **68a**–**68f**

Oligothiophene-functionalized truxene derivatives **67** were previously synthesized by the Suzuki cross-coupling reactions[68]. The 1,3-dipolar cycloaddition reaction of **67a**–**67f** with C_{60} and *N*-methylglycine allows to obtain a family of star-shaped donor–π-acceptor materials. UV-Vis spectra of **68a**–**68f** show that in the ground state there is no significant intramolecular electronic communication or charge transfer between the fullerenes and the donor moieties. On the other hand, intramolecular and intermolecular singlet energy transfer from a photoexcited π-conjugated oligomer to a covalently bonded C_{60} moiety occurs in the excited states for all C_{60} adducts **68a**–**68f** as indicated by the quenching of the fluorescence of the adducts. A comparison of the emission quenching of **68a**–**68d** indicates that the intramolecular energy transfer distinctly depends on the oligothiophene bridge length.

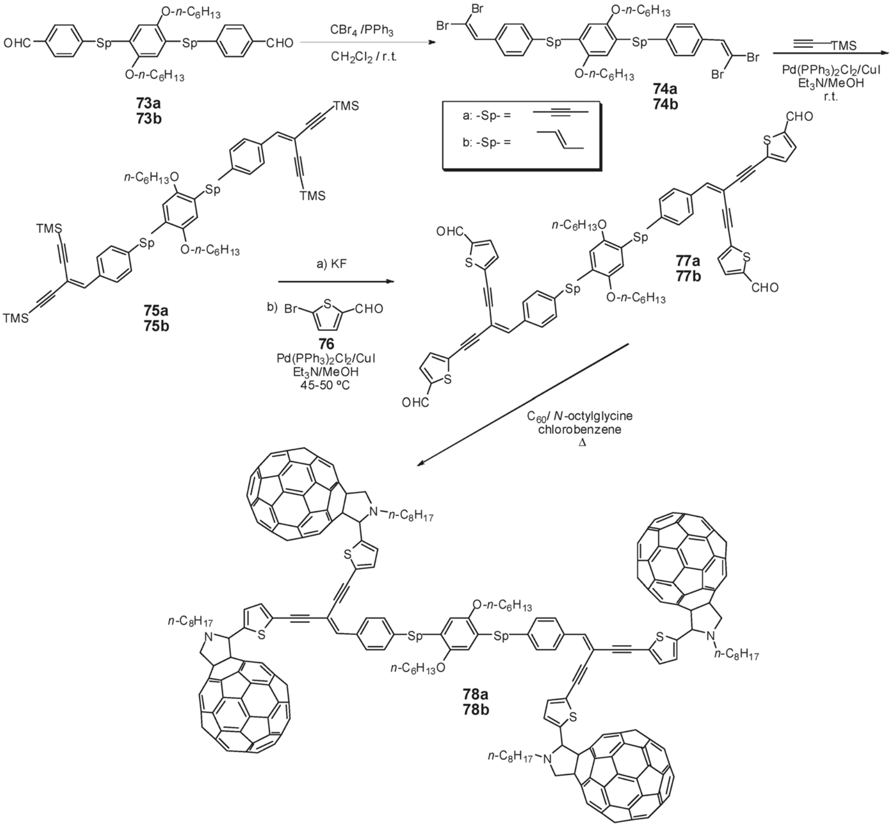
Otsubo, Aso and co-workers have also reported the synthesis of oligothiophene multifullerene ensembles **72a**, **72b** (Scheme 14) as high-performance photovoltaic materials[69]. Tetraaldehydes **71a**, **71b** can be obtained by Stille coupling of tributyltin derivative **69** respectively with (bromoquaterthienyl)benzenedialdehyde **70a** or (bromooctithienyl)benzenedialdehyde **70b** in the presence of catalytic tetrakis(triphenylphosphine)palladium(0) in refluxing toluene. Further treatment of tetraaldehydes **71a**, **71b** with [60]fullerene and *N*-methylglycine in *o*-dichlorobenzene at 140 °C afforded the corresponding pentads **72a**, **72b**. These materials were incorporated in devices with the structure of Al/pentad **72**/Au. Upon illumination from the Al side with 10 μW cm^{-2} monochromatic light the device fabricated with **72b** showed a significant photocurrent. A similar device fabricated with **72a** hardly responded to photostimulation probably due to the aggregation observed on the film caused by its poor solubility. It is worth mentioning that in previous solar cells based on oligothiophene–C_{60} dyads and C_{60}–oligothiophene–C_{60} triads, for oligothiophenes with similar lengths, triads exhibit a better performance in electron transport due to the improved fullerene network. Thus, a better photoresponse for the pentads in compari-



