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[60]Fullerene-based electron acceptors

Beatriz M. Illescas, Nazario Martín [*]

Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, 28040 Madrid, Spain

Abstract

Although C_{60} is a good electron acceptor molecule, most of its derivatives show decreased electronegativity in comparison to parent C_{60}. The chemical modification of fullerenes has allowed us to enhance the electron acceptor ability of substituted fullerenes, thus making it feasible to modulate their electronic properties. Some of the most significant examples of the different strategies followed in this sense are highlighted in this review. *To cite this article: B.M. Illescas, N. Martín, C. R. Chimie 9 (2006)*.

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[60]Fullerene is a molecule with a remarkable electron acceptor character which has been skilfully used for the preparation of a wide variety of different electroactive systems [1]. According to theoretical calculations, it exhibits a triply degenerated LUMO (t_{1u}) comparatively low in energy. Therefore, C_{60} behaves like an electronegative molecule which reversibly accepts up to six electrons in solution [2]. The cyclic voltammetry and the electron affinity measured for [60]fullerene clearly confirm that it is a moderate electron acceptor comparable to other organic molecules such as benzo- and naphtho-quinones. [3] This electron-accepting ability of C_{60} to form stable multianions [4] is in sharp contrast to the ability to generate the very unstable cationic species [5].

It is well known that most of the [60]fullerene derivatives present poorer electron acceptor properties than the parent C_{60} as a consequence of the saturation of a double bond of the C_{60} framework that raises the LUMO energy [6]. Therefore, different strategies have been followed for increasing the electron acceptor character in fullerene derivatives, which have been mainly focused on (*i*) the presence of electronegative atoms directly linked to the C_{60} core, (*ii*) electron acceptor groups, (*iii*) periconjugative effect, (*iv*) pyrrolidinium salts, (*v*) the presence of heteroatoms as constituents of the fullerene framework (heterofullerenes) and (*vi*) fluorofullerenes [7]. Some of these aspects have previously been reviewed [1] and, therefore, in this paper we will highlight the most remarkable examples reported during the last years.

A structurally simple type of electron acceptor organofullerenes is [60]fullerene-*p*-benzoquinone systems (**1a–c, 2**) which have been prepared from substituted

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[*] Corresponding author.
E-mail address: nazmar@quim.ucm.es (N. Martín).

o-quinodimethanes by reaction with C_{60} (Fig. 1) [8,9]. These cycloadducts (**1a–c, 2**) show three or four reduction waves at potential values similar to those of C_{60}, which should be attributed to the fullerene moiety [8, 9b, c]. The reduction waves, as expected, are shifted to more negative values in comparison to the parent C_{60}, due to the saturation of a double bond [10]. In addition, another reduction wave appears at potential values very close to the first reduction potential of the C_{60} moiety. The CV values were rationalised on the basis of theoretical calculations [9b] and, according to the molecular orbital distribution, the attachment of the first electron in the reduction process takes place either in the *p*-benzoquinone fragment or in the C_{60} cage. Thus, whereas the introduction of two bromine atoms linked to the C_{60} moiety in **1c** causes the stabilization of the LUMO of this moiety, the presence of a benzene ring fused to the quinone moiety in **1b**, in contrast, produces a destabilization of the LUMO of the organic addend [11] which now lies above those of the C_{60} core. By comparison, the first reduction potential found for **2** [9c] can be considered as the sum of two different effects: the presence of the bromine atoms which shifts the reduction potential towards more positive values (stabilization of the LUMO) and the fused benzene ring which raises the LUMO energy [11].

Therefore, depending upon the nature of the substituents on the *p*-benzoquinone ring, it is possible to address the attachment of the first electron in the reduction process either to the C_{60} core or to the organic addend [9b].

Diekers et al. [12] reported the synthesis and electrochemical study of other Diels–Alder C_{60}–acceptor dyads bearing either an anthraquinone (**3a**) or a dicyano-*p*-quinonediimine DCNQI (**3b**) fragment which contain a rigid linkage between the redox active centres. The electrochemical study of these compounds shows that the reduction processes are highly localised either on the fullerene core or on the addend, depending on the relative electron affinities. Thus, in the case of **3a**,

the first reduction is fullerene based, while for **3b** the attachment of the first electron is addend-based. ESR spectroscopic data allowed unambiguous assignment of the location of each reduction step being consistent with the electrochemical observations, with the exception of that for the penta-anion of **3b**, which shows that spin localization occurs exclusively on the anthraquinone moiety. This observation suggests that a diamagnetic tetra-anion is present on the fullerene group and an unpaired spin is localised on the addend, contrary to the electrochemically predicted electron distribution with a fullerene trianion and a quinone dianion.

Other [60]fullerene-based electron acceptors have also been prepared by following Prato's procedure [13,14].

The interesting redox properties of compounds **4–6** can also be understood in terms of the LUMO's energies as described above for the related systems. Thus, the attachment of the first electron in the reduction process takes place in the organic addend in compounds **4**, **5** and **6b–c**, while for the anthraquinone derivative **6a** the first reduction process is fullerene-based.

Dyads **2** (Fig. 1) and **6b** (Fig. 2) have been studied in the search for a possible electron transfer from the photoexcited fullerene moiety to the covalently linked electron-acceptor [15]. Formation of the fullerene triplet excited state rather than an intramolecular electron-transfer was observed, which can be accounted for by the inability of C_{60} to form stable cationic species [5, 16].

Anthraquinone (AQ) and 11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCAQ) were also used as acceptor moieties for the design of C_{60}-based triads constituted by fullerene and AQ (**7a**) or TCAQ (**7b**) as acceptor units, which are weaker and stronger acceptors, respectively, relative to the parent C_{60}, and ferrocene as donor unit [17]. The electrochemical study of these triads shows the presence of three one-electron reduction steps, all of them taking place at the [60]fullerene moiety, at potential values quite similar to those

