The importance of the linking bridge in donor–C_{60} electroactive dyads

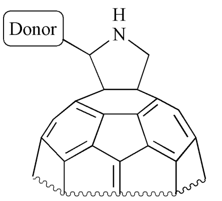
Fernando Langa,*[a] Pilar de la Cruz,[a] Juan L. Delgado,[a] María J. Gómez-Escalonilla,[a]
Araceli González-Cortés,[b] Antonio de la Hoz[c] and Vicente López-Arza[d]

[a] *Facultad de Ciencias del Medio Ambiente, Universidad de Castilla-La Mancha, 45071 Toledo, Spain. E-mail: flanga@amb-to.uclm.es; Fax: +34 9 2526 8840; Tel: +34 9 2526 8843*
[b] *Facultad de Química, Universidad Complutense, 28040 Madrid, Spain*
[c] *Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha, 45071 Ciudad Real, Spain*
[d] *Escuela de Ingenieros Técnicos Industriales, Universidad de Castilla-La Mancha, 45071 Toledo, Spain*

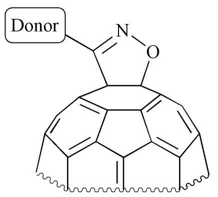
Received (in Montpellier, France) 6th July 2001, Accepted 17th September 2001
First published as an Advance Article on the web 20th December 2001

The synthesis, spectroscopic characterization, electrochemistry and photophysical measurements of three 2-methoxyphenylfullerene derivatives are described and their properties compared. Cyclic and Osteryoung square-wave voltammetry studies indicate that the pyrazolino[60]fullerene shows improved electron affinity in comparison to the parent C_{60}. Preliminary photophysical studies suggest the occurrence of an electron transfer process.

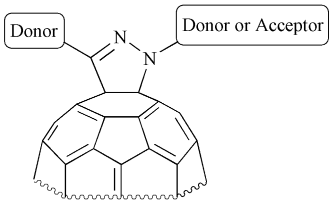
The dramatic increase in research into fullerenes since 1991 continues unabated[1] and intense effort is now focused on new fullerene-based materials and devices.[2] Due to their unique electrochemical[3] and photophysical properties,[4] the design of covalently linked donor–[60]fullerene systems that are capable of undergoing photoinduced electron transfer[5] has been extensively studied in recent years. C_{60} is an excellent electron acceptor, as demonstrated by cyclic voltammetry experiments in which six reversible one-electron reduction waves were observed.[6] However, the majority of C_{60} derivatives have a lower electronegativity than the parent system and attempts to increase the electron affinity of C_{60} have only met with partial success. Indeed, only a few examples of derivatives that exhibit better reduction potentials than the parent C_{60} have been described.[7] An improvement in the electron-accepting properties of fullerene derivatives may therefore lead to more efficient behavior in charge transfer processes.[8]



