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Pyrazolino [60]fullerenes: synthesis and properties

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Abstract

We describe our contribution to the functionalization of fullerenes by 1,3-dipolar cycloaddition reactions in the preparation of pyrazolino [60]fullerenes. Several advantages that are inherent in the use of nitrile imines, with respect to other procedures for the derivatization of C_{60} , will be discussed. Electrochemical and photochemical properties of this new family of fullerene derivatives suggest that they are good candidates for incorporation into new donor–acceptor assemblies. **To cite this article:** F. Langa, F. Oswald, *C. R. Chimie* 9 (2006).

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1. Introduction

The dramatic increase in research into fullerenes, particularly C_{60} , since the first multigram preparation in 1990 [1] continues today [2]. Several years have been spent developing new procedures for the functionalization of these materials and intense effort is currently focussed on the design and synthesis of new fullerene derivatives with specific properties, particularly in the fields of medicinal chemistry [3,4] and materials science [5–7].

Among the many reactions available for the preparation of fullerene derivatives, cycloaddition reactions—principally 1,3-dipolar cycloadditions—represent a powerful tool due to the fact that C_{60} behaves as an electron-deficient olefin.

The addition of a 1,3-dipole to an alkene to give a five-member ring is a classic organic reaction. Indeed, 1,3-dipolar cycloaddition reactions are useful for the

formation of carbon–carbon bonds and for the preparation of heterocyclic compounds. Unlike the Diels–Alder reaction, the 4π -electron component contains three atoms and at least one of these is a heteroatom; such a component is called a 1,3-dipole and can be classified into two types depending on the electronic structure. The first type of 1,3-dipole is isoelectronic with the allyl anion. These compounds are characterized by a system of four π -electrons in three parallel atomic p_z -orbitals. The second type of 1,3-dipole, which is called the propargyl-allenyl type, contains an additional π -orbital orthogonal to the allyl anion-type molecular orbital. In one canonical form this type of dipole contains a triple bond. Allyl-type dipoles are bent whereas propargyl-allenyl types are linear.

The transition state of the concerted 1,3-dipolar cycloaddition is controlled by the frontier molecular orbitals of the substrates. A classification of the 1,3-dipolar cycloaddition has been performed on the basis of the relative frontier molecular orbital energies between the alkene and the 1,3-dipole. The type I cycloaddition is governed by an interaction between the HOMO of the dipole and

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the LUMO of the alkene. In type II additions, the energy level of the frontier orbitals of both dipole and alkene are similar, which makes interactions between both $\text{HOMO}_{\text{dipole}}\text{-LUMO}_{\text{alkene}}$ and $\text{HOMO}_{\text{alkene}}\text{-LUMO}_{\text{dipole}}$ important. Type III reactions are based on the interaction between the LUMO of the dipole and the HOMO of the alkene. The rate of the reaction depends on the gap between the controlling orbitals, with smaller gaps associated with faster cycloadditions. Substitution of these systems by electron-donating or electron-withdrawing groups on the dipole and/or the alkene may change the relative frontier orbital energies and result in a change in the rate and reaction type.

The low value of the LUMO level of C_{60} (-2.88 eV) suggests that a type I interaction should be the most favoured approach in reactions where C_{60} is the dipolarophile and, consequently, those dipoles with higher HOMO levels should react more easily with C_{60} . In this way, diazomethanes [8], azides [9,10], azomethine ylides [11–16] and nitrile oxides [16–22] have been used for the preparation of fullerene derivatives in attempts to increase the solubility of C_{60} in common solvents, to diminish the aggregation to make materials that are easier to handle or to prepare tailor-made novel fullerene derivatives for specific applications in medicinal or material chemistry.

The formation of fulleropyrrolidines using 1,3-dipolar cycloadditions between fullerene and azomethine ylides, which was developed by Prato, has been widely used [23]. Azomethine ylides can be generated in situ from a wide variety of readily available starting materials. For example, *N*-methyl fulleropyrrolidine can be obtained by the cycloaddition between C_{60} and the azomethine ylide resulting from decarboxylation of *N*-methylglycine in the presence of paraformaldehyde in refluxing toluene. The simplicity of this procedure and the good yields achieved explain the popularity of this approach in fullerene chemistry. Fulleropyrrolidines have been widely used in different areas of chemistry. For example, water soluble or protein-modified fulleropyrrolidines have been prepared for medical applications [24–27]. In 1993, C_{60} was proposed as an inhibitor of HIV protease [24] and, more recently, fulleropyrrolidine derivatives bearing two ammonium groups on the surface of the fullerene sphere showed significant anti-HIV activity [25]. In spite of its wide applicability, the resulting fulleropyrrolidine is obtained as a racemic mixture due to the stereogenic centre being formed at C-2 of the pyrrolidine ring and the the C_{60} cage loses part of its electron affinity compared to pristine C_{60} (vide infra).

The design of covalently linked donor-fullerene systems that are capable of undergoing photoinduced electron transfer has been extensively studied in recent years as a result of the unique photophysical [28,29] and electrochemical [30] properties exhibited by fullerenes. Cyclic voltammetry experiments have shown that C_{60} is an excellent electron acceptor [31]. One drawback, however, is that most of the fullerene adducts reported to date show worse electron-accepting capacity than the parent C_{60} [32] as a consequence of the saturation of one double bond and the loss of conjugation. Many efforts have been made in order to increase the electron affinity of C_{60} [33–37] (see Section 3).

In this contribution we have aimed to provide an introduction to the synthesis of pyrazolino [60]fullerene systems and to present interesting electrochemical and photophysical properties of this family of compounds. Certain applications of these materials in photovoltaic devices are also covered in an effort to stimulate new work with these compounds in the field of materials science.

2. Synthesis

The first 1,3-dipolar cycloadditions to C_{60} were described in the early days of fullerene chemistry. However, the first example of a reaction between a nitrile imine and C_{60} was not described until 1994, when Mathews et al. [38] prepared a mixture of bisadducts **1** by reaction of C_{60} and 1,3-diphenylnitrile imine, generated in situ from benzhydrazidoyl chloride, in the presence of triethylamine during 10 days. This C_{60} bisadduct was characterized by FAB mass spectrometry and IR spectroscopy as well as by proton and carbon NMR spectroscopy. The monoadduct was not isolated during this procedure (Fig. 1).

In 1995, Matsubara et al. [39] described the preparation of a 1,3-diphenyl-2-pyrazolinofullerene. Furthermore, the synthesis and electrochemical and photochemical properties of some 2-pyrazoline ring-fused C_{60} derivatives **2a–c** were described in 1996 [40] by the same authors. These adducts were prepared by cycloaddition of C_{60} to nitrile imines generated in situ from the corresponding *N*-chlorobenzylidene derivatives in the presence of triethylamine in refluxing benzene for 2 hours (Fig. 2). The benzylidene derivatives can be obtained in two steps from the corresponding acid chloride and hydrazine, followed by reaction with phosphorus pentachloride.

Another approach to 2-pyrazolines involves the use of azomethine imines. Hydrazones give a thermal 1,2-hydrogen shift to afford azomethine imine intermedi-

ates that can undergo a 1,3-dipolar cycloaddition [41, 42] and this procedure has been used, for example, to prepare bipyrazoles from pyrazolylhydrazones under microwave irradiation. The synthesis involved [3 + 2] cycloadditions with alkenes after an efficient hydrazone-azomethine imine tautomerization (Fig. 3). It should be noted that this reaction does not proceed under classical heating conditions [43].

This procedure was used to react different pyrazolylhydrazones (which are readily prepared from aldehydes in almost quantitative yields) with C_{60} under microwave irradiation to form the corresponding fullerene cycloadducts [44]. However, the yields obtained in these reactions were lower than 6%.

A more useful and alternative route to the pyrazolino [60]fullerenes **3a–c** (see Fig. 4) involved the use of nitrile imines as dipoles, but in this case the procedure was modified in that the dipoles were prepared in a one-pot procedure starting from hydrazones. These 1,3-dipoles were generated in situ directly from the hydrazones and *N*-bromosuccinimide in the presence of

triethylamine and then reacted with C_{60} under microwave irradiation [44]. The corresponding adducts **3a–c** were obtained in 20–38% yield.

A modification of this procedure was used for the preparation of various pyrazolino fullerenes **4a–f** [45] bearing different functional groups as substituents. Such a modification avoids the use of microwave irradiation and the reaction can be carried out at room temperature. The starting hydrazones were treated with *N*-chlorosuccinimide in the presence of pyridine; the resulting chloro-derivatives were directly treated with triethylamine and C_{60} at room temperature to give the corresponding cycloadducts **4a–f** in good yields (Fig. 5).