1a: R = H
1b: R = -(CH=CH)$_2$-
1c: R = Br

2

3a: X = O
3b: X = N(CN)
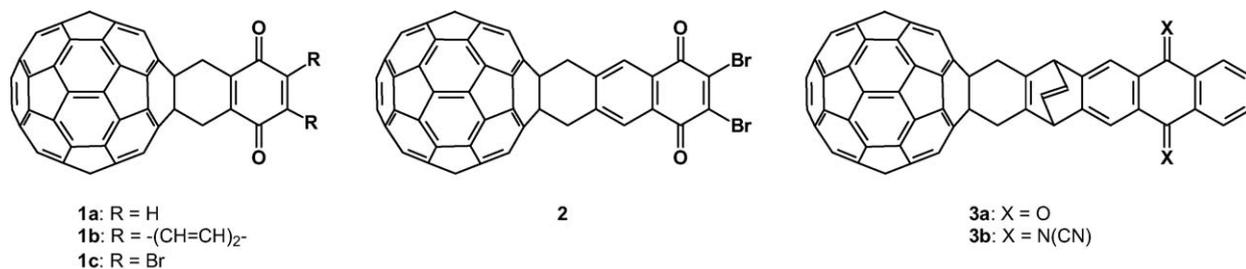
Fig. 1. Examples of [60]fullerene-*p*-benzoquinone (**1a–c, 2, 3a**) and [60]fullerene–DCNQI (**3b**) acceptors.
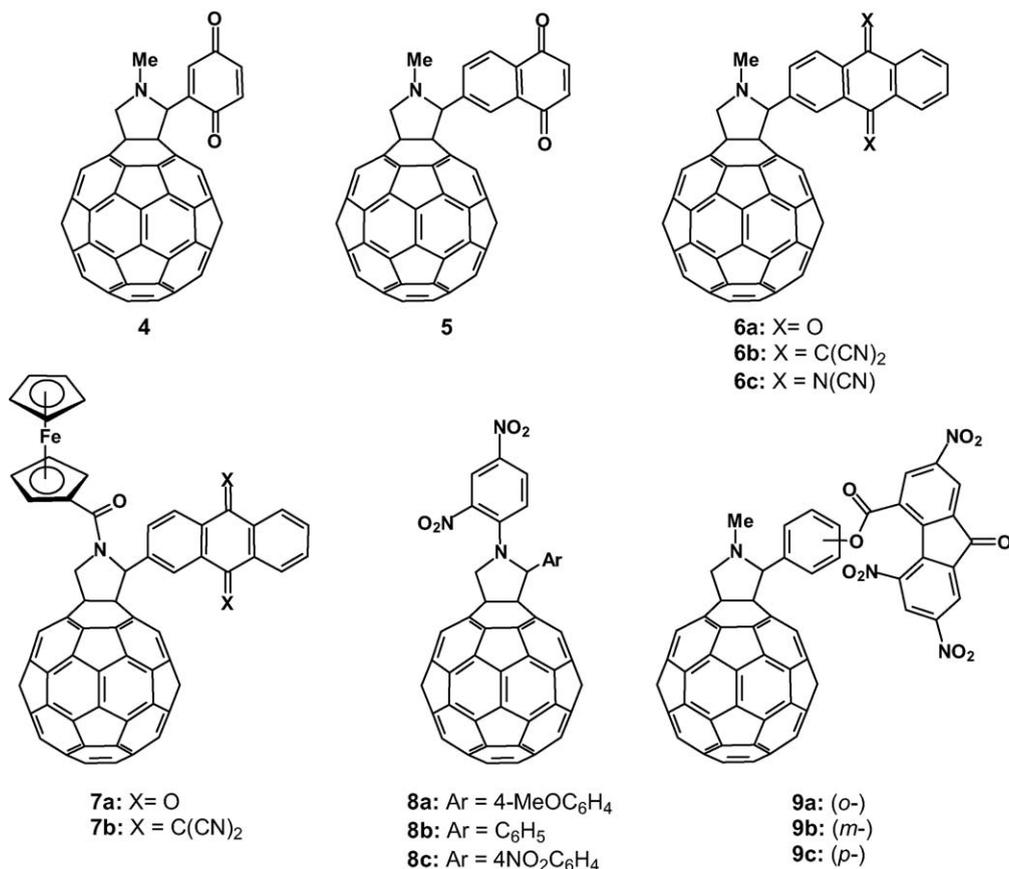
Fig. 2. Different fulleropyrrolidines endowed with strong electron-accepting moieties.

found for the parent C_{60}. A possible reasoning for this observation stems from a combination of, first, the carbonyl group linked to the pyrrolidine nitrogen [18] and, second, the electronic effect of the electron-acceptor unit bound to the pyrrolidine ring.

The photophysical study of these triads (**7a–b**) revealed that only a reaction between Fc as donor and C_{60} as acceptor takes place, despite the fact that the reduction potential of TCAQ in triad **7b** renders to be easier than the fullerene first reduction [17].

In compounds **8a–c**, the presence of the nitro substituents in the *N*-phenyl ring has a striking influence on the reduction potential values [19]. Derivative **8c**, containing a second electron-withdrawing 4-nitrophenyl group, resulted to be a slightly better acceptor than the parent C_{60}. The electrochemical behaviour observed for **8a–c** has been rationalised on the basis of PM3 calculations finding a correlation of the first reduction potential with the LUMO level of these compounds.

The synthesis of novel trinitrofluorenone–C_{60} (TNF–C_{60}) acceptors in which the two subunits are

placed at different distances (**9a–c**) has been recently reported [20]. The electrochemical study of these dyads shows a first reduction potential which is TNF-based and appears 220–260 mV anodically shifted in comparison with reference compound *N*-methylfulleropyrrolidine. The photorefractive properties of these compounds as sensitisers in poly(*N*-vinylcarbazole)-based composite materials have also been studied, finding some advantages with respect to the use of the parent C_{60}.

A simple procedure to improve electron affinity of [60]fullerene derivatives in comparison to the parent C_{60} consists on the incorporation of electronegative atoms or electron-deficient carbon atoms directly connected to the C_{60} core. In this sense, apart from isoxazolofullerenes (see Fig. 3), triazolino and pyrazolino [60]fullerenes (see Fig. 4) have also been reported. Other electron-withdrawing substituents directly connected to the C_{60} cage [21] or through a methano bridge [21c] also present stronger acceptor properties than the parent C_{60}.