A



B



C

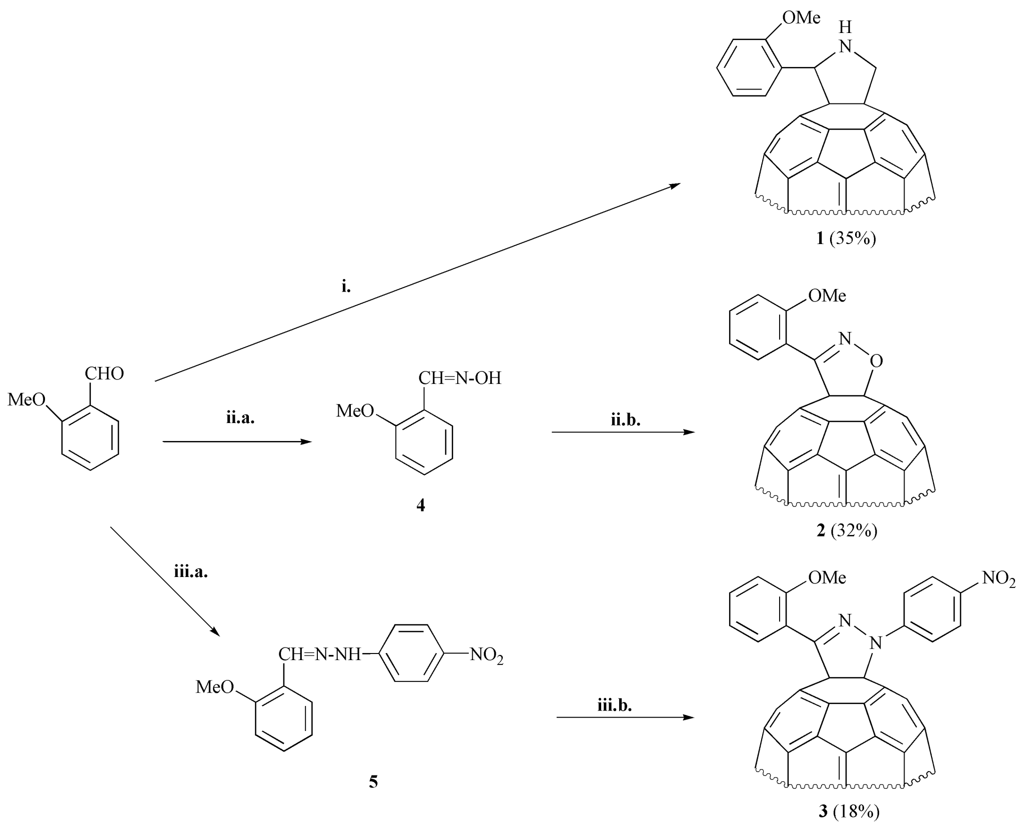
The 1,3-dipolar cycloaddition between azomethine ylides and C_{60} to afford pyrrolidino[60]fullerenes (**A**), a technique first developed by Prato, has for many years been the most widely used approach to link a donor to the fullerene cage.[9] The popularity of this method is due to the simplicity of the procedure and the good yields of isolated products. However, derivatization of C_{60} through this spacer causes a decrease in the electron affinity of the C_{60} sphere and leads to a displacement of reduction potentials to more negative values (by about 150 mV).[10] In this respect, the inductive effect of organic groups attached to the C_{60} core has proven to be the most important factor in determining the redox properties of organofullerenes. Indeed, we[11] and others[12] have shown that isoxazolo[60]fullerenes (**B**) are similar, or even better, acceptor systems than the parent C_{60}, depending on the nature of the organic addend. These fullerene derivatives can be easily synthesized by 1,3-dipolar cycloaddition reactions involving nitrile oxides, which can in turn be prepared from oximes. In contrast, the functionalization of C_{60} with 1,3-nitrile imines to give pyrazolino[60]fullerenes (**C**) has not been widely exploited.[13] We recently described the facile one-pot synthesis of such pyrazolyl-pyrazolino[60]fullerene systems from the corresponding hydrazones under microwave irradiation.[14]

We decided to compare the electrochemical and photophysical properties of cycloadducts formed by the incorporation of the same substituent into the molecule by different approaches. The work reported here describes the synthesis of three 2-methoxyphenylfullerene derivatives: the pyrrolidino[60]fullerene **1**, the isoxazolo[60]fullerene **2** and the pyrazolino[60]fullerene **3**. The spectroscopic and electrochemical properties of these donor–C_{60} derivatives are also described in order to assess how the spacer affects the properties of the molecule when a weak donor, such as the 2-methoxy group, is incorporated within the system.