This synthetic strategy was used in conjunction with a wide variety of hydrazones to prepare numerous different pyrazolino [60]fullerenes. For example, an oligophenylenevinylene (OPV) trimeric subunit was attached to C_{60} through a pyrazoline ring [46] (compound **5**) and a number of new phenylenevinylene (PV) fullerenden-

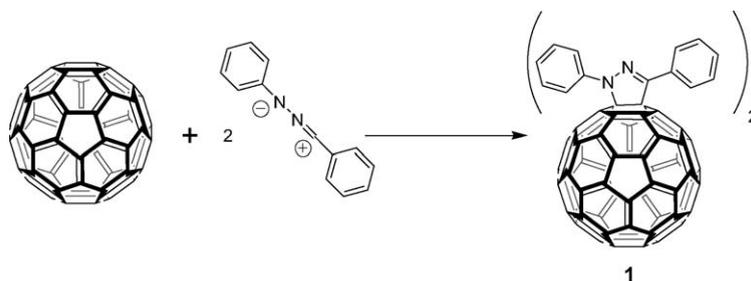


Fig. 1. Synthesis of compound **1**.

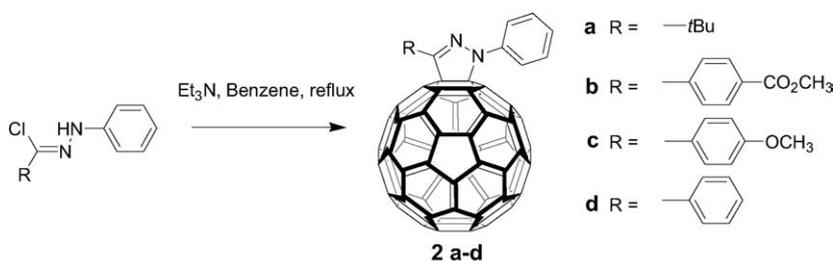


Fig. 2. Synthesis of compounds **2a–d**.

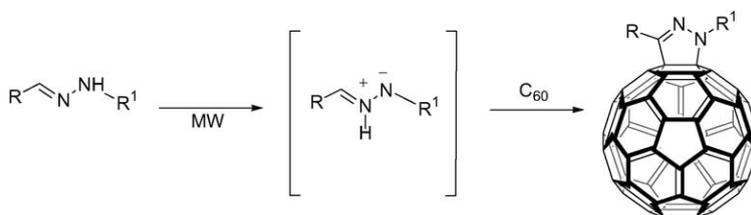
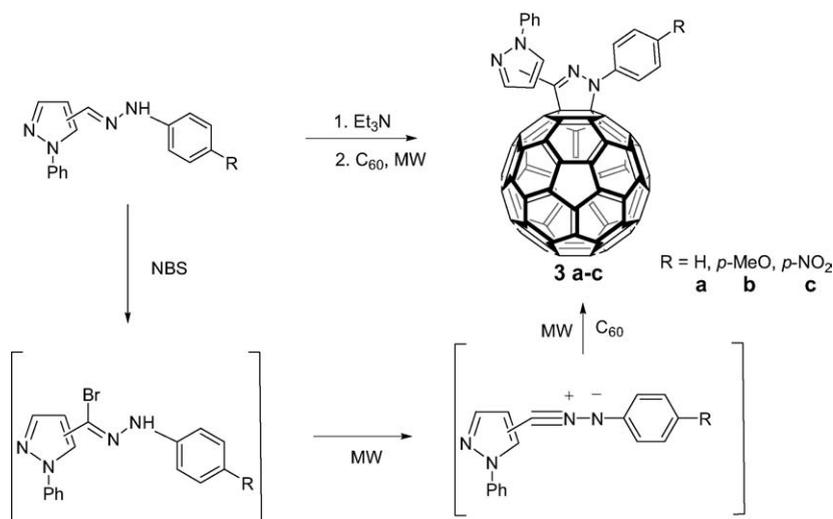
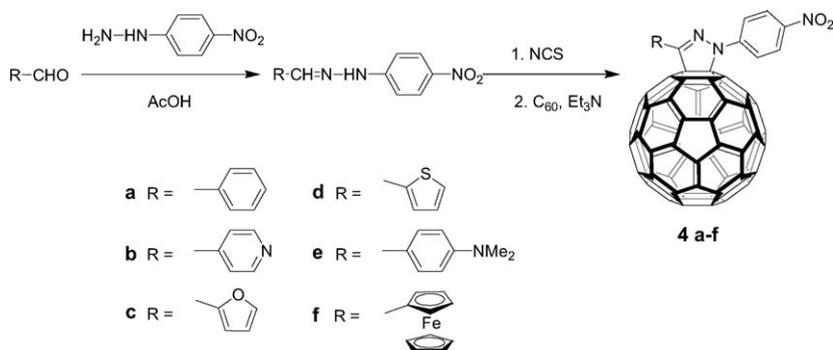


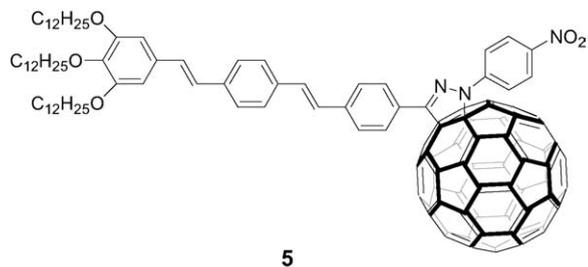
Fig. 3. [3 + 2] cycloaddition to fullerene after hydrazone–azomethine imine tautomerization.

Fig. 4. Synthesis of compounds **3a–c**.Fig. 5. Synthesis of compounds **4a–f**.

dimers have been synthesized [47] (compounds **6a–b**) (Fig. 6).

In 2002, symmetrically substituted oligophenylenevinylene derivatives bearing terminal *p*-nitrophenylhydrazone groups were prepared and used for the synthesis of dumb-bell-shaped bis-(pyrazolino [60]fullerene)-oligophenylenevinylene systems [48] (compounds **7**). Unlike other functionalization methods, the formation of stereoisomers does not occur and this method allows pure cycloadducts to be obtained in good yields (Fig. 7).

One drawback of this functionalization method is that, although the reaction is general for any kind of aldehyde (*C*-side of the final pyrazolino [60]fullerene), in terms of the *N*-side the route is limited by the availability of the starting hydrazine to form the hydrazone. As indicated above, substituents that raise the energy of the dipole LUMO should make the cycloaddition easier and, consequently, frontier orbital theory predicts that

Fig. 6. Structure of compound **5**.

N-*p*-nitrophenyl hydrazones should react more slowly than *N*-phenyl or *N*-*p*-methoxyphenyl derivatives. Despite the fact that *N*-phenyl and *N*-*p*-methoxyphenyl pyrazolino [60]fullerenes have been prepared, the best results were obtained from *p*-nitrophenyl hydrazones [49] as, in this case, the nitrile imine intermediate is stabilized by the *p*-nitrophenyl group [50].

A simple procedure that allows the preparation of pyrazolino [60]fullerene with substitution on the *N*-side

of the pyrazoline ring was developed [51] and involves reduction with tin of the *p*-nitrophenyl moiety (Fig. 8). This method enabled the introduction of a range of desirable moieties on the *N*-side of the pyrazolino [60] fullerene system by functionalization of the amino group. The resulting *N*-anilinyrpyrazolino [60]fullerenes **9a–e** are convenient synthons for the preparation of other fullerene derivatives with the appropriate functionality for a given application (Fig. 9).

Ruthenocene has been used as a new fragment in [60]fullerene-donor dyads [52]. A 2-pyrazolino [60] fullerene was synthesized by following the previously described procedure. For the sake of comparison, the pyrrolidinofullerene was also prepared (Fig. 10).

The gas phase geometries and the electronic structures of **12** and **13** were studied by density functional theory methods using the B3PW91/LanL2DZ model as implemented in the Gaussian 03 program. The optimized geometry of **13** is shown in Fig. 11 and resembles that calculated for analogous ferrocene derivatives using the B3LYP/3-21G* model [53]. The two carbon

atoms in the C₆₀-pyrrolidine junction were out of the C₆₀ sphere by 0.35 Å, and the ruthenocene moiety was located away from C₆₀ in such a way that the distance between the C₆₀ spheroid centre and the ruthenium atom was 8.37 Å. The geometry of the analogous 2-pyrazolinofullerene is significantly different, as shown in Fig. 11. The calculated geometry of **12** was dictated by the conjugation of the ruthenocene moiety with the pyrazoline ring, which was almost coplanar (ca. 10°) with the cyclopentadiene ring linked to it. This geometrical arrangement reduced the distance from ruthenium to the centre of C₆₀ to 7.55 Å.