10a: n = 0
10b: n = 1

11a: R = H

11b: R =

11c: R =

12a: 4-(N-phenyl)pyrazolyl
12b: 5-(N-phenyl)pyrazolyl

13

14a: X = O
14b: X = C(CN)$_2$
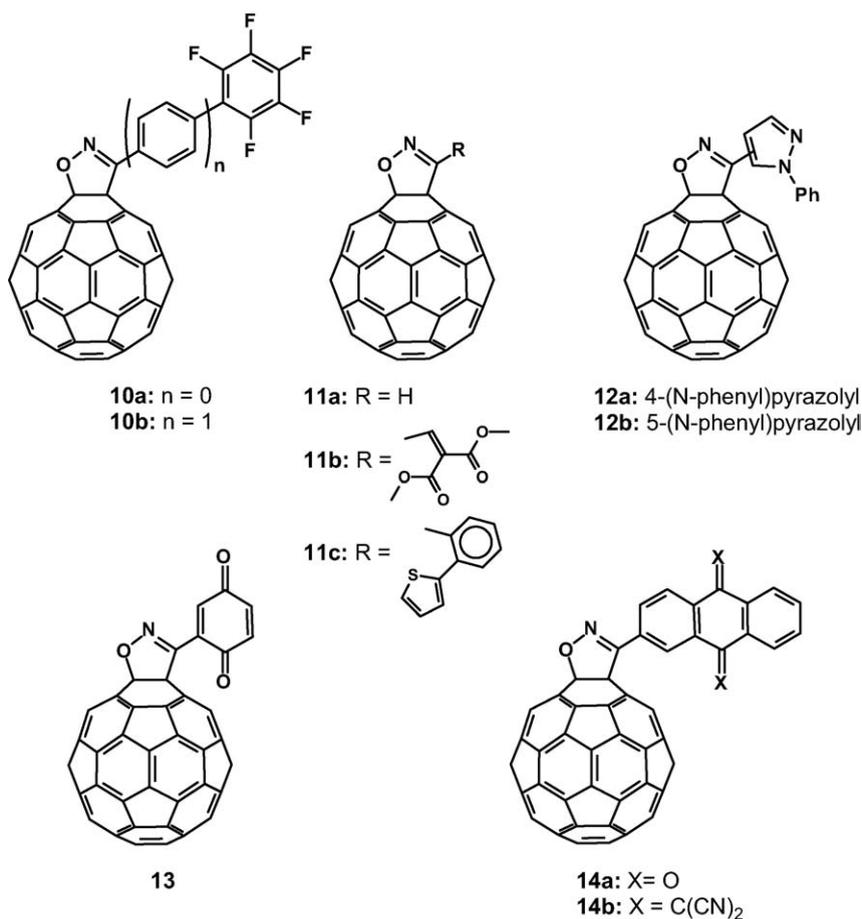
Fig. 3. Examples of isoxazolofullerenes as electron acceptors.

The introduction of an acceptor substituent as the pentafluorophenyl group in compounds **10a–b** also led to an anodic shift of the reduction potentials of these compounds of 40–70 mV relative to the naked C$_{60}$ [22]. To study the substituents' effects on the redox properties of isoxazolofullerenes, Irngartinger et al. [23] prepared a series of these derivatives. Thus, for compound **11a**, with R = H, the electrochemical study showed a shift of 50 mV to more positive values compared to C$_{60}$ for the first reduction potential, due to the strong electron-withdrawing effect of the heterocycle. A remarkable anodic shift of the reduction potential is also observed for diester derivative **11b** (80 mV relative to pristine C$_{60}$). For other substituents studied, the authors concluded that, not only the donor or acceptor characteristics of the substituent, but also the distances or geometries have an influence on the redox properties of the adducts, as shown by CV experiments. Thus, for example, compound **11c** shows a redox potential which is 40 mV cathodically shifted relative to **11a**. This behaviour

can be explained in terms of through-space interactions between the heterocycle and the fullerene surface, which are favoured by the orientation of the addend.

In the same way, donor–acceptor dyads **12a–b** show an anodic shift of 50–70 mV of the reduction potential values in comparison to the parent C$_{60}$ [24].

The enhanced electron accepting properties of isoxazolo[4′,5′:1,2][60]fullerenes related to C$_{60}$ prompted us to synthesise derivatives **13–14** bearing strong electron acceptor addends [14] (Fig. 3).

In contrast to the above mentioned pyrrolidino [3′,4′:1,2][60]fullerenes endowed with acceptor moieties (Fig. 2), these isoxazolofullerenes exhibit reduction potentials which are anodically shifted (70–110 mV) in comparison with the parent C$_{60}$, which indicates that they are stronger electron acceptors than [60]fullerene. This finding can be accounted for by the presence of the oxygen atom directly linked to the C$_{60}$ cage as well as by the electronic effect of the organic addend covalently attached to the isoxazole ring.
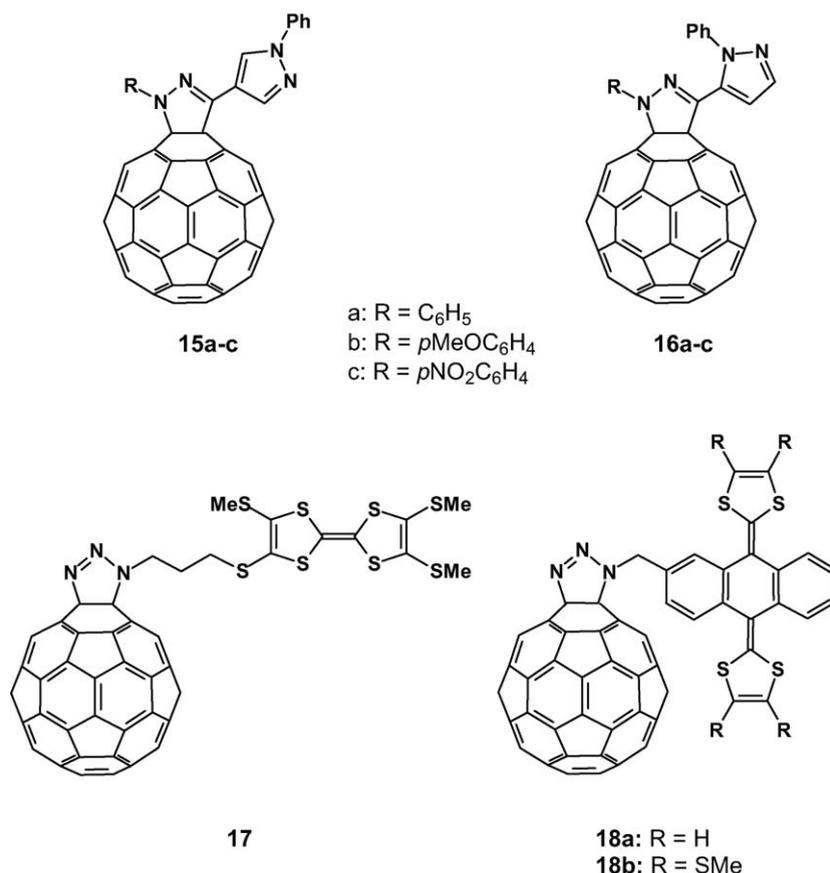
Fig. 4. Examples of pyrazolino[60]fullerenes (**15**, **16**) and triazolino[60]fullerenes bearing TTF (**17**) and exTTF (**18a,b**) units.

Similar effects on the reduction potentials can be observed in pyrazolino[60]fullerenes (**15–16**), which are easily prepared in one pot by 1,3-dipolar cycloaddition reaction from suitably functionalised hydrazones (Fig. 4) [25].