Results and discussion

The syntheses of the target molecules **1**, **2** and **3** were performed according to Scheme 1. Pyrrolidino[60]fullerene **1** was prepared by a 1,3-dipolar cycloaddition reaction between the appropriate azomethine ylide (generated *in situ* from glycine

DOI: 10.1039/b106012k



Scheme 1 (i) C_{60}, H_2NCH_2COOH, toluene, microwave irradiation, (ii.a) $H_2NOH \cdot HCl$, CH_3COONa, EtOH, H_2O; (ii.b) NBS, C_{60}, Et_3N, benzene, microwave irradiation; (iii.a) 4-NO_2–C_6H_4–$NHNH_2$, EtOH, AcOH, reflux; (iii.b) NBS–benzene, C_{60}, Et_3N, microwave irradiation.

and 2-methoxybenzaldehyde) and C_{60} according to the well-established procedure first reported by Prato *et al.*[15] The cycloaddition proceeded in moderate yield (35% overall, 92% based on reacted C_{60}) by reaction of 2-methoxybenzaldehyde with glycine and [60]fullerene (Scheme 1, path i). Isoxazolo[60]fullerene **2** was synthesized (32% overall yield, 75% based on reacted C_{60}) in one pot by reacting 2-methoxybenzaldoxime (**4**; prepared in 81% yield by the reaction of 2-methoxybenzaldehyde with hydroxylamine hydrochloride; Scheme 1, path ii.a) with NBS in the presence of Et_3N. The resulting product was reacted *in situ* with C_{60} under focused microwave irradiation[16] according to our previously described procedure (Scheme 1, path ii.b).[11a] Finally, pyrazolino[60]fullerene **3** was prepared by a 1,3-dipolar cycloaddition between the corresponding nitrile imine and C_{60} under microwave irradiation according to our previously published method for other pyrazolino derivatives.[14] Firstly, 4-nitrophenylhydrazone (**5**; prepared in 80% yield by reaction of 2-methoxybenzaldehyde with 4-nitrophenylhydrazine; Scheme 1, path iii.a) was reacted with NBS in benzene. Et_3N and C_{60} were then added to the reaction mixture, which was irradiated for 40 min (210 W power in a focused microwave reactor) to afford **3** (Scheme 1, path iii.b) in 18% yield (82% based on reacted C_{60}). In all cases, cycloadducts were purified by column chromatography (silica gel, toluene–chloroform 2 : 1 for **1** and toluene–hexane 9 : 1 and 2 : 1, respectively, for **2** and **3**), followed by centrifugation in hexane, methanol and diethyl ether.

The novel compounds **1**, **2** and **3** were characterized by ^1H NMR, ^{13}C NMR, FT-IR, and UV-vis spectroscopy as well as by FAB-MS. The FAB mass spectra of adducts **1**, **2** and **3** show the MH^+ peaks together with several fragmentation peaks. All of the organofullerenes synthesized showed a weak absorption band at around 430 nm in their UV-vis spectra, which is a typical feature of 1,2-dihydrofullerenes.

The electrochemical properties of compounds **1**–**3** were studied by cyclic voltammetry (CV) and Osteryoung square-wave voltammetry (OSWV) at room temperature. The samples were dissolved in 1,2-dichlorobenzene–acetonitrile (4 : 1) and tetrabutylammonium perchlorate (TBAP) was used as the supporting electrolyte. The results of the OSWV studies are summarized in Table 1 and Fig. 1 along with, for the sake of comparison, the data for C_{60} itself.

The cyclic voltammogram of pyrrolidino[60]fullerene **1** shows four reversible reduction peaks and retains the electrochemical pattern of C_{60}. However, as previously described for other fullereno derivatives, the reduction potentials are shifted to more negative values when compared to those of C_{60}. In contrast, a different trend is found for isoxazolo[60]fullerene **2**. In this case, the reduction potentials are slightly shifted to more positive values in comparison to the parent C_{60} and this behavior is similar to that described recently, by ourselves and others, for this kind of fullerene derivative.[11,12]

Finally, pyrazolo[60]fullerene **3** shows four reversible reduction potentials, which are assigned to the C_{60} cage, as well as a fifth reduction potential situated between the second and the third potentials of C_{60}. This fifth potential is assigned to the reduction of the nitrophenyl group. Interestingly, compound **3** shows an anodic shift relative to both C_{60} and

Table 1 Redox potentials (OSWV) of organofullerenes **1**–**3** and C_{60}[a]

	E^1_{red}	E^2_{red}	E^3_{red}	E^4_{red}
C_{60}	−0.99	−1.42	−1.87	−2.41
1	−1.10	−1.51	−2.04	−2.36
2	−0.97	−1.37	−1.88	−2.36
3	−0.95	−1.38 (−1.64)	−1.80	−2.30

[a] V *vs.* $Ag/AgNO_3$; GCE as working electrode; 0.1 M TBAP; ODCB–MeCN (4 : 1); scan rate: 100 mV s^{-1}.