This methodology can also be used for the functio-

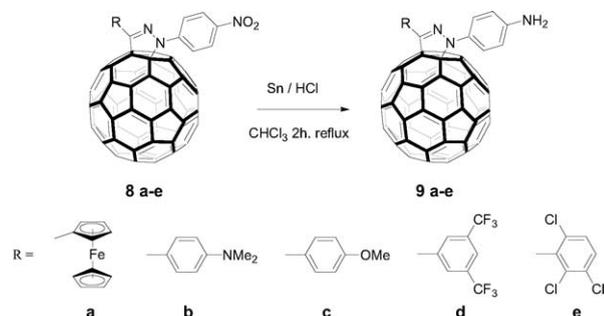


Fig. 8. Synthesis of compounds **9a–e**.

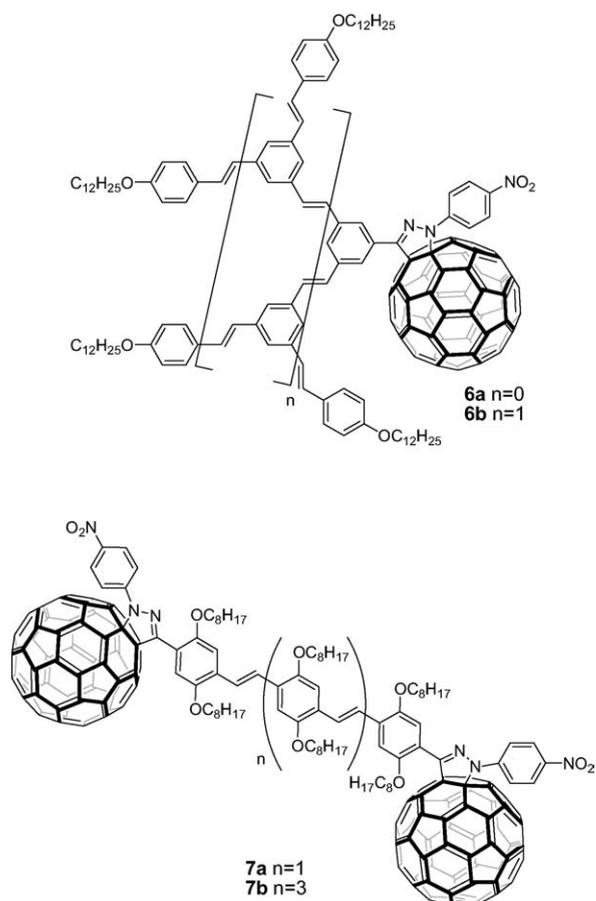


Fig. 7. Structures of compounds **6** and **7**.

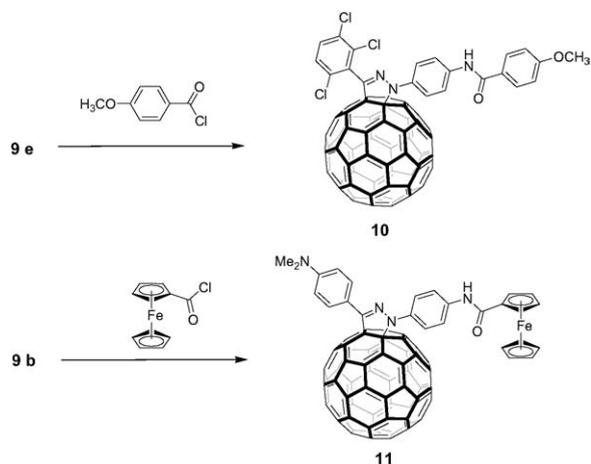


Fig. 9. Synthesis of compounds **10** and **11**.

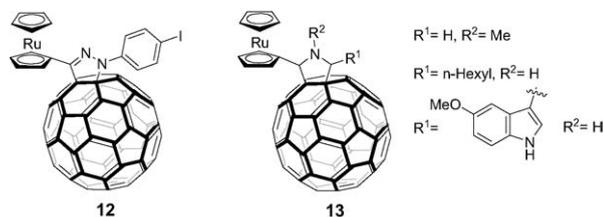


Fig. 10. Structures of compounds **12** and **13**.

nalization of single-walled carbon nanotubes (SWNTs): two soluble, photoactive single-walled carbon nanotubes containing *n*-pentyl esters at the tips and 2,5-diarylpyrazoline units on the walls of the tubes were synthesized by 1,3-dipolar cycloaddition of nitrile imines to the sidewalls of SWNTs [54] (Fig. 12). The success of the synthesis was demonstrated by solution ^1H - and ^{19}F -NMR as well as by UV-Vis and FT-IR spectroscopy. These two compounds were selected to have soluble single-walled carbon nanotubes substituted either with an electron-poor (3,5-bistrifluoromethylphenyl, **14**) or electron-rich (4-*N,N*-dimethylaminophenyl, **15**) unit on the C atom of the pyrazoline ring. Laser flash photolysis in dynamic flow of these carbon nanotubes in acetonitrile revealed the formation of several transient species that decayed in the microsecond time scale. All of the available data – including the photochemistry of model compounds, quenching experiments with electron donors and acceptors and the influence of acids – are compatible with the occurrence of electron transfer from the electron-rich substituents of the pyrazoline unit to the electron-acceptor terminal that incorporates electron-poor aryl rings and nanotube walls.

It has been demonstrated that this method is a general and versatile procedure for the functionalization of fullerenes and carbon nanotubes in a one-pot reaction starting from the corresponding hydrazone. The hydrazones are stable compounds and are readily available from aldehydes in almost quantitative yield.

A new synthetic route has recently been investigated by Reinov et al. [55]. In this procedure, nitrile imines were generated by the thermal decomposition of 2,5-diaryltetrazoles. Cycloadducts containing aryl and hetaryl substituents, such as thienyl and pyridyl, in the pyrazoline fragment were synthesized using this method (Fig. 13). The availability of 2,5-diaryltetrazoles with various structures

generates a greater possibility for functionalization of the fullerene spheroid than other procedures, which are limited by the availability of the appropriate hydrazone halides.

Finally, Wang et al. [56] prepared [60]fullerene-fused pyrazolines by the reaction of C_{60} with alkyl diazoacetates under solid-state high-speed vibration milling (HSVM) conditions as well as in toluene solution. The 2-pyrazolines were obtained through isomerization of the corresponding 1-pyrazolines, which were formed directly by the 1,3-dipolar cycloadditions of alkyl diazoacetates generated in situ from glycine ester hydrochlorides and sodium nitrite with C_{60} (Fig. 14).

3. Electrochemical properties

The study of the electrochemical properties of fullerenes [57] has been a field of intense research since these materials were first reported in 1990 [58]. As a consequence of its LUMO triple degeneracy, C_{60} can be reduced up to the hexa-anion [59] by a stepwise reduction. The reductions were found to be reversible and the different potentials appeared to be almost equidistant. The low value of the first reduction potential of C_{60} , which is similar to that of quinones, makes it an interesting partner in the preparation of donor–acceptor (D–A) systems due to the interesting electronic and optical properties that these materials can display. As a result, several groups have focussed their attention on the preparation of C_{60} –donor dyads [29,60–66] and the study of the existence of inter- or intramolecular electronic interactions between donor and C_{60} in both the ground and excited states.

The characteristic features of the electrochemical properties of C_{60} are also seen in monoadducts. However, the reduction potentials of the monoadducts are about 100 mV more negative than those of C_{60} [30,