These pyrazolino derivatives present a remarkable advantage over the isoxazolino[60]fullerenes mentioned above to obtain electroactive compounds due to the possibility of preparing donor–donor–C_{60} or donor–acceptor–C_{60} triads by modification of the nature of the substituents linked to the sp^3 nitrogen atom. All compounds **15a–c** and **16a–c** possess better electron affinity than the corresponding pyrrolidino[60]fullerene (by up to 170 mV), and all except **16b** present an anodically shifted first reduction potential (up to 80 mV) in comparison with the parent C_{60}. The inductive effect of the substituents must be one of the most important factors in determining the observed redox behaviour [25b].

Fullerotriazolines (**17–18**) [26,27] can also be utilised to form fullerene derivatives with enhanced elec-

tron accepting properties. These compounds are thermally labile intermediates in the reaction of C_{60} with azides [28]. As intermediates, they are of interest as precursors by thermal nitrogen extrusion of azafulleroids (opened 5,6-adducts) and fulleroaziridines (closed 6,6-adducts) [29].

The voltammogram of compound **17** shows, apart from the two reversible one-electron oxidation waves yielding the radical cation and dication of the TTF moiety [E^1_{ox} = 0.57 V and E^2_{ox} = 0.70 V (vs. SCE)], four quasireversible one-electron steps on the reduction side. These reduction waves correspond to the fullerene reductions [–0.57, –0.97, –1.52 and –2.00 V (vs. SCE)] and are remarkably shifted to more positive values (~100 mV) relative to other 1,2-dihydrofullerenes such as pyrrolidino[3′,4′:1,2][60]fullerenes as well as to the parent C_{60} (–0.60 mV vs. SCE). This shift can be explained by the electronegative character of the two nitrogen atoms covalently linked to the C_{60} core. Interestingly, the photophysical study of this compound shows than fullerotriazoline-TTF dyad gives rise to a reduced

HOMO–LUMO energy gap (–5.12 eV) relative to previously reported fulleropyrrolidine–TTF dyads (–5.35 eV) [18,30]. This has a large effect on the electron transfer rates, which are similar to those observed in systems where the spatial separations between the donor and acceptor are markedly decreased [31]. Thus, increasing the electron accepting behaviour of the C_{60} moiety in C_{60}-based dyads such as fullerotriazolines **17** and **18a–b** can be used as a useful tool to improve (*i*) the dynamics of the forward electron transfer and (*ii*) the lifetime of the charge separated (CS) state. However, it should be stated that these advantages are only observed if the forward electron transfer is located in the normal Marcus region and the back electron transfer in the inverted Marcus region [32].

For dyads **18a–b** the reduction potentials are also anodically shifted by 10–30 mV in comparison to pristine C_{60} [27]. Steady-state fluorescence experiments and transient absorption spectroscopy results in the formation of a radical pair, showing the characteristic fingerprint of $C_{60}^{\bullet-}$ and exTTF$^{\bullet+}$, with lifetimes in the

range of hundred of nanoseconds, nearly two orders of magnitude larger than those found for **17**.

A different approach for the preparation of electron acceptor organofullerenes is based on the periconjugative effect [33]. Thus, some quinone-type methanofullerenes were prepared (**19–21**) [34,35] (Fig. 5).

In principle, the intramolecular electronic interaction (periconjugation) between the p_z–π orbitals of the olefinic carbons of the quinone moiety and the adjacent carbon atoms of C_{60}, separated by a spiro carbon atom, results in more extended conjugated molecules showing good acceptor properties. In agreement with these predictions, the CV data of compounds **19–20** showed a less negative first reduction potential than the parent C_{60}, thus being stronger acceptor molecules than C_{60}. In contrast, compounds **21** showed a more negative first reduction potential than naked C_{60}, which has been accounted for by the steric hindrance between the "peri" hydrogens of the organic addend and the surface of the ball leading to a significant deviation from the orthogonality and hence to the loss of periconjugation.

19a: R = H
19b: R = Me
19c: R = But
19d: R = Ph

20

21a: X = O
21b: X = C(CN)$_2$
21c: X = N(CN)

22

23
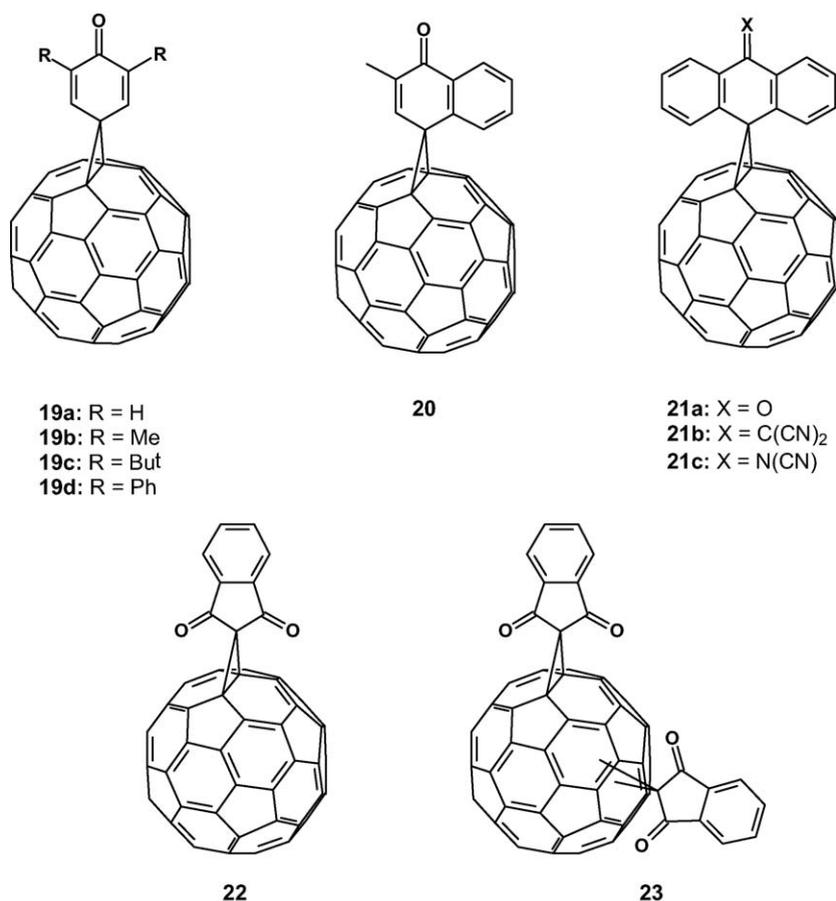
Fig. 5. Spiro methanofullerene derivatives showing periconjugative effect.
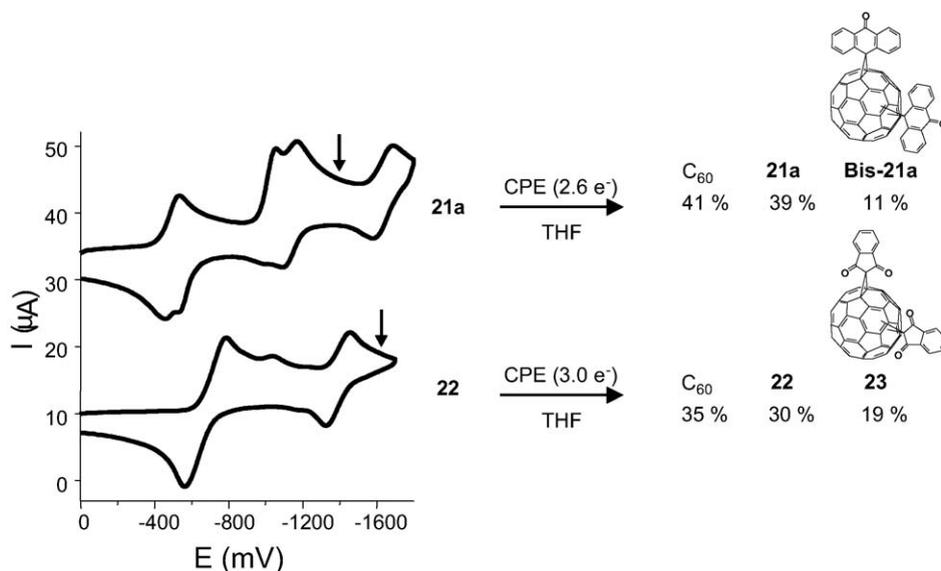
Fig. 6. Cyclic voltammetry of compounds **21a** and **22** in THF and CPE results.