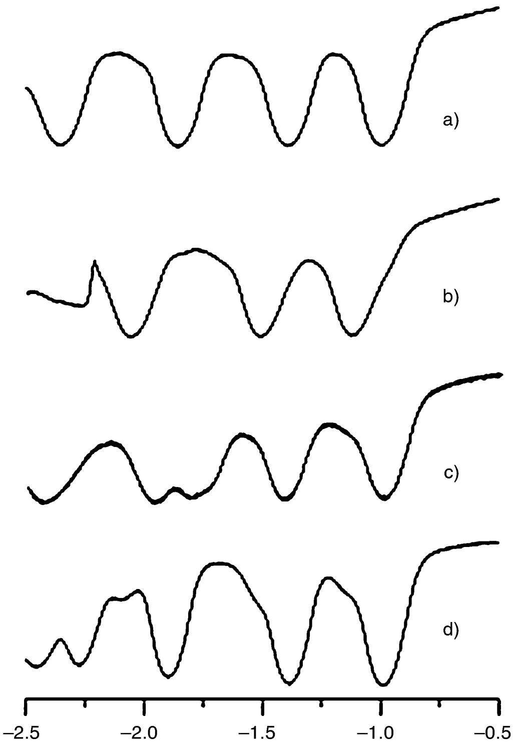


Fig. 1 Osteryoung square-wave voltammograms of C_{60} (a), **1** (b), **2** (c) and **3** (d).

compound **2**. The inductive effect of the nitrogen atom, which is close to the C_{60} cage, is thought to be responsible for this improved electron affinity.

The fluorescence spectra of fullerene derivatives **1**, **2**, **3** and, for the sake of comparison, the model *N*-methylpyrrolidino-[60]fullerene (**6**),[15] were measured at room temperature in toluene and benzonitrile with excitation at 430 nm (Table 2, Fig. 2). Solutions with the same absorbance were employed so that the fluorescence intensity and the quantum yields could be correlated.

When toluene was used as the solvent [Fig. 2(a), Table 2], the reference compound **6** presented a maximum at 717 nm and while compound **1** showed a maximum at 718 nm, which is in the expected region for this type of system.[8] The emission of **1** shows a similar intensity to that of the model compound **6**, indicating that **1** does not undergo photoinduced charge transfer under these conditions. On using solutions with the same absorbance, the fluorescence intensities were also found to be similar, indicating that the quantum yield should be almost equal.

A similar pattern was observed for the isoxazolo dyad **2** but the intensity of the emission was slightly lower and the maximum appeared at 706 nm. Finally, pyrazolino[60]fullerene **3** showed a maximum at 709 nm and a stronger reduction in the fluorescence emission with respect to the model compound **6** was observed [see Fig. 2(a) and Table 2].

Table 2 Fluorescence data of compounds **1**, **2**, **3** and **6**

	λ/nm (Rel. int.)	
	Toluene	Benzonitrile
1	718 (0.462)	722 (0.438)
2	706 (0.372)	710 (0.320)
3	709 (0.307)	705 (0.205)
6	717 (0.481)	722 (0.462)

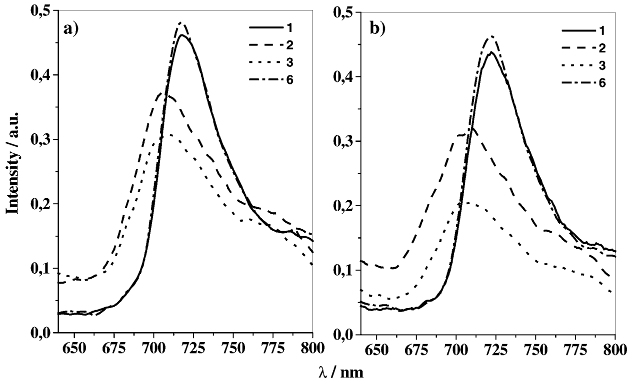


Fig. 2 Fluorescence spectra of compounds **1**–**3** and **6** in (a) toluene and (b) benzonitrile.