SCHEME 14
Synthesis of oligothiophene–multifullerene ensembles **72a**, **72b**

son with the triads was expected; however, the photocurrent of the device with pentad **72b** is less than that observed for a triad with a oligothiophene with 16 thiophene units. AFM images of the active films of both devices indicate that the effect of the increased fullerene content in pentad on photovoltaic performance is cancelled by poor morphology of the film.

Very recently, the synthesis and study of two novel multifullerene ensembles **78a**, **78b**, in which the C_{60} units are covalently connected through thiophene rings in the periphery of the central core of the OPE or OPV oligomers, have been reported (Scheme 15)[70]. The tetrafullerene derivatives were obtained from the diformylated oligomers **73a**, **73b** following a multistep route. Treatment of oligomers **73a**, **73b** with tetrabromomethane and triphenylphosphine in dichloromethane gave the corresponding



Scheme 15
Synthesis of multifullerene ensembles **78a**, **78b**

vinylbenzene derivatives **74a**, **74b**, which were subsequently reacted with (trimethylsilyl)acetylene under Sonogashira conditions to give compounds **75a**, **75b**. In situ deprotection of their TMS groups with KF followed by Sonogashira cross-coupling with 2-bromo-5-formylthiophene (**76**) gave compounds **77a**, **77b** bearing a tetraaldehyde functionality for the reaction with [60]fullerene under the Prato conditions. Thus, further treatment of tetraaldehydes **77a**, **77b** with [60]fullerene and *N*-octylglycine in chlorobenzene afforded the corresponding tetrafullerene ensembles **78a**, **78b**.

Photophysical measurements of **78a**, **78b** in solution show a very fast deactivation of the singlet excited state of the oligomer core that generates a mixture of charge-separated states, which is more pronounced for the stronger donor **78b**. These systems **78a**, **78b** were tested in organic solar cells showing no significant photovoltaic effect due to the absence of long-lived charge carriers in thin films. Nevertheless, PV devices constructed from blends of oligomer **77b** and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) showed relatively high photocurrent of 2 mA cm^{-2} providing that long-lived charge carriers are generated in these mixtures.

From all these studies it can be concluded that long oligothiophene-multifullerene molecules show a great potential as efficient single-component materials for photovoltaic devices. Nevertheless, for further development of analogues with better performance higher processability is required.

CONCLUSION

Combination of monodisperse π-conjugated oligomeric systems with C_{60} fullerene offers the opportunity to obtain hybrid systems with excited state interactions suitable for fundamental photophysical studies. It has been shown that recombination dynamics measured in solid films are slower than that observed in solutions as a consequence of trapping free carriers in film defects. Therefore, the transient absorption studies of solid molecular films are important in order to develop solar cells based upon this type of molecular donor–acceptor structures.

Synthetic strategies have been developed that allow obtaining sophisticated conjugated oligomer-multifullerene ensembles for various applications such as models to study controlled molecular motion on surfaces or materials for photovoltaic applications.

We are grateful to the program for the funding of research groups UCM-BSCH (Group No. 910759) and to the MCyT of Spain (CTQ2007-60459) for generous support of this work. R. Bazaco is grateful to the Comunidad de Madrid for a doctoral fellowship.