Theoretical calculations on compounds **19a–c** indicate that the attachment of the first electron causes the homolytic cleavage of one of the bonds connecting the addend to C_{60}. This ring opening has been supported by EPR measurements and explain the irreversible electrochemical behaviour of these compounds [34b].

This bond cleavage leading to an irreversible electrochemical behaviour related these compounds with the retro-Bingel reaction, an electrochemical reduction reaction which efficiently removes the cyclopropane ring adduct from the fullerene surface resulting in the formation of the parent C_{60} [36]. Thus, we decided to study some of these derivatives (**19a, d, 20, 21a, 22, 23**) under controlled potential electrolysis (CPE) for potential adduct removal. It is remarkable that all these compounds except **21a** show stronger electron-accepting properties that the parent C_{60} [37].

Reductive electrolysis of these methanofullerenes led to different results. Thus, CPE of **20, 21a, 22**, and **23** in dichloromethane results in removal of the addend to form C_{60}. An alternative reaction pathway was observed for **19a, d** and **20** which leads to the formation of methanofullerene–CH_2Cl products of unspecified structure. Reductive electrolysis in THF shows clean adduct removal for **20** and **21a, 22–23**. Another reaction pathway was observed for **21a** and **22** in THF, an intramolecular addend crossover reaction leading to bis-adducts (Fig. 6). The regioisomer distribution of these bis-adducts obtained by electrolysis was determined for compound **22** and resulted to be clearly different from

that obtained by the regular synthetic route. The electrochemical formation of the *cis*-3 bis-adduct as one of the predominant regioisomers is particularly remarkable [38].

In order to investigate more deeply these new electrochemically-induced reactions we prepared compounds **24–26** containing a nitrophenyl group which exhibits a strong and easily recognizable ESR signal when reduced [39] (Fig. 7).

The electrochemistry of these products showed a similar behaviour for **24** and **25**, exhibiting three fullerene reductions and one reversible nitrobenzene reduction. Compound **26** shows more chemical irreversibility due, probably, to the major extent in which the retro-Bingel reaction occurs (Fig. 8). Typically, each compound was subjected to CPE at a potential ca. 100–150 mV more cathodic than every reduction wave and then analysed by ESR spectroscopy. Reoxidation at 0 V was usually performed after bulk electrolysis at the third of fourth reduction potential followed by analysis of the products.

CPE of methanofullerene **24** presented, after reoxidation and purification, analysis of the reaction mixture by HPLC and MALDI-TOF, the formation of a small amount of C_{60} (5%) and recovery of 40% of starting material. CPE for compounds **25** and **26** resulted in the recovery of C_{60} (23% for **25** and 52% for **26**), formation of bisadducts (18% for **25** and 11% for **26**) and the starting material (40% for **25**) or an uncharacterised material (37% for **26**).

24 25 26
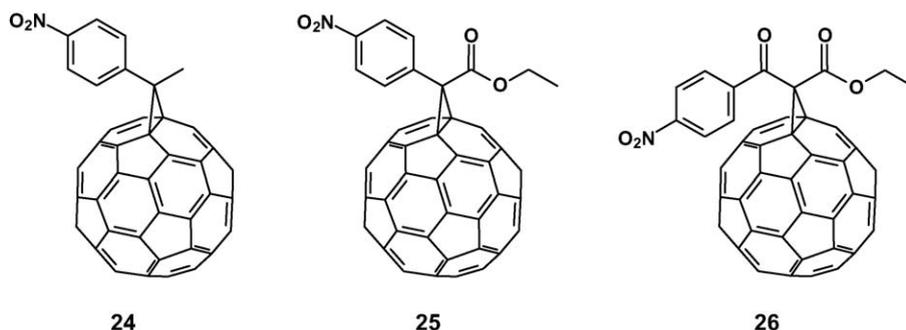
Fig. 7. Methanofullerenes endowed with an ESR active nitrophenyl group.
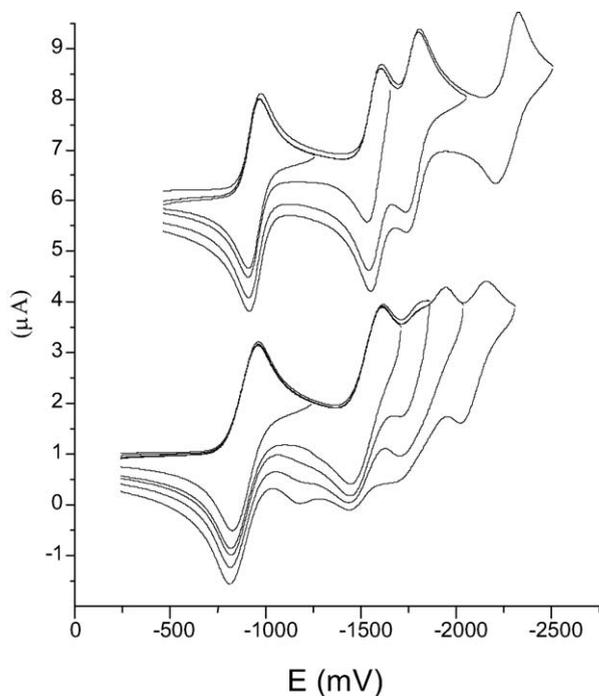
Fig. 8. Cyclic voltammetry of compounds **25** and **26** in TFH vs. Fc.