When benzonitrile was used as the solvent [Table 2, Fig. 2(b)], the maximum in **1** was red-shifted to 722 nm and the emission intensity remained practically unaffected (95%) with respect to that found in toluene (considered as 100%). The reference compound **6** shows the same behavior (relative intensity 96%). Previous studies on the photochemical properties of **6** indicated that the pyrrolidine ring nitrogen is not involved in charge transfer[17] and this fact explains why compound **1** shows similar emission behavior in toluene and benzonitrile. A similar red shift, with the maximum at 710 nm, was observed for compound **2** and a slight decrease in the fluorescence was observed, being 85% with respect to that found in toluene. In contrast, the maximum for compound **3** was blue-shifted to 705 nm in benzonitrile. In addition to this blue shift, a substantially lower fluorescence intensity (60% with respect to that in toluene) was observed.

The quenching of the fluorescence in pyrazolino[60]fullerene **3** as the polarity of the solvent is increased, suggests the occurrence of an electron transfer (ET) process from the lone pair of the sp^3 nitrogen atom to the C_{60} cage in benzonitrile. Such a process should be facilitated by the close proximity of these two moieties. Sun *et al.* observed a similar effect in a number of aminofullerene derivatives.[17]

Addition of TFA to benzonitrile solutions of **1** and **3** (*ca.* 10^{-7} M) produces opposite effects: for compound **1**, the addition of TFA ($[\mathrm{TFA}]/[\mathbf{1}] = 530$) caused a weak quenching of the fluorescence (by 30%) and the maximum was blue-shifted from 723 to 713 nm [Fig. 3(b)]. This phenomenon can be explained in terms of the formation of the pyrrolidinium salt of **1** (pyrrolidinium salts have shown better electron affinities than C_{60}[7a] and ET from donors in donor–pyrrolidinium[60]fullerene salts has been observed)[8] and the possibility

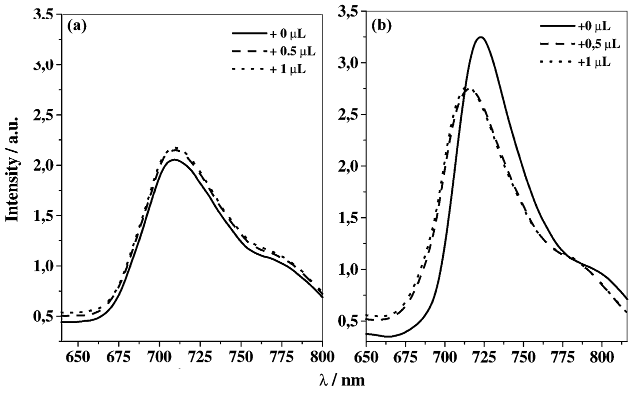
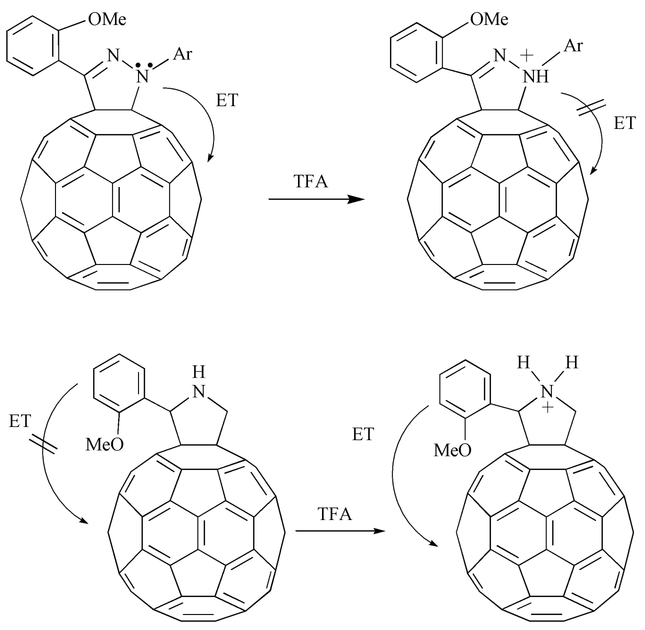