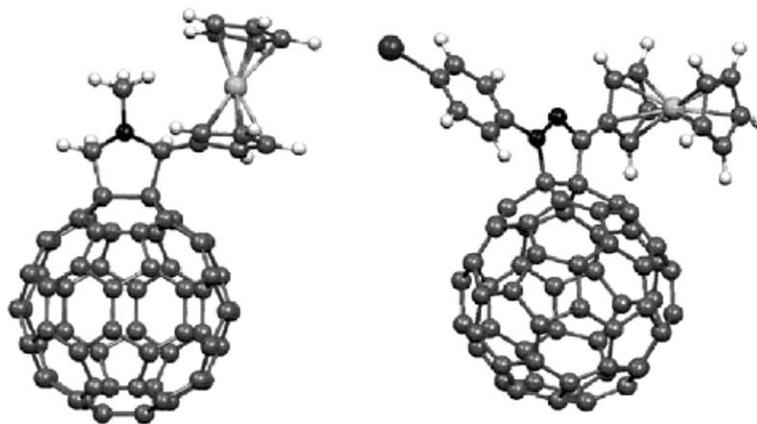
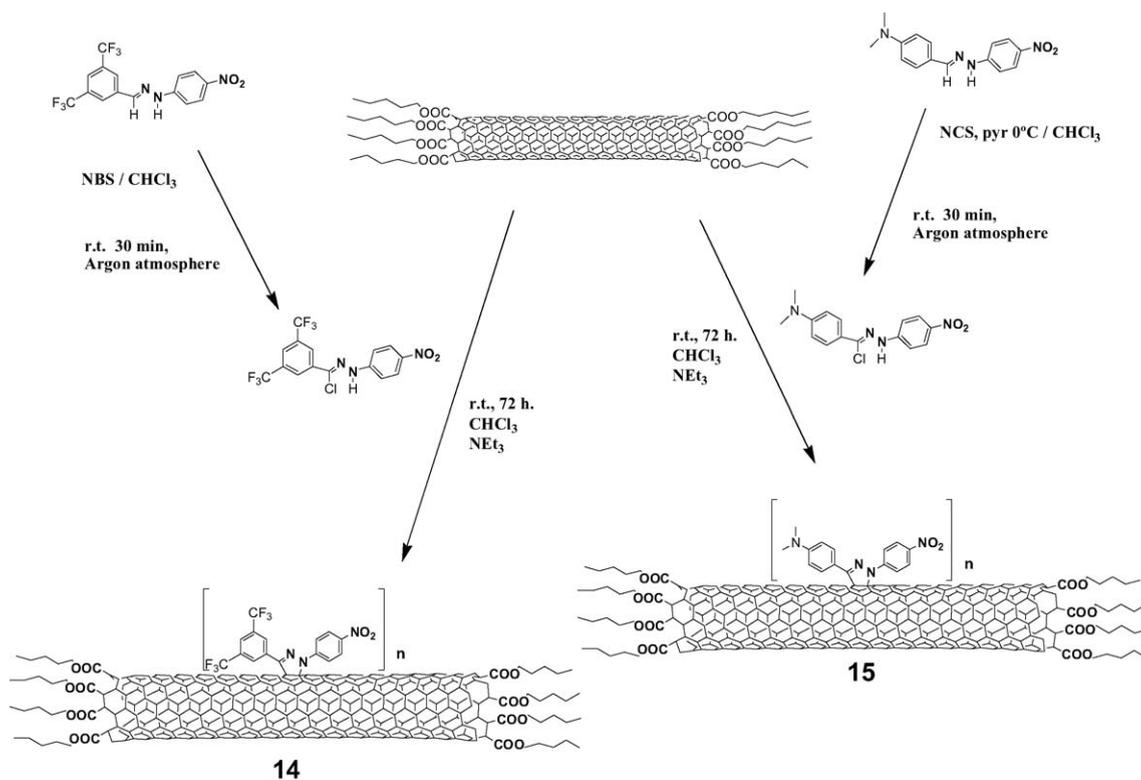
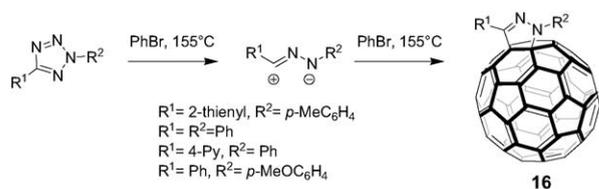


Fig. 11. Optimized geometries of compounds **13** (left) and **12** (right) calculated using B3PW91/LanL2DZ.

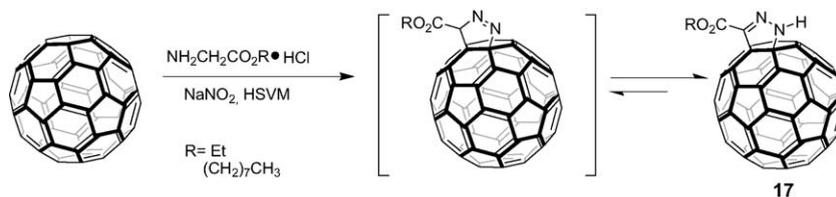
Fig. 12. Synthesis of compounds **14** and **15**.Fig. 13. Synthesis of compound **16**.

67] – a consequence of the saturation of one double bond – and a great deal of effort has been spent on attempts to increase the electron affinity of C_{60} . Wudl et al. described the synthesis of a methanofullerene bearing two cyano groups [33] and this showed a first reduction potential that was 156 mV more positive than the parent C_{60} . Several heterofullerenes [34] and multi-

fluorinated derivatives [35,36] exhibit better electron affinity than pristine fullerene. Another example is represented by a series of pyrrolidinium salts that showed better electron-accepting properties than the corresponding pyrrolidines. This behaviour was attributed to the inductive effect of the heteroatoms on the fullerene sphere [37].

Consequently, one possible way to prepare functionalized fullerenes with a better, or at least equivalent, electron affinity to the parent C_{60} would be to use electronegative or electron-deficient atoms directly connected to the fullerene cage – as in the addition of nitrile oxides to form isoxazolinofullerene [16–20,68,69] or the addition of nitrile imines to prepare pyrazolinofullerenes.

The most simple pyrazolino [60]fullerene prepared to date, methyl derivative **18**, was synthesized and its

Fig. 14. Synthesis of compound **17**.

electrochemical behaviour studied [70] by Osteryoung square wave (OSWV) and cyclic voltammetry (CV). This compound showed four reversible reduction waves and one irreversible reduction wave attributed, respectively, to the fullerene core and the *p*-nitrophenyl moiety. Compared to the parent C₆₀, this adduct showed similar values for the first and the second fullerene-based reduction waves in an *o*-dichlorobenzene (ODCB)/acetonitrile (4:1) mixture ($E_{\text{red}}^1 = -0.63$ V and $E_{\text{red}}^2 = -1.04$ V for **18** compared to -0.64 and -1.05 V, respectively, for C₆₀) [70] (Fig. 15).

3.1. Influence of the nature of the heterocycle

In order to compare the electrochemical properties of different fullerene derivatives with a heterocyclic five-member ring linked to the C₆₀ cage, the synthesis, spectroscopic characterization, electrochemistry and photochemical measurement of three 2-methoxyphenylfullerene derivatives **19–21** with pyrrolidine, isoxazalone and pyrazoline rings were undertaken and their properties compared [71]. Cyclic and Osteryoung square wave voltammetry studies indicated that pyrazolino [60]fullerene **21** had improved electron affinity in comparison with the parent fullerene (Table 1).

Cyclic and Osteryoung square wave voltammetry studies on pyrrolidino [60]fullerene **19** showed four reversible reduction peaks and confirmed that these derivatives retain the electrochemical pattern of C₆₀. However, as previously described for other fullerene derivatives, the reduction potentials are shifted to more negative values compared to those of C₆₀. A different trend was found for isoxazolo [60]fullerene **20**, for which reduction potentials were shifted to slightly more positive values than the parent C₆₀. This behaviour is similar to that described previously for this class of fullerene derivative [72–75]. Finally, pyrazolino [60]fullerene presented four reversible reduction potentials corresponding to the fullerene core and a fifth reduction potential located between the second and third potential of C₆₀. Comparison of the three derivatives indicates that the

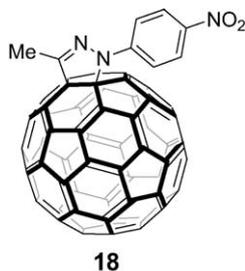


Fig. 15. Structure of compound **18**.

electron affinity follows a particular order (*p*-nitrophenylpyrazolinofullerene > isoxazolinofullerene >> pyrrolidinofullerene) as a consequence of the strength of the $-I$ effect of the heterocyclic ring on the C₆₀ cage (Fig. 16).

From this study, it can be concluded that in those cases where a high electron affinity of the C₆₀ cage is a desired property, the preparation of pyrazolino [60]fullerenes shows advantages with respect to other functionalization procedures.

3.2. Substitution on the C-side of the pyrazoline

The influence that the substituent on the C-side of the pyrazoline ring has on the electrochemical properties of *p*-nitrophenyl-substituted pyrazolino [60]fullerenes has been studied in compounds **4a–f** (Table 2) [45]. The influence of strong electron donors (e.g., ferrocene or *N,N*-dimethylaniline) and an electron acceptor (e.g., pyridine) was studied. The introduction of an electron-acceptor moiety (4-pyridinyl) in compound **4b** resulted in the most positive first reduction potential in this series of compounds. Indeed, the electron affinity of this compound was better than parent C₆₀ itself. When electron donors like *N,N*-dimethylaniline (**4e**) or furan (**4c**) were introduced at the C atom of the pyrazolino ring, the most negative values in this series were found, with first reduction potentials similar to the parent C₆₀. Although the differences between derivatives were small (~ 40 mV), the influence that the nature of the substituent on the C-side of the pyrazoline has on the electron affinity of C₆₀ can be explained in terms of through-bond or through-space interactions between the substituent and the fullerene cage. Comparison of the reduction potentials of the *p*-nitrophenyl moiety of these compounds shows a shift to more negative values as the electron-donor ability of the substituent on the other side of the molecule was increased. This reduction potential was shifted by 60 mV when a strong electron-donor was linked to the pyrazoline ring. This fact demonstrates electronic communication between the C-substituent and the sp³ nitrogen atom of the pyr-

Table 1

Redox potential (OSWV) of organofullerenes **19–21** and C₆₀ measured at room temperature in *o*-dichlorobenzene (ODCB)/acetonitrile (4:1)^a

Compounds	E_{red}^1	E_{red}^2	E_{red}^3	E_{red}^4
C ₆₀	-0.99	-1.42	-1.87	-2.41
19	-1.10	-1.51	-2.04	-2.36
20	-0.97	-1.37	-1.88	-2.36
21	-0.95	-1.38	-1.80	-2.30

^a Experimental conditions: V vs. Ag/AgCl; GCE as working electrode; 0.1 M TBAP; scan rate: 100 mV/s.