ESR spectroscopy allowed unambiguous assignment of the sites of reduction and monitoring of the reactive intermediates resulting from subsequent reductions. ESR spectra for the reduction of **26** in THF is shown if Fig. 9. The ESR signals during the different stages of the electrolysis showed how spin localization changed from fullerene to nitrobenzene-based and allowed the measurement of electronic effects induced by electron withdrawing substituents. The simulated spectrum (Fig. 9, e) clearly shows that the radical generated contains a single spin 1/2 nucleus, most probably a proton, which exhibits a hyperfine coupling constant of 0.40 G. A possible structure for this radical is shown in Fig. 9. Exactly how this transformation takes place is not presently known in detail, but it fits well with the ESR

observations and with the known formation of C_{60} via the retro-Bingel reaction as a final product after reoxidation.

Fulleropyrrolidinium salt derivatives of C_{60} have also shown to have enhanced electron-accepting properties with respect to both the parent pyrrolidine derivatives and C_{60}. Remarkably, CV measurements of compounds **27a–c** (Fig. 10) performed at low temperatures and fast scan rates, using ultramicroelectrodes, have allowed the observation for the first time in fullerene derivatives, of six C_{60}-centred reductions [40]. Since the chemistry of fulleropyrrolidines is very rich [18], formation of pyrrolidinium ions, especially in donor–bridge–acceptor dyads, is a valuable methodology to modulate the electronic properties of the C_{60} moiety.

In order to promote water solubility and to preclude fullerene clustering in aqueous media, bis(pyrrolidinium) salts (**28a–d**) [41] were also investigated. Considering the reduction potential of C_{60} (–0.35 vs. SCE) and that of the monopyrrolidinium salt (–0.29 vs. SCE), reduction potentials of bis(pyrrolidinium) salts **28** are between –0.32 and –0.34 V vs. SCE. This enhanced electronegativity can be reasonably interpreted in terms of inductive effects which leads to a decrease of the electron density within the fullerene π-system.

For the development of novel donor–acceptor arrays that display improved performance, the use of a fulleropyrrolidinium acceptor clearly has a distinct advantage over fulleropyrrolidine (**29–31**) [42]. Interestingly, the fulleropyrrolidinium-based dyads reveal faster charge separation dynamics, relative to the fulleropyrrolidine analogues, a trend that parallels their better acceptor properties. Regarding charge recombination, formation of the zwitterionic fullerene π-radical anion appears to be a key factor for stabilizing the charge-separated state.

The CV study of a series of novel bisfulleropyrrolidines (**32**) and bisfulleropyrrolidinium ions (**33**) has also been reported [43]. The eight possible stereo-
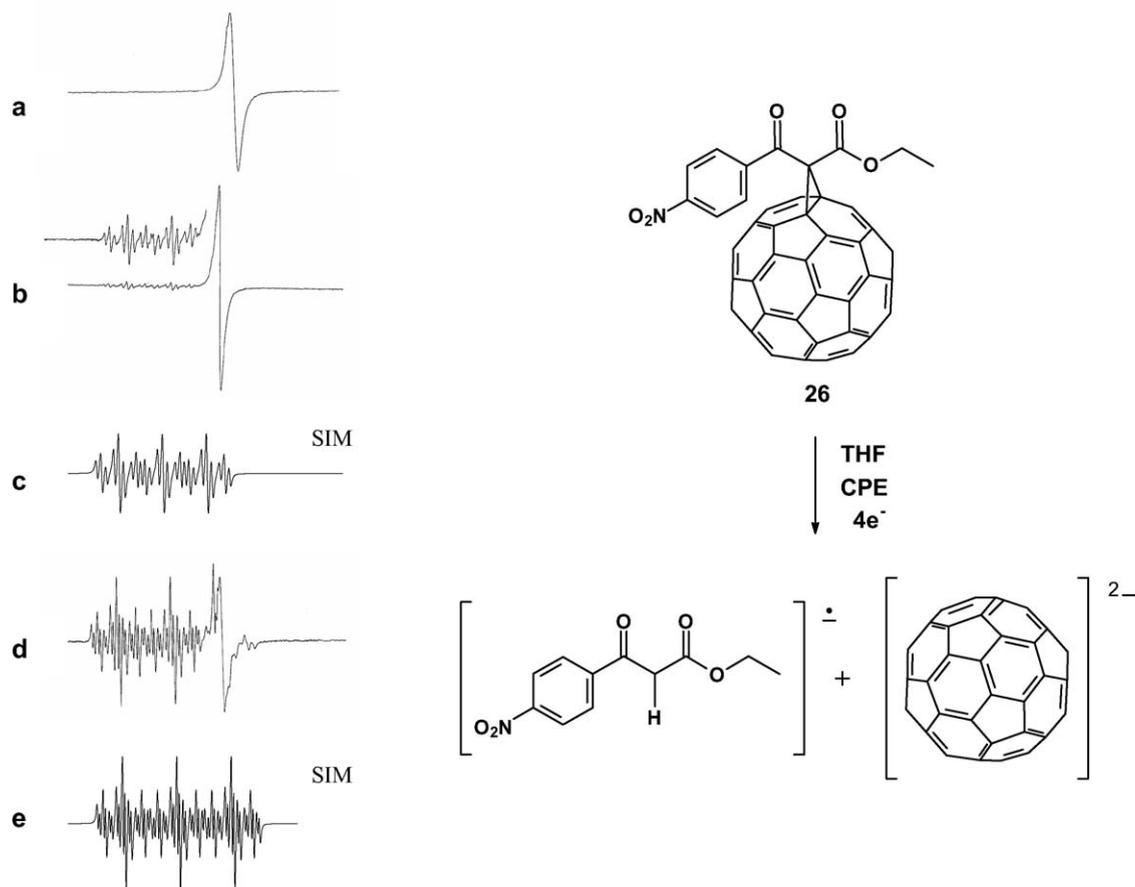
Fig. 9. Experimental and simulated ESR spectra of 26 in THF solution.

isomers of each series were systematically investigated. The stabilizing effect of positive charges produced a significant enhancement of the electronegative properties in **33**. The study evidenced that in both **32** and **33**, the CV pattern and, in particular, the potential separation between the second and third reductions, changes significantly with the addition pattern. A sequential π-electron model that simulates the effect of subsequent reductions of C_{60} bis-adducts gives a good correlation ($r > 0.96$) with the cyclic voltammetry data when the molecules are divided in two sets dependent on the location of the addends in the same or in opposite hemispheres.