Fig. 3 Fluorescence spectra of a solution of (a) **3** and (b) **1** upon addition of increasing amounts of trifluoroacetic acid: (——) 0 µL, (------) +0.5 µL (+6.5×10^{-6} equiv.), (·····)+1 µL (+1.3×10^{-5} equiv.).



Scheme 2 Proposed mechanism for the quenching of the ET process in compound **3**.

that a weak ET process from the 2-methoxyphenyl moiety can occur (Scheme 2). On the other hand, addition of TFA to a solution of **3** ([TFA]/[**3**] = 450) in benzonitrile resulted in a slight increase in the fluorescence [Fig. 3(a)], which suggests quenching of the ET process by virtue of the fact that the nitrogen lone pair is no longer available (Scheme 2). The addition of base (pyridine) reversed this process and quenching of the fluorescence was observed once again.

Conclusions

We have shown that the use of pyrazolino[60]fullerenes as building blocks for donor–C_{60} systems has several advantages over other fullereno derivatives: (i) they can be prepared in one step from hydrazones by a simple procedure; (ii) the derivatives show improved electron affinities, even when compared to C_{60}; (iii) the preliminary photophysical studies suggest that an electron transfer process from the nitrogen atom to the C_{60} cage occurs in the pyrazolino[60]fullerene system.

Experimental

General

All cycloaddition reactions were performed under argon. Reactions under microwave irradiation were carried out in a focused reactor—Maxidigest MX-350 from Prolabo—equipped with an infrared temperature detector. The irradiation power and temperature were controlled with the program MPX-2 from PACAM. C_{60} was purchased from MER Corporation (Tucson, AZ) and the other starting materials were purchased from ACROS. Cycloaddition reactions were monitored by TLC using Merck silica gel 60-F_{254}. ^1H and ^{13}C, NMR spectra were recorded on a Varian Mercury 200 spectrometer. UV-vis absorption spectra were obtained using a Shimadzu spectrophotometer. FT-IR spectra were recorded on a Nicolet Impact 410 spectrophotometer using KBr disks. Fluorescence spectra were obtained on a JASCO FP-750 spectrophotometer.

FAB mass spectra were obtained on a VG AutoSpec instrument, using 3-nitrobenzyl alcohol as a matrix. Cyclic voltammetry measurements were carried out using a BAS 100 potentiostat with a BAS MF-2062 Ag/0.01 M $AgNO_3$, 0.1 M TBAP in MeCN reference electrode, an auxiliary electrode consisting of a Pt wire and a Metrohm 6.0805.010 conventional glassy carbon electrode (3 mm o.d.) as the working electrode, which was directly immersed in the solution. A 10 mL electrochemical cell from BAS (model VC-2) was also used. The reference potential was shifted by 290 mV towards a more negative potential compared with the Ag/AgCl scale. $E_{1/2}$ values were taken as the average of the anodic and cathodic peak potentials. The scan rate used was 100 mV s^{-1}.