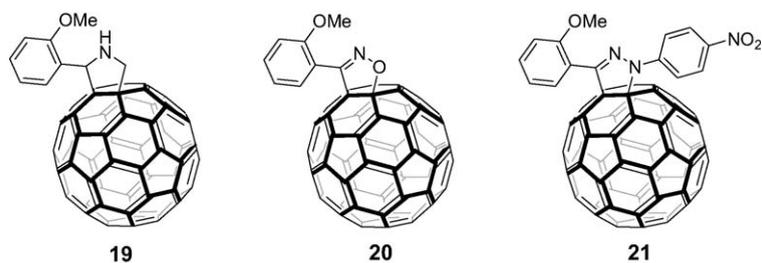


Fig. 16. Structures of compounds 19–21.

Table 2

Redox potential (OSV) of organofullerenes **4a–f** and C_{60} measured at room temperature in *o*-dichlorobenzene (ODCB)/acetonitrile (4:1) ^a

Compounds	E_{red}^1	E_{red}^2	E_{red}^3	E_{red}^4	E_{red}^5
C_{60}	-0.95	-1.36	–	-1.83	-2.29
4a	-0.93	-1.33	-1.70	-1.87	-2.24
4b	-0.91	-1.32	-1.66	-1.82	-2.22
4c	-0.95	-1.36	-1.70	-1.84	-2.33
4d	-0.92	-1.32	-1.70	-1.85	-2.22
4e	-0.95	-1.35	-1.72	-1.91	-2.28
4f	-0.94	-1.35	-1.72	-1.92	-2.30

^a Experimental conditions: V vs. Ag/AgCl; GCE as working electrode; 0.1 M TBAP; scan rate: 100 mV/s.

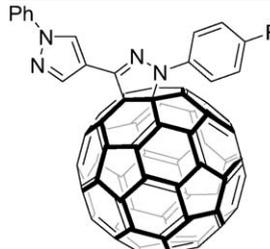
azoline ring. As a consequence, the electron-transfer process from this nitrogen atom should be favoured when an electron-donor is incorporated into the *C*-side of the pyrazoline ring.

3.3. Substitution on the N-side of the pyrazoline

The electrochemical behaviour of a series of pyrazolopyrazolino [60]fullerenes (**3a–c**) was investigated by cyclic voltammetry [49]. The first reduction potential of **3c**, which is attributed to the fullerene moiety, showed an anodic shift of up to 80 mV compared to the parent C_{60} (Table 3). This difference became less pronounced as the *N*-phenyl group attached to the nitrogen atom of the pyrazoline ring became more electron rich as a consequence of the conjugation of the aryl group [76].

Table 3

Redox potential (OSV) of organofullerenes **3a–c** and C_{60} measured at room temperature in *o*-dichlorobenzene (ODCB)/acetonitrile (4:1) ^a

	R	E_{red}^1	E_{red}^2	E_{red}^3	E_{red}^4
	C_{60}	-0.59	-0.98	-1.48	-2.95
	3a H	-0.55	-0.97	-1.46 (-1.71)	-2.22
	3b <i>p</i> -MeO	-0.57	-0.99	-1.44 (-1.74)	-2.23
	3c <i>p</i> -NO ₂	-0.51	-0.91	-1.19 (-1.73)	-2.21

3 a-c

^a Experimental conditions: V vs. Ag/AgNO₃; GCE as working electrode; 0.1 M TBAP; scan rate: 100 mV/s.

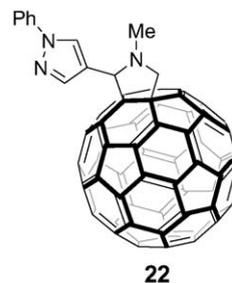


Fig. 17. Structure of compound 22.

Fulleropyrrolidine **22** (Fig. 17) was synthesized and the electrochemical properties were compared to those of the corresponding pyrazolino [60]fullerene.

As expected, it was found that the fulleropyrrolidine has a markedly more negative value for the first reduction potential than the pyrazolino [60]fullerene. The formation of the pyrrolidine ring usually leads to a displacement of the reduction potentials to more negative values, which results from a decrease in the electron affinity of the fullerene cage [77].

Interestingly, aminopyrazolino [60]fullerenes [51] showed different electrochemical behaviour depending on the solvent used for the studies (Table 4). In the less polar mixture (ODCB/CH₂Cl₂), compounds **9a–e** showed reduction potentials that were shifted to more positive values than that in the parent C_{60} . The materi-

Table 4

 $E_{1/2}$ values measured as the average of the anodic and cathodic peak potentials (CV) of compounds **9a–e** and C_{60} at room temperature ^a

Compounds	ODCB/Acetonitrile 4/1					ODCB/CH ₂ Cl ₂ 4/1
	E^1_{red}	E^2_{red}	E^3_{red}	E^1_{ox}	E^2_{ox}	
C_{60}	-0.94	-1.36	-1.84	–	–	-0.94
9a	-1.01	-1.41	-1.91	0.13 ^c	0.39 ^b	-0.91
9b	-1.00	-1.40	-1.90	0.16	0.32 ^b	-0.88
9c	-1.00	-1.39	-1.90	0.37 ^b	0.57 ^b	-0.89
9d	-0.98	-1.39	-1.91	0.30 ^b	–	-0.89
9e	-1.00	-1.40	-1.89	0.32 ^b	–	-0.89

^a Experimental conditions: V vs. Ag/AgNO₃; GCE as working electrode; 0.1 M TBAP; scan rate: 100 mV/s. ^b Irreversible. ^c Reversible, corresponding to the ferrocene addend.

als exhibited an improved electron affinity compared to the parent fullerene. However, in the most polar solvent mixture (ODCB/acetonitrile), the reduction potentials were shifted to slightly more negative values compared to C_{60} . This phenomenon was explained in terms of possible electronic interactions between the fullerene cage and the aniline substituent in the ground state, which should be stabilized in the more polar solvent.

As shown above, when compared to other C_{60} derivatives, pyrazolino [60]fullerenes must be considered as interesting electroactive compounds. Unlike other fullerene adducts, most of these compounds showed similar or better electron-accepting properties than the parent fullerene, thus making them good candidates for the preparation of new electroactive fullerene assemblies.

4. Photophysical properties

Fullerenes are characterized by excited levels that are relatively low in energy. The singlet and triplet excited states of C_{60} are localized, respectively, at 1.7 eV [78] and 1.5 eV [79] above the ground state. In addition, the positions of these low-lying electronic states in functionalized fullerenes are not significantly different to that in the parent C_{60} . The singlet excited state of fullerenes is partially deactivated to the ground state through a radiative process that leads to the emission of fluorescence at 700 nm [78,80,81]. The main deactivation process for the fullerene singlet excited state is the intersystem crossing pathway that leads to the formation of the triplet excited state [79] (Fig. 18).

The fact that fullerenes are good acceptors with low-energy electronic levels is an important aspect for the photochemistry of fullerene derivatives: the excitation of a molecule in the presence of fullerene (whether it is covalently attached or not) can be followed by two processes other than deactivation by fluorescence. The first involves an electron transfer (ET) and the second

an energy transfer (EN) (Fig. 19). These two processes are in competition with one another.

The fluorescence spectra of three different types of fullerene derivatives **19**, **20**, **21** and the model *N*-methylpyrrolidino [60]fullerene were recorded at room temperature in toluene and benzonitrile with excitation at 430 nm. Solutions with the same absorbance were employed so that the fluorescence intensity and quantum yield could be correlated.

When toluene was used as the solvent, the model compound presented a maximum at 717 nm while **19** showed a maximum at 718 nm – both values are in the expected region for this system [82]. The emission of **19** was of a similar intensity to that of the reference *N*-methylpyrrolidino [60]fullerene, indicating that **19** did not undergo photoinduced charge transfer under these conditions. The fluorescence intensities were found to be similar and this shows that the quantum yields are almost equal. A similar pattern was observed for **20** but the intensity of the emission was slightly lower and the maximum appeared at 706 nm. Pyrazolino [60]fullerene **21** showed a maximum at 709 nm and a marked reduction in the fluorescence emission was observed in comparison with the reference material.

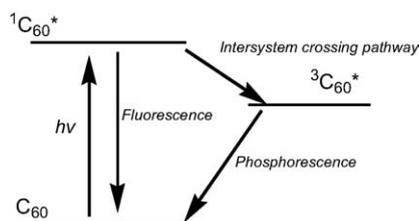


Fig. 18. Deactivation process for the fullerene singlet excited state.