REFERENCES

1. For a comprehensive treatment of the semiconductor device physics of conjugated polymers, see: Greenham N. C., Friend R. H.: *Solid State Phys.* **1995**, *49*, 1.
2. Sheats J. R., Barbara P. F.: *Acc. Chem. Res.* **1999**, *32*, 191.
3. Brabec C. J., Sariciftci N. S., Hummelen J. C.: *Adv. Funct. Mater.* **2001**, *11*, 15.
4. Nelson J.: *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 87.
5. Sariciftci N. S.: *Mater. Today* **2004**, *7*, 36.
6. Sariciftci N. S., Smilowitz L., Heeger A. J., Wudl F.: *Science* **1992**, *258*, 1474.
7. Yu G., Gao J., Hummelen J. C., Wudl F., Heeger A. J.: *Science* **1995**, *270*, 1789.
8. Shaheen S. A., Brabec C. J., Sariciftci N. S., Padinger F., Fromherz T., Hummelen J. C.: *Appl. Phys. Lett.* **2001**, *78*, 841.
9. a) Marcos Ramos A., Rispens M. T., van Duren J. K. J., Hummelen J. C., Janssen R. A. J.: *J. Am. Chem. Soc.* **2001**, *123*, 6714; b) Cravino A., Zerza G., Neugebauer H., Maggini M., Bucella S., Menna E., Svensson M., Andersson M. R., Brabec C. J., Sariciftci N. S.: *J. Phys. Chem. A* **2002**, *106*, 70; c) Zhang F., Svensson M., Andersson M. R., Maggini M., Bucella S., Menna E., Inganäs O.: *Adv. Mater.* **2001**, *13*, 1871.
10. Cravino A., Sariciftci N. S.: *J. Mater. Chem.* **2002**, *12*, 1931.
11. Müllen K., Wegner G. (Eds): *Electronic Materials: The Oligomer Approach*. Wiley-VCH, Weinheim 1998.
12. Müllen K., Wegner G.: *Adv. Mater.* **1998**, *10*, 433.
13. Segura J. L., Martín N.: *J. Mater. Chem.* **2000**, *10*, 2403.
14. Janssen R. A. J., Christiaans M. P. T., Pakbaz K., Moses D., Hummelen J. C., Sariciftci N. S.: *J. Chem. Phys.* **1995**, *102*, 2628.
15. a) Ouali L., Krasnikov V. V., Stalmach U., Hadziioannou G.: *Adv. Mater.* **1999**, *11*, 1515; b) Veenstra S. C., Malliaras G. C., Brouwer H. J., Esselink F. J., Krasnikov V. V., van Hutten P. F., Wildeman J., Jonkman H. T., Sawatzky G. A., Hadziioannou G.: *Synth. Met.* **1997**, *84*, 971; c) Pasimeni L., Maniero A. L., Ruzzi M., Prato M., Da Ros T., Barbarella G., Zambianchi V.: *Chem. Commun.* **1999**, 429; d) Hadziioannou G.: *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2000**, *41*, 797; e) Andreev A. Y., Matt G., Sitter H., Brabec C. J., Badt C., Neugebauer H., Sariciftci N. S.: *Synth. Met.* **2001**, *116*, 235.
16. Segura J. L., Martín N., Guldi D. M.: *Chem. Soc. Rev.* **2005**, *34*, 31.
17. Figueira-Duarte T. M., Gégout A., Nierengarten J.-F.: *Chem. Commun.* **2007**, 109.
18. a) McConnell H. M.: *J. Phys. Chem.* **1961**, *35*, 508; b) Barbara P. F., Meyer T. J., Ratner M. A.: *J. Phys. Chem.* **1996**, *100*, 13148.
19. Schuster G. B.: *Acc. Chem. Res.* **2000**, *33*, 253.
20. Gray H. B., Winkler J. R.: *Annu. Rev. Biochem.* **1996**, *65*, 537.
21. Arrhenius T. S., Blanchard-Desce M., Dvolaitzky M., Lehn J.-M., Malthête J.: *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 5355.
22. a) Molmlin R. E., Danliker P. J., Barton J. K.: *Angew. Chem. Int. Ed.* **1997**, *36*, 2715; b) Meade T. J., Kayyem J. F.: *Angew. Chem. Int. Ed.* **1995**, *34*, 352.