Bourgeois et al. ([44]) have reported positive shifts in the fullerene reduction potential ($\Delta E = 90$ mV) of a C_{60}–dibenzo–18–crown–6 conjugate (**34**) (Fig. 11) upon complexation of a potassium cation due to the electrostatic effect of K^+ bound in close proximity to the carbon sphere. Similar effects have also been observed by D'Souza in compound **35** by complexation with differ-

ent cations [45]. It is important to note, however, that in these systems (**34**, **35**) the first reduction potential value of the fullerene unit is cathodically shifted in comparison with pristine C_{60} due to the saturation of two double bonds of the fullerene cage which raises the LUMO energy in these compounds. Similarly, the positive shift in potential observed for the reduction of **37** relative to the uncomplexed compound **36** is attributed to an electrostatic effect able to counterbalance the electronic interactions between the bis(2,9-diphenyl-1,10-phenanthroline)Cu(I) core and the C_{60} units that tend to negatively shift the reduction potentials [46].

An attractive alternative to isocyclic fullerenes, as components of multiredox and light-responsive systems, are heterofullerene building blocks (i.e. $C_{59}N$) [47]. In azaheterofullerene derivatives, substitution of a carbon atom with nitrogen alters the redox potential and the excited state energies of the fullerene ([48]. Significantly, $C_{59}N$ derivatives render better electron acceptors than C_{60} and C_{60} derivatives that bear similar

27a: R$_1$ = (CH$_2$O)$_3$CH$_3$; R$_2$ = H
27b: R$_1$ = CH$_3$; R$_2$ = CH$_2$O(CH$_2$CH$_2$O)$_2$CH$_3$
27c: R$_1$ = (CH$_2$CH$_2$O)$_3$CH$_3$; R$_2$ = CH$_2$O(CH$_2$CH$_2$O)$_2$CH$_3$

28a: equatorial
28b: trans-4
28c: trans-3
28d: trans-2
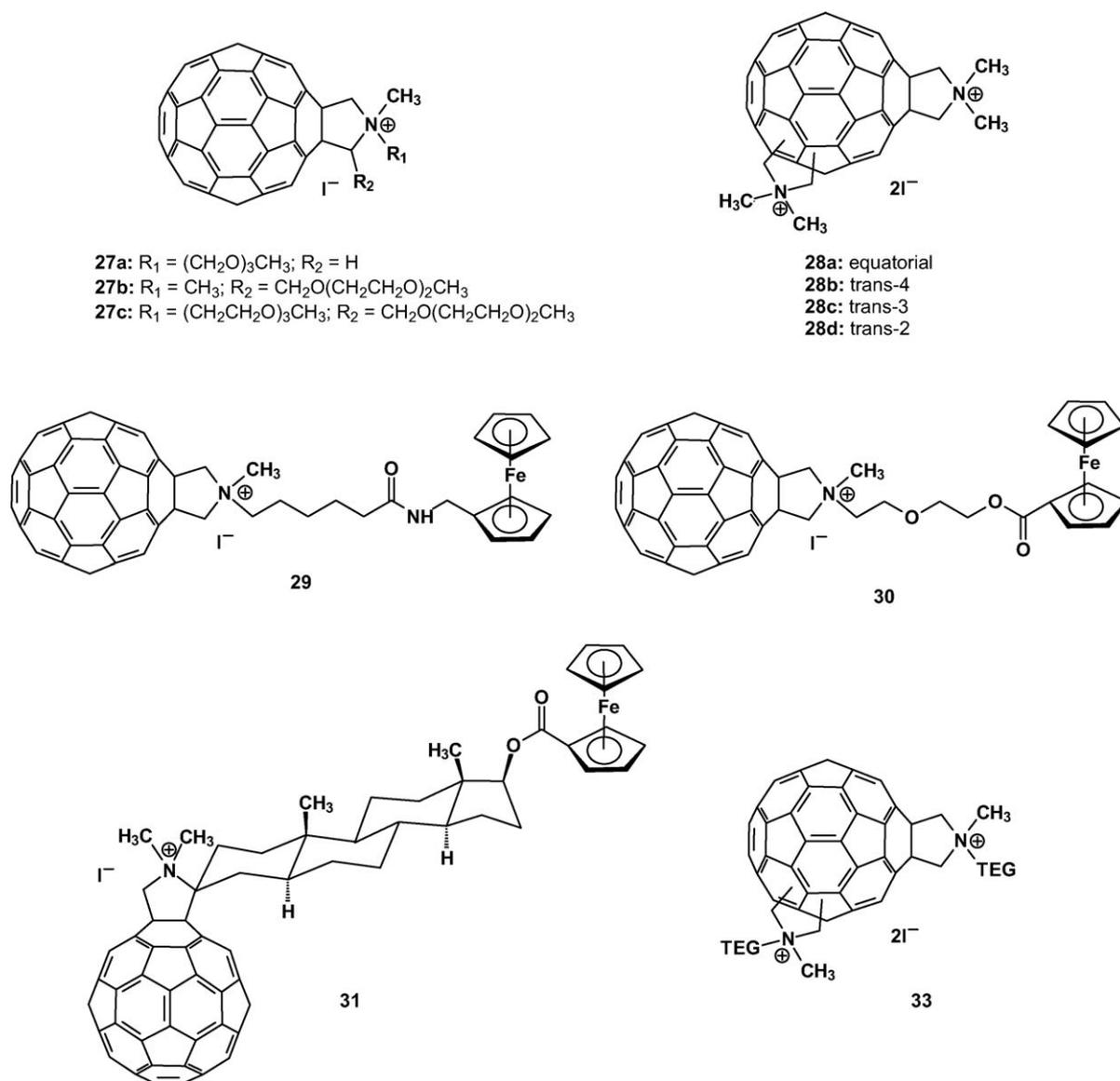
Fig. 10. Fulleropyrrolidinium salts with enhanced electron-accepting properties.

addends. The simplest azaheterofullerene can only be isolated as its corresponding dimer (**38**) (Fig. 12). The C–H bonded monomer, HC$_{59}$N, has also been characterised [48]. The monomeric C$_{59}$N$^+$ cation, which is isoelectronic with C$_{60}$, can be isolated as a carborane anion salt [C$_{59}$N$^+$] [Ag(CB$_{11}$H$_6$Cl$_6$)$^-_2$] [49]. The synthesis involves a rare example of oxidation of an sp^3–sp^3 C–C bond to produce a carbenium ion.