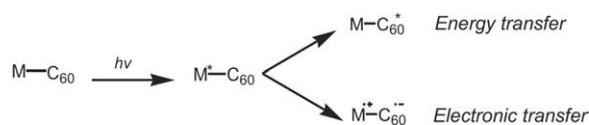


Fig. 19. Other deactivation processes.

When benzonitrile was used as the solvent, the maximum of **19** was red shifted to 722 nm and the emission intensity remained virtually unchanged with respect to that found in toluene (considered as 100%). The reference compound showed the same type of behaviour.

A similar red shift and a slight decrease in the fluorescence emission (85% with respect to that found in toluene) were found in the case of **20**. In contrast, the maximum for pyrazolino [60]fullerene **21** was blue shifted to 705 nm. In addition, a substantially lower fluorescence intensity (60% with respect to that found in toluene) was observed. The quenching of the fluorescence in **21** as the polarity of the solvent increased suggests the occurrence of an electron-transfer process from the lone pair of the sp^3 nitrogen atom to the C_{60} cage when the sample is dissolved in benzonitrile.

Interestingly, the addition of trifluoroacetic acid (TFA) to benzonitrile solutions of **19** and **21** produced the opposite effect. In the case of compound **19** the addition of TFA resulted in a weak quenching of the fluorescence and the maximum was blue shifted. This behaviour can be explained in terms of the formation of the pyrrolidinium salt and the possibility that a weak electron-transfer process can occur from the 2-methoxyphenyl moiety. The addition of TFA to a solution of **21** in benzonitrile resulted in a slight increase in the fluorescence. Such an increase suggests quenching of the electron-transfer process because the nitrogen lone pair is no longer available (Fig. 20).

Compound **23** exhibited a faint fluorescence band in CH_2Cl_2 at room temperature ($\lambda_{max} = 706$ nm) and the emission quantum yield was about two orders of magnitude lower than that of **24**. The fluorescence intensity

was dependent on solvent polarity, with lower polarity solvents giving rise to stronger emission (Fig. 21a). Fluorescence enhancement was observed on addition of TFA and the addition of about 30% TFA (v/v) led to an intensity plateau (Fig. 21b). The luminescence signal reverted to its initial intensity after extraction of the CH_2Cl_2 /TFA solution with saturated aqueous NaOH. These results all suggest that the lowest fullerene singlet excited state was quenched by electron transfer from the lone pair of the pyrazoline sp^3 nitrogen, a situation analogous to that seen in similar substituted fullerenes [73,83–87]. Accordingly, fulleropyrazoline **23** (Fig. 22) was described as a redox dyad in which the electron donor and acceptor units were linked through an sp^3 carbon as a very simple spacer, as suggested by Sun and Bunker for aminofullerene derivatives [84].

The fluorescence spectra of **4a–f** [45] were measured in both toluene and benzonitrile upon excitation at 430 nm at room temperature. The solutions studied had the same absorbance so that the fluorescence intensity and quantum yields could be correlated.

The fluorescence spectrum of pyrazolino [60]fullerene **4a** in toluene was similar to those of other fullerene derivatives, with an emission maximum at 705 nm and a shoulder at 772 nm due to the intersystem crossing into the excited triplet state.

The intensities of the emission maxima in **4b**, **4c** and **4d** were lower and the maxima were red shifted with respect to those of **4a**. This trend indicates that the excited state had been partially quenched. Evidence for emission was not found when the strong donors *N,N*-dimethylaniline (**4e**) or ferrocene (**4f**) were linked to the

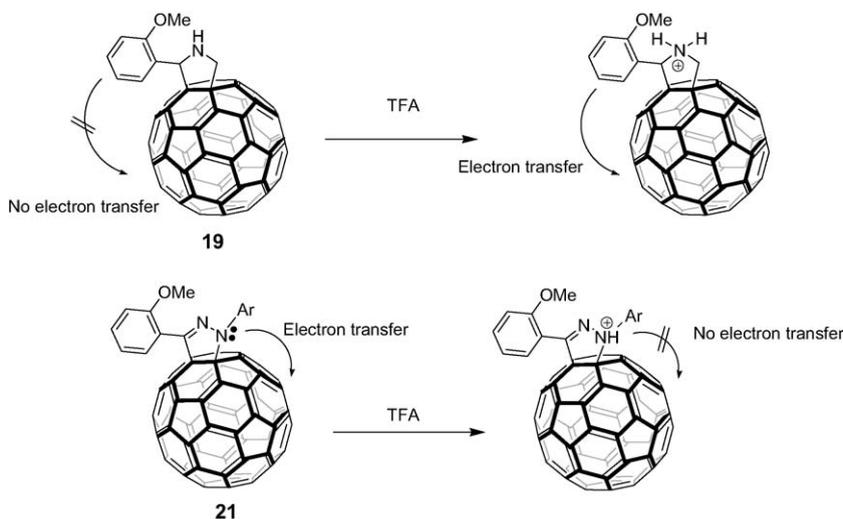


Fig. 20. Proposed mechanism for the quenching of the electron transfer.

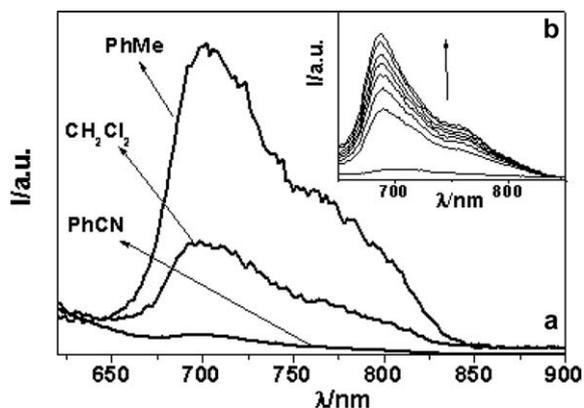


Fig. 21. (a) Fluorescence spectra of **23** in various solvents under the same experimental conditions; $\lambda_{\text{exc}} = 430$ nm, $A = 0.400$. (b) Inset: Fluorescence spectrum of **23** in CH_2Cl_2 upon addition of increasing amount of acid up to 30% (v/v); $\lambda_{\text{exc}} = 424$ nm.

pyrazolino [60]fullerene system. This quenching was explained in terms of a photoinduced electron-transfer (PET) process, which is not common in non-polar solvents like toluene. On the other hand, the fluorescence intensity in benzonitrile was lower and was also associated with solvatochromic red shifts of the maxima in all cases. This solvatochromic effect in benzonitrile when compared to toluene was assigned to a weak CT character. The quenching of the fluorescence was attributed to a weak PET interaction that occurs on increasing the polarity of the solvent and this would be expected to lead to increased stability of the separated charge state.

Addition of TFA to a benzonitrile solution of **4e** ($R = N,N$ -dimethylaniline) caused an enhancement in the fluorescence, suggesting quenching of the PET process as the lone electron pairs of the two nitrogen atoms (N,N -dimethylaniline group and pyrazoline ring) become unavailable. One (or both) of the electron pairs

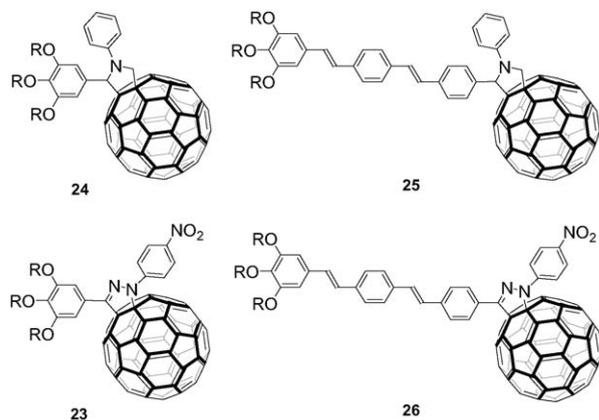


Fig. 22. Structures of compounds **23**–**26**.

should be responsible for the PET process; the addition of base (pyridine) caused quenching of the fluorescence, indicating the reversibility of the process.

The photochemical behaviour of pyrazolino [60]fullerenes **3a–c** was investigated [49]. These compounds share common absorption bands but the peak at 425 nm, which is characteristic of [6,6]-bridged mono-adducts, only appeared as a shoulder in the spectrum of the nitro adduct **3c** due to the absorption of the nitrophenyl group. A band at around 687 nm, attributed to the $0-0^*$ transition, was also observed. A weak, broad band was observed in the 450–650-nm region. This band was stronger in dyads containing an electron-donating substituent on the nitrogen atom of the pyrazoline ring (e.g., **3b**). Similar bands have been reported for intramolecular charge transfer in some C_{60} -based dyads [88–90] or intermolecular charge transfer interactions with other donors [91]. These broad absorptions were red-shifted on increasing the polarizability of the solvent. This fact suggests that weak charge-transfer complexes are formed in the ground state. The intensity of this band was found to increase with the polarity of the solvent, supporting the formation of a charge-transfer complex in more polar solvents. This band was not observed in **3c** because the electron-withdrawing moiety on the nitrogen atom of the pyrazoline ring inhibited the formation of a charge-transfer complex in this derivative.