23. a) Jortner J., Ratner M. (Eds): *Molecular Electronics*. Blackwell, Oxford 1997; b) Petty M. C., Bryce M. R., Bloor D. (Eds): *An Introduction to Molecular Electronics*. Oxford University Press, New York 1995.
24. a) Davis W. B., Svec W. A., Ratner M. A., Wasielewski M. R.: *Nature* **1998**, *396*, 60; b) Davis W. B., Ratner M. A., Wasielewski M. R.: *J. Am. Chem. Soc.* **2001**, *123*, 7877.
25. Ramos A. M., Meskers S. C. J., Van Hal P. A., Knol J., Hummelen J. C., Janssen R. A. J.: *J. Phys. Chem. A* **2003**, *107*, 9269.
26. Giacalone F., Segura J. L., Martín N., Guldi D. M.: *J. Am. Chem. Soc.* **2004**, *126*, 5340.
27. Giacalone F., Segura J. L., Martín N., Ramey J., Guldi D. M.: *Chem. Eur. J.* **2005**, *11*, 4819.
28. Martín N., Sánchez L., Herranz M. A., Illescas B., Guldi D. M.: *Acc. Chem. Res.* **2007**, *40*, 1015.
29. De la Torre G., Giacalone F., Segura J. L., Martín N., Guldi D. M.: *Chem. Eur. J.* **2005**, *11*, 1267.
30. Figueira-Duarte T. M., Rio Y., Listrti A., Delavaux-Nicot B., Holler M., Marchioni F., Ceroni P., Armaroli N., Nierengarten J.-F.: *New J. Chem.* **2008**, *32*, 54.
31. Ikemoto J., Takimiya K., Aso Y., Otsubo T., Fujitsuka M., Ito O.: *Org. Lett.* **2002**, *4*, 309.
32. Lindsey J. S., Schreiman I. C., Hsu H. C., Kearney P. C., Marguerettaz A. M.: *J. Org. Chem.* **1987**, *52*, 827.
33. a) Paulson B., Pramod K., Eaton P., Closs G., Miller J. R.: *J. Phys. Chem.* **1993**, *97*, 13042; b) Xu J., Li H.-L., Zhang Y.: *J. Phys. Chem.* **1993**, *97*, 11497; c) Carter M. T., Rowe G. K., Richardson J. N., Tender L. M., Terrill R. H., Murray R. W.: *J. Am. Chem. Soc.* **1995**, *117*, 2896.
34. a) Barigelletti F., Flamigni L., Guardigli M., Juris A., Beley M., Chodorowski-Kimmens S., Collins J.-P., Sauvage J.-P.: *Inorg. Chem.* **1996**, *35*, 136; b) Schlicke B., Belser P., De Cola L., Sabbioni E., Balzani V.: *J. Am. Chem. Soc.* **1999**, *121*, 4207.
35. a) Benniston A. C., Goulle V., Harriman A., Lehn J.-M., Marczinke B.: *J. Phys. Chem.* **1994**, *98*, 7798; b) Osuka A., Tanabe N., Kawabata S., Yamazaki I., Nishimura Y.: *J. Org. Chem.* **1995**, *60*, 7177.
36. a) Grosshenny V., Harriman A., Ziessel R.: *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1100; b) Grosshenny V., Harriman A., Ziessel R.: *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2705.
37. Sun M., Song P., Chen Y., Ma F.: *Chem. Phys. Lett.* **2005**, *416*, 94.
38. Nakamura T., Fujitsuka M., Araki Y., Ito O., Ikemoto J., Takimiya K., Aso Y., Otsubo T.: *J. Phys. Chem.* **2004**, *108*, 10700.
39. Nakamura T., Ikemoto J., Fujitsuka M., Araki Y., Ito O., Takimiya K., Aso Y., Otsubo T.: *J. Phys. Chem.* **2005**, *109*, 14365.
40. Kanato H., Takimiya K., Otsubo T., Aso Y., Nakamura T., Araki Y., Ito O.: *J. Org. Chem.* **2004**, *69*, 7183.
41. Nakamura T., Kanato H., Araki Y., Ito O., Takimiya K., Otsubo T., Aso Y.: *J. Phys. Chem.* **2006**, *110*, 3471.
42. Kanato H., Narutaki M., Takimiya K., Otsubo T., Harima Y.: *Chem. Lett.* **2006**, *35*, 668.
43. Negishi N., Yamada K., Takimiya K., Aso Y., Otsubo T., Harima Y.: *Chem. Lett.* **2003**, *32*, 404.
44. Ie Y., Kawabata T., Kaneda T., Aso Y.: *Chem. Lett.* **2006**, *35*, 1366.
45. Xiao X., Nagahara L. A., Rawlet A. M., Tao N.: *J. Am. Chem. Soc.* **2005**, *127*, 9235.
46. Winters M. U., Dahlstedt E., Blades H. E., Wilson C. J., Frampton M. J., Anderson H. L., Albisson B.: *J. Am. Chem. Soc.* **2007**, *129*, 4291.