Recently, Hauke et al. [50] have reported a novel series of fluorophore-heterofullerene conjugated (**39**) in which the flexibility of the acetyl-group linker opens the way for conformations with π–π stacking interactions between the chromophores. Photophysical stea-

dy-state and time-resolved measurements clearly show the photosensitization effect of the fluorophores that act as an antenna system and transmit their excited-state energy to the covalently attached C$_{59}$N moiety. This approach offers a viable alternative for developing well-defined architectures, bearing a C$_{59}$N core, which give rise to sequential energy and electron transfer processes [50].

Summary and perspectives

Although fullerene C$_{60}$ is known to exhibit a good electron acceptor ability, the chemical modification of
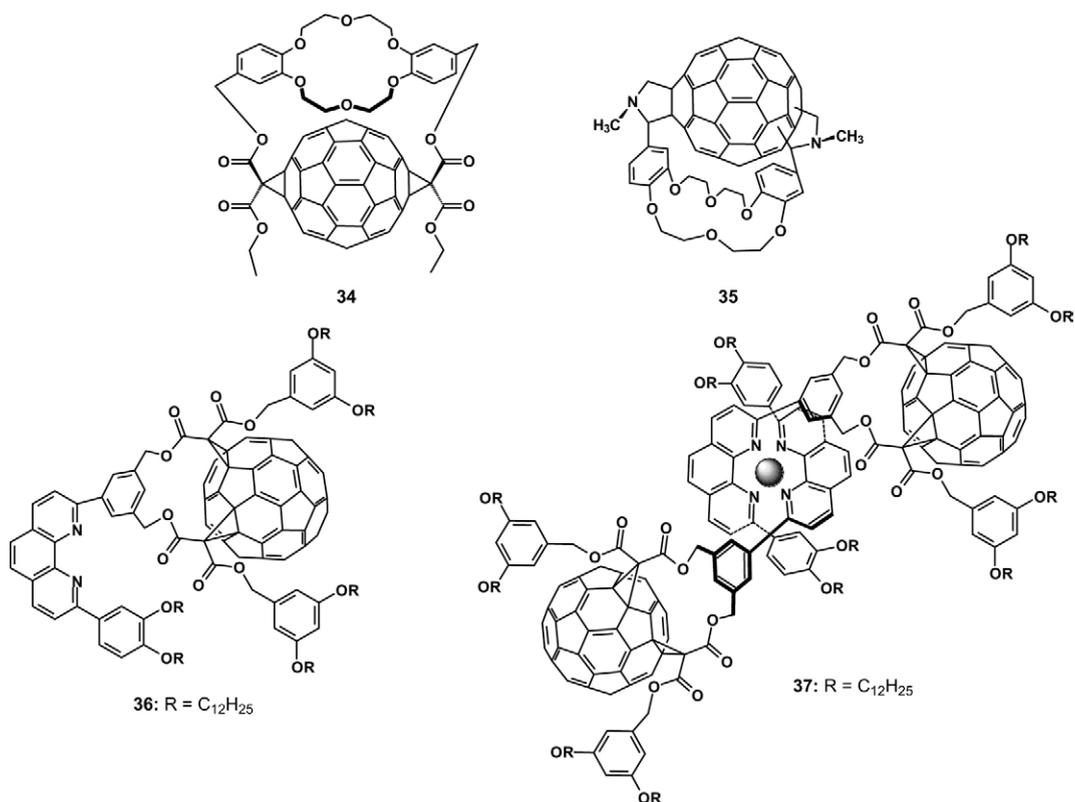
Fig. 11. Representative examples of fullerene complexes with better reduction potentials than pristine [60]fullerene.
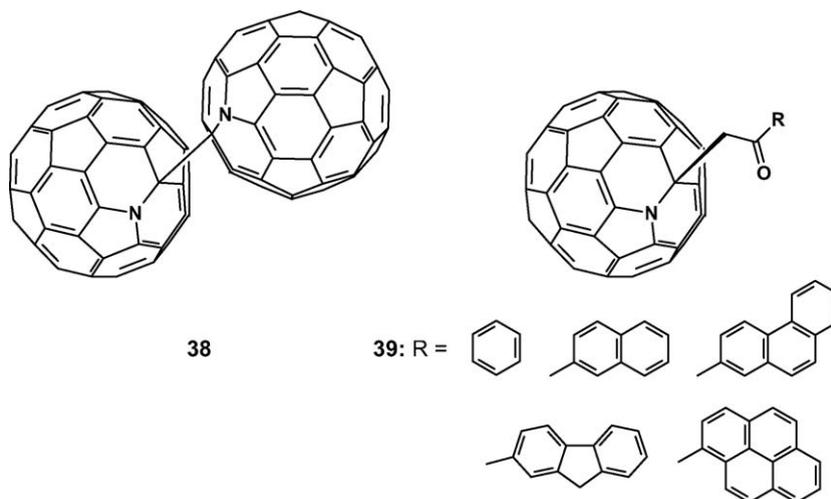
Fig. 12. Dimer (**38**) and monomers (**39**) azaheterofullerenes show good electron-acceptor properties.

fullerenes has been skilfully used to enhance the electronegative character of substituted fullerenes. Different strategies have been developed mainly involving the presence of exohedral or constituent electronegative or electron withdrawing groups either as neutral or charged species and some of the most significant examples have been highlighted in this review. The remarkable negative inductive effect of these substituents on the fullerene network compensates the saturation of a double bond of the fullerene structure in the functiona-

lization process resulting in stronger electron acceptors than the parent C_{60}. Other different and more subtle strategy is based on the periconjugative effect. However, more work is needed in order to clarify the extent of this through space electronic interaction.

Improved C_{60}-based electron acceptors have been covalently connected to different electron donor units and faster photoinduced charge separation processes have been observed. These remarkable photophysical features are of interest for the design of novel fullerene derivatives with improved properties for the preparation of photovoltaic devices.

In summary, highly efficient electron acceptor fullerenes are able to act as real electron-accepting sponges forming multianion species with theoretical and synthetic interest, which have only been scarcely studied. Furthermore, the synthesis of modified fullerenes showing stronger electron accepting character than pristine C_{60} is still a challenge for the design of new molecules of interest in fields such as artificial photosynthetic systems and photovoltaic devices where electron transfer from a donor unit to the fullerene core plays a key role.

Acknowledgements

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