The effect of solvent on the fluorescence has also been studied in fullerene derivatives. Previous studies on the photochemical properties of N -methylpyrrolidino [60]fullerenes indicated that the nitrogen atom of the pyrrolidine ring is not involved in charge transfer [84, 88]. The fluorescence spectrum of fulleropyrrolidine **22** in cyclohexane was found to be independent of the excitation wavelength and similar to the spectrum of the reference unsubstituted N -methylfulleropyrrolidine. The fluorescence study showed that this compound does not undergo photoinduced charge transfer in non-polar solvents.

An increase in the solvent polarity caused quenching of the fluorescence. This quenching, as well as the red shift observed in the more polar solvent benzonitrile, was ascribed to a weak charge transfer interaction in the excited state between the C_{60} and the pyrazole substituent.

The fluorescence spectra of the pyrazolino [60]fullerenes **3a–c** were recorded in different solvents. These compounds all showed a weak fluorescence compared to the fulleropyrrolidine discussed above. The fluorescence experiments demonstrated efficient deactivation of the

fullerene singlet excited state in pyrazolinofullerene derivatives when compared to fulleropyrrolidine derivatives. The fluorescence quenching of these compounds was attributed to an intramolecular electron-transfer process from the pyrazole substituent to the C₆₀ cage.

A series of isoindazole–C₆₀ dyads based on pyrazolino [60]fullerene has been prepared [70] (Fig. 23).

The fluorescence spectra of the dyads **29a–c** and the model compound *N*-methylpyrazolino [60]fullerene (**18**) were measured in polar and non-polar solvents. The toluene solutions gave peaks at 697 nm due to the fullerene moiety. Fluorescence was not observed in the 500–600 nm region for **29a–c**, indicating that energy transfer takes place efficiently from the excited singlet state of the isoindazole (or hydrazone) moiety to the fullerene moiety. Appreciable substituent effects were not observed in compounds **29a–c**. In contrast, in the more polar solvent (benzonitrile) the fluorescence intensities of the fullerene moieties at 697 nm changed considerably from **18** (reference) and **29c** to **29a** and **29b**. As the electron-donating ability of the substituents of the isoindazole moiety increased, the fluorescence intensity decreased significantly.

This trend was confirmed by the shortening of fluorescence lifetimes, which allowed the evaluation of intramolecular charge-separation rates and efficiencies via the excited singlet states of the fullerene moiety. The yields of the triplet states in the polar solvent decreased with electron-donating ability. This observation is consistent with the competitive formation of the charge-se-

parated state by intersystem crossing from the excited states. Thus, isoindazole [60]fullerene **29b** can be considered as a molecular switch with an AND logic gate.

The fluorescence emission behaviour of two pyrazolino [60]fullerene phenylenevinylene dendrimers (**6a** and **6b**) has been studied [47]. The fluorescence emission was strongly quenched (around 60% for **6a** and 50% for **6b**) compared to the corresponding starting hydrazones, indicating significant interaction between the singlet excited state of the phenylenevinylene moiety and the fullerene ground state. Moreover, different behaviour was observed for the generation one (**6a**) and generation two (**6b**) dendrimers. Dendrimer **6a** showed emission at 694, 707 (ascribed to the fullerene cage as a consequence of an energy transfer), 965 and 983 nm. These bands were not observed for **6b**, suggesting that an electron transfer might occur in this case. The fluorescence spectra were taken at different concentrations and were independent of the concentration—indicating that the process taking place was intramolecular.

The pyrazolino [60]fullerene phenylenevinylene dendrimer **6a** has been studied in solid molecular films for the first time [92]. Good-quality Langmuir–Blodgett (LB) films and cast-dropped films were prepared in order to compare their photophysical (Fig. 24), electrochemical and structural properties. These studies show how the assembly of the donor–acceptor dyads in thin films seem to favour the photoinduced electron transfer with respect to that observed in solutions. This difference in behaviour was related to intermolecular effects, as sug-

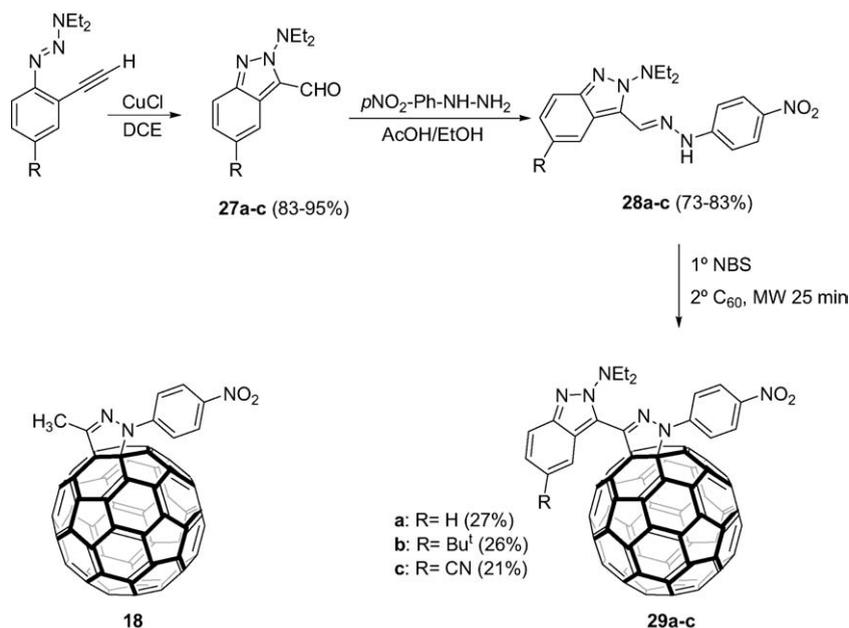


Fig. 23. Synthesis of compounds **29a–c** and structure of **18**.

gested by the steady-state photophysical outcomes of LB and cast dropped films, as well as the electrochemical behaviour of the LB films, in which the electron affinities of the fullerene redox states were markedly improved. However, a competitive energy transfer between the two chromophores was also assumed and this was optimized in case of the LB film due to the favourable intermolecular alignment. Finally, in an effort to further understand the structural aspects related to the properties outlined above, the structural organisation of the fullerodendrimer in the films has been elucidated by reflection–absorption infrared spectroscopy. This investigation showed that the dyad achieved a preferential intermolecular order in the LB film due to anchoring of the $-\text{NO}_2$ group on the substrate. In contrast, cast films of **6a** consisted of molecules that were randomly orientated but more efficiently packed. Atomic force microscopy topographic images show that the LB films present a growing aggregation on increasing the number of monolayers, but homogeneity was attained throughout the film. In contrast, the cast films consisted of dispersed and aggregated crystallites.

A new pyrazolino [60]fullerene (**26**) in which an OPV unit (3PV) is linked to a fulleropyrazoline (**23**) moiety has been prepared [46]. The corresponding fulleropyrrolidines **25** and **24** were also synthesized for comparison purposes.

The photophysical properties of **23**, **25** and **26** were studied in three different solvents of increasing polarity, as well as at two different temperatures (298 and 77 K). In the case of **23**, a photoinduced pyrazoline-to- C_{60} electron transfer was observed at room temperature in all solvents. This transfer could be blocked by the addition of acid or on conversion to a rigid matrix at 77 K. In **25**, an OPV-to- C_{60} energy transfer was found in all solvents and this was followed by charge separation in PhCN to a significant extent. Compound **26** was arranged in such a way that the C_{60} unit could act either as an energy (for the OPV moiety) or electron (for the pyrazoline moiety) acceptor following excitation with light. Excitation of the OPV moiety or the fullerene chromophore triggered distinct photo processes. In addition to the choice of excitation wavelength, control over electron transfer was achieved by varying several parameters (or combinations of parameters) such as solvent polarity, acidity and temperature.