47. Handa S., Giacalone F., Haque S. A., Palomares E., Martín N., Durrant J. R.: *Chem. Eur. J.* **2005**, *11*, 7440.
48. a) Beckers E. H. A., Van Hal P. A., Dhanabalan A., Meskers S. C. J., Hummelen J. C., Janssen R. A. J.: *J. Phys. Chem. A* **2003**, *107*, 6218; b) Negishi N., Takimiya T., Otsubo T., Harima Y., Aso Y.: *Chem. Lett.* **2004**, *33*, 654.
49. Guldi D. M., Luo C., Swartz A., Gómez R., Segura J. L., Martín N.: *J. Phys. Chem. A* **2004**, *108*, 455.
50. a) Liu S.-G., Rivera J., Liu H., Raimundo J.-M., Roncali J., Gorgues A., Echegoyen L.: *J. Org. Chem.* **1999**, *64*, 4884; b) Martineau C., Blanchard P., Rondeau D., Delaunay J., Roncali J.: *Adv. Mater.* **2002**, *14*, 283.
51. a) Nierengarten J.-F., Gu T.: *Helv. Chim. Acta* **2004**, *87*, 2948; b) Atienza C., Insuasty B., Seoane C., Martín N., Ramey J., Rahman G. M. A., Guldi D. M.: *J. Mater. Chem.* **2005**, *15*, 124.
52. Van der Pol C., Bryce M. R., Wielopolski M., Atienza-Castellanos C., Guldi D. M., Filippone S., Martín N.: *J. Org. Chem.* **2007**, *72*, 6662.
53. Segura J. L., Martín N.: *Chem. Soc. Rev.* **2000**, *29*, 13.
54. Zhou N., Wang Li, Thompson D. W., Zhao Y.: *Tetrahedron Lett.* **2007**, *48*, 3563.
55. Shirai Y., Zhao Y., Cheng L., Tour J. M.: *Org. Lett.* **2004**, *6*, 2129.
56. Zhao Y., Shirai Y., Slepkov A. D., Cheng L., Alemany L. B., Sasaki T., Hegmann F. A., Tour J. M.: *Chem. Eur. J.* **2005**, *11*, 3643.
57. Slepkov A. D., Hegmann F. A., Zhao Y., Tykwinsky R. R., Kamada K.: *J. Chem. Phys.* **2002**, *116*, 3834.
58. Shirai Y., Osgood A. J., Zhao Y., Kelly K. F., Tour J. M.: *Nano Lett.* **2005**, *5*, 2330.
59. Shirai Y., Morin J.-F., Sasaki T., Guerrero J. M., Tour J. M.: *Chem. Soc. Rev.* **2006**, *35*, 1043.
60. Tour J. M.: *J. Org. Chem.* **2007**, *72*, 7477.
61. Atienza C. M., Fernández G., Sánchez L., Martín N., Dantas I. S., Wienk M. M., Janssen R. A. J., Rahman G. M. A., Guldi D. M.: *Chem. Commun.* **2006**, 514.
62. Delgado de la Cruz J. L., Hahn U., Nierengarten J.-F.: *Tetrahedron Lett.* **2006**, *47*, 3715.
63. Gégout A., Holler M., Figueira-Duarte T. M., Nierengarten J.-F.: *Eur. J. Org. Chem.* **2008**, 3627.
64. Gutiérrez-Nava M., Accorsi G., Masson P., Armaroli N., Nierengarten J.-F.: *Chem. Eur. J.* **2004**, *10*, 5076.
65. Hahn U., Gégout A., Duhayon C., Coppel Y., Saquet A., Nierengarten J.-F.: *Chem. Commun.* **2007**, 516.
66. Hahn U., Maisonhaute E., Amatore C., Nierengarten J.-F.: *Angew. Chem. Int. Ed.* **2007**, *46*, 951.
67. Wang J.-L., Duan X.-F., Jiang B., Gan L.-B., Pei J., He C., Li Y.-F.: *J. Org. Chem.* **2006**, *71*, 4400.
68. Pei J., Wang J.-L., Cao X.-Y., Zhou X.-H., Zhang W.-B.: *J. Am. Chem. Soc.* **2003**, *125*, 9944.
69. Negishi N., Takimiya K., Otsubo T., Harima Y., Aso Y.: *Synth. Met.* **2005**, *152*, 125.
70. Fernández G., Sánchez L., Veldman D., Wienk M. M., Atienza C., Guldi D. M., Janssen R. A. J., Martín N.: *J. Org. Chem.* **2008**, *73*, 3189.