Syntheses

2-Methoxybenzaldoxime (4). A solution of 2-methoxybenzaldehyde (1 g, 7 mmol) in ethanol (5 mL) was added to a solution of hydroxylamine hydrochloride (0.647 g, 7 mmol) and sodium acetate (0.574 g, 7 mmol) in water (5 mL). The solution was heated under reflux for 10 min. The crude product was purified by recrystallization from ethanol to afford the product **4** in 81% yield. FT-IR (KBr) ν/cm^{-1} 3168.1, 2870.5, 1627.4, 1599.7, 1496.2, 1465.1, 1439.0, 1320.2, 1304.9, 1258.4, 1199.3, 1171.9, 1111.3, 1051.1, 972.1, 949.1, 875.4, 786.4; ^1H NMR ($CDCl_3$) δ 3.88 (s, 3H), 6.95 (dd, $J = 8.1$, $J = 7.7$ Hz, 2H), 7.35 (t, $J = 8.1$ Hz, 1H), 7.67 (d, $J = 7.7$ Hz, 1H), 8.49 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 157.8, 146.9, 131.4, 127.4, 120.6, 111.3, 55.7; Anal. calc. for $C_8H_9NO_2$: C, 63.56, H, 6.00, N, 9.27; found: C, 63.50, H, 5.99, N, 9.15%.

3-(2-Methoxyphenyl)-1,*N*-(4-nitrophenyl)hydrazone (5). A solution of 2-methoxybenzaldehyde (1 g, 7 mmol), 4-nitrophenylhydrazine (1.124 g, 7 mmol) and two drops of acetic acid in ethanol (10 mL) was heated under reflux for 10 min. The crude product was purified by recrystallization from ethanol to afford compound **5** in 80% yield. FT-IR (KBr) ν/cm^{-1} 3270.0, 1586.7, 1493.9, 1460.8, 1314.9, 1235.4, 1102.8, 1016.6, 824.3, 744.7, 697.7, 532.6; ^1H NMR ($CDCl_3$) δ 3.88 (s, 3H), 6.93 (d, $J = 7.7$ Hz, 1H), 7.02 (dd, $J = 7.7$, $J = 7.3$ Hz, 1H), 7.11 (d, $J = 9.1$ Hz, 2H), 7.36 (d, $J = 8.1$, $J = 7.3$ Hz, 1H), 7.99 (d, $J = 8.1$ Hz, 1H), 8.1 (br s, 1H), 8.18 (d, $J = 9.1$ Hz, 2H), 8.25 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 157.6, 149.8, 137.8, 131.1, 126.5, 126.3, 122.8, 121.2, 111.8, 55.8; Anal. calc. for $C_{14}H_{13}N_3O_3$: C, 61.99, H, 4.83, N, 15.49; found: C, 61.78, H, 5.06, N, 15.65%.

2′-(2-Methoxyphenyl)pyrrolidino[3′,4′ : 1,2][60]fullerene (1). A solution of C_{60} (100 mg, 0.138 mmol), glycine (21 mg, 0.277 mmol) and 2-methoxybenzaldehyde (47 mg, 0.345 mmol) in toluene (50 mL) was stirred under reflux for 18 h. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel using a toluene–chloroform (2 : 1) mixture as eluent to yield 42 mg of **1** (35%, 92.5% based on reacted C_{60}). Further purification of the solid was achieved by centrifuging three times with methanol and once with diethyl ether. FT-IR (KBr) ν/cm^{-1} 2919.3, 2839.8, 1633.9, 1460.8, 744.7, 526.0; ^1H NMR ($CDCl_3$) δ 3.82 (s, 3H), 4.87 (d, $J = 11.3$ Hz, 1H), 5.12 (d, $J = 11.3$ Hz, 1H), 6.08 (s, 1H), 6.95 (d, $J = 8.06$ Hz, 1H), 7.06 (dd, $J = 7.33$, $J = 7.33$ Hz, 1H), 7.33 (dd, $J = 8.06$, $J = 8.06$ Hz, 1H), 7.72 (d, $J = 7.33$ Hz, 1H); ^{13}C NMR ($CDCl_3$–CS_2, 1 : 1) δ 157.8, 156.7, 154.4, 147.3, 146.4, 146.2, 145.5, 144.6, 142.8, 142.4, 142.3, 140.4, 136.2, 134.4, 131.1, 129.8, 128.5, 125.5, 121.4, 111.6, 63.0, 55.3; UV-vis (CH_2Cl_2) λ_{max}/nm (log ε) 705.0 (3.1), 662.5 (3.1), 431.0 (3.5), 308.0 (4.32), 256.5 (4.7); MS *m*/*z* 870 $[M+H]^+$, 720 $[C_{60}]^+$.