The incorporation of both of these features within a C_{60} unit was reported for the first time in compound **26**. These changes introduced a very interesting pattern in terms of the photophysical properties in the solution, making **26** a fullerene-based molecular switch in which

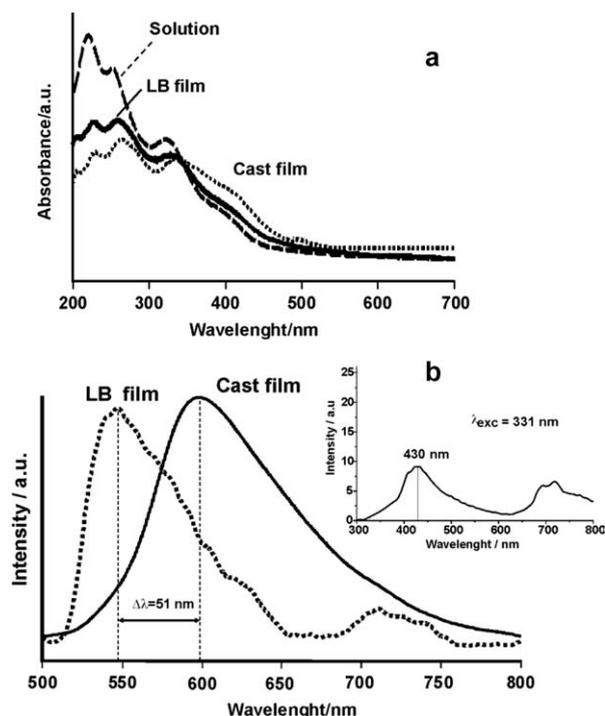


Fig. 24. (a) Steady-state UV-Vis absorption; (b) fluorescence spectra of **6a** in molecular films at $\lambda_{\text{exc}} = 488$ nm (spectra corrected to arbitrary units). Inset: fluorescence spectrum of a ca. 10^{-5} M CH_2Cl_2 solution excited at 331 nm.

the switchable parameters are photoinduced processes. The incorporation of **26** into photovoltaic devices resulted in a lower light-to-current efficiency than in **25**. This lower efficiency is due to the fact that charge separation involving the fullerene moiety and the pyrazoline nitrogen atom was unable to contribute to the photocurrent and, as such, the pyrazoline unit can act as an electron trap.

From a photochemical point of view, the behaviour of systems that incorporate a pyrazolino [60]fullerene moiety is complex. As discussed above, the pyrazoline ring itself should be considered as a photoactive unit and should be taken into account during the study of photoinduced processes.

Symmetrically substituted oligophenylenevinylene (OPV) derivatives bearing terminal *p*-nitrophenylhydrazone groups have been prepared and used for the synthesis of dumb-bell-shaped bis(pyrazolino [60]fullerene)–OPV systems **7a** and **7b** [48]. The photochemical behaviour and the self-assembly on surfaces of these triads have been investigated [93]. In these triad arrays, the OPV-type fluorescence was dramatically quenched as a consequence of ultrafast OPV-to- C_{60} singlet energy transfer. In turn, the fullerene singlet state was

quenched by a pyrazoline-to- C_{60} electron transfer process, in line with the behaviour of the corresponding reference fullerene molecule. The occurrence of electron transfer in the multicomponent arrays was evidenced by recovery of fullerene fluorescence at 77 K in CH_2Cl_2 and in toluene at 298 K. Under these conditions, the OPV-to- C_{60} energy transfer was not affected. The rate of this process turned out to be higher for the OPV trimer **7a** than for the corresponding pentameric OPV array **7b**, a situation in agreement with energy-transfer theory expectations. Scanning tunneling microscopy (STM) and scanning force microscopy (SFM) revealed that the bis(pyrazolino [60]fullerene)–OPV can self-assemble into ordered layered crystalline architectures on the basal plane of highly oriented pyrolytic graphite (HOPG) (Fig. 25).

Plastic solar cells were fabricated [94] using a low-band-gap alternating copolymer of fluorene and a donor–acceptor–donor moiety (APFO-Green1, **31**), blended with [6,6]-phenyl- C_{61} -butyric acid methylester or 3'-(3,5-bis-trifluoromethylphenyl)-1'-(4-nitrophenyl)pyrazolino [60]fullerene (**30**) as electron acceptors (Fig. 26). Devices based on APFO-Green1 (**31**) blended with the latter fullerene exhibited outstanding photovoltaic behaviour in the infrared range, where the external quantum efficiency was as high as 8.4% at 840 nm and 7% at 900 nm. This represents a demonstration of efficient photocurrent spectral response at a wavelength in the infrared range, with an onset at about 1 μm . A photocurrent density of 1.76 mA/cm², open-circuit voltage of 0.54 V and power conversion efficiency of 0.3% were achieved under the illumination of AM1.5 (1000 W/m²) from a solar simulator. These results were attributed to the LUMO energy match between the electron donor and acceptor, which supplies sufficient driving force for charge separation, but may be also attrib-

uted to a suitable interpenetrating network geometry in the devices.

In an effort to improve the performance of the plastic solar cells, the synthetic strategy developed for C_{60} fullerene was used to functionalize C_{70} . However, while reaction with C_{60} led to the formation of only one compound, reaction with C_{70} resulted in the formation of an isomeric mixture, which was nevertheless incorporated into photovoltaic cells [95]. A broad photocurrent spectral response in the wavelength range $300 < \lambda < 1000$ nm was obtained in these solar cells made with the low band-gap alternating copolymer of fluorene and a donor–acceptor–donor moiety (APFO-Green1 **31**) blended with 3'-(3,5-bis-trifluoromethylphenyl)-1'-(4-nitrophenyl)pyrazolino [70]fullerene (**32**) as an electron acceptor. In this case, a photocurrent density of 3.4 mA/cm², open circuit voltage of 0.58 V and

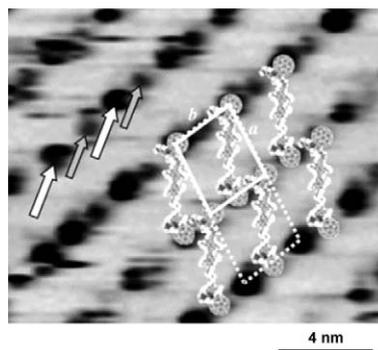


Fig. 25. STM current images of **7b** physisorbed at the solution–HOPG interface: zoom-in of a monocrystalline area. Arrows indicate dark spots, which are ascribed to fullerenes. Molecular shape and dimensions were obtained from energy minimization of a single isolated molecule using commercial software. For the sake of clarity, the alkyl chains are not shown. The 1×1 unit cell is drawn with a solid line and the 2×1 superstructure with a dashed line.

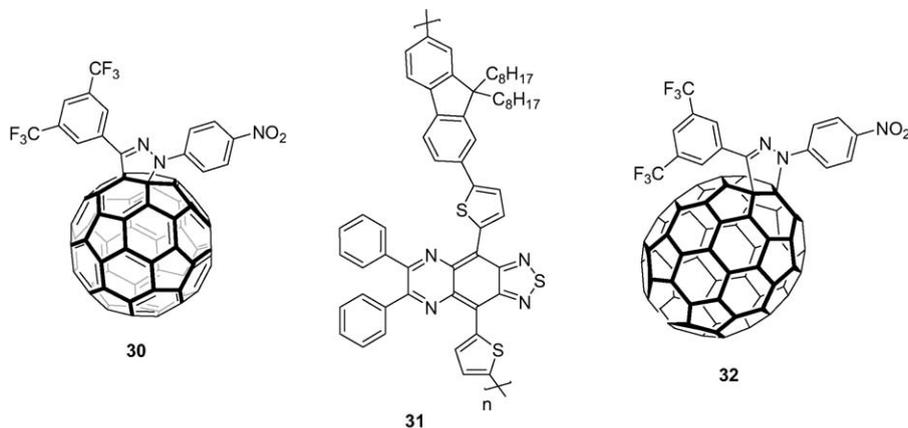


Fig. 26. Structures of compounds **30–32**.

power conversion efficiency of 0.7% were achieved under the illumination of AM1.5 (1000 W/m²) from a solar simulator. These results were attributed to efficient charge separation at the interface due to better matching of the LUMO levels of APFO-Green1 **31** and **32**, and also to a very significant photocurrent contribution from **32** due to its high charge transfer efficiency.

The overall results were better than those obtained in previous work on an APFO-Green1:**30**-based solar cell [94], which was the first demonstration of efficient infrared photocurrent spectral response with an onset photocurrent generation of 1 μm.

5. Concluding remarks

The cycloaddition of nitrile imines to [60]fullerene to afford pyrazolino [60]fullerene is a general and versatile procedure for the functionalization of C₆₀. This method has several advantages over other derivatization procedures: (1) hydrazones are readily available in one step from aldehydes in almost quantitative yields; (2) the cycloadducts are obtained in good yields; (3) the formation of stereoisomers does not occur—in contrast to other functionalization methods—and, most importantly, (4) unlike other fullerene derivatives, pyrazolino [60]fullerenes have reduction potentials similar to the parent C₆₀, which has proven to be an excellent three-dimensional electron acceptor. The electrochemical and photophysical properties of this new family of fullerene derivatives indicate that they are excellent candidates for the preparation of tailor-made donor–acceptor dyads or donor–donor–acceptor triads for photoinduced electron-transfer processes of interest in artificial photosynthetic systems and optoelectronic devices.

Acknowledgments

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