3′-(2-Methoxyphenyl)isoxazolo[4′,5′ : 1,2][60]fullerene (2). C_{60} (50 mg, 0.069 mmol) and Et_3N (21 mg, 0.21 mmol) were added to a stirred solution of anisaldoxime **4** (32 mg, 0.21 mmol) and NBS (38 mg, 0.21 mmol) in benzene (45 mL). The solution was irradiated for 10 min at 210 W power. The product was purified by flash chromatography on silica gel using a mixture of toluene–hexane (9 : 1) as eluent to yield 20 mg of **2** (32%, 75% based on reacted C_{60}). Further purification of the solid was achieved by centrifuging three times with methanol and once with diethyl ether. FT-IR (KBr) ν/cm^{-1} 2919.3, 2839.8, 1525.4, 1235.4, 751.4, 526.0; ^{1}H NMR ($CDCl_3$) δ 3.82 (s, 3H), 7.05 (d, $J = 8.4$ Hz, 1H), 7.13 (dd, $J = 7.7$, $J = 7.7$ Hz, 1H) 7.51 (dd, $J = 8.4$, $J = 7.7$ Hz, 1H), 7.67 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR ($CDCl_3$–CS_2, 1 : 1) δ 149.8, 147.9, 147.3, 146.3, 145.9, 145.5, 144.4, 142.9, 142.5, 141.8, 140.6, 140.2, 137.1, 135.7, 132.2, 131.7, 121.1, 111.7, 55.4; UV-vis (CH_2Cl_2) $\lambda_{\max}$/nm ($\log \varepsilon$) 686.0 (3.4), 457.0 (4.0), 425.0 (4.14), 316.0 (5.4), 255.5 (5.04); MS m/z 870 $[M + H]^+$, 720 $[C_{60}]^+$.

3′-(2-Methoxyphenyl)-1′-(4-nitrophenyl)pyrazolino[4′,5′ : 1,2]-[60]fullerene (3). C_{60} (50 mg, 0.069 mmol) and Et_3N (21 mg, 0.21 mmol) were added to a stirred solution of hydrazone **5** (56 mg, 0.21 mmol) and NBS (38 mg, 0.21 mmol) in benzene (45 mL). The solution was irradiated for 40 min at 210 W power. The product was purified by flash chromatography on silica gel using a mixture of toluene–hexane (2 : 1) as eluent to yield 16 mg of **3** (18%, 82% based on reacted C_{60}). Further purification of the solid was achieved by centrifuging three times with methanol and once with diethyl ether. FT-IR (KBr) ν/cm^{-1} 2916.5, 2843.8, 1985.7, 1640.9, 784.6, 522.9; ^{1}H NMR ($CDCl_3$) δ 3.08 (s, 3H), 7.05 (d, $J = 8.4$ Hz, 1H), 7.15 (dd, $J = 7.3$, $J = 6.8$ Hz, 1H), 7.52 (dd, $J = 6.8$, $J = 8.4$ Hz, 1H), 7.67 (d, $J = 7.3$ Hz, 1H), 8.24 (d, $J = 9.5$ Hz, 1H), 8.31 (d, $J = 9.5$ Hz, 1H); ^{13}C NMR ($CDCl_3$–CS_2, 1 : 1) δ 158.4, 150.1, 147.7, 142.1, 141.9, 137.3, 135.0, 132.0, 131.9, 125.4, 120.9, 118.9, 111.7, 55.4; UV-vis (CH_2Cl_2) $\lambda_{\max}$/nm ($\log \varepsilon$) 689.0 (2.7), 426 8 (3.3), 324.0 (4.1), 256.5 (4.7); MS m/z 990 $[M + H]^+$, 720 $[C_{60}]^+$.

Acknowledgement

Support of this work by the DGESIC of Spain (PB 97-0429) is gratefully acknowledged.

References

1 T. Braun, A. P. Schubert and R. N. Kostoff, *Chem. Rev.*, 2000, **100**, 23.

2 (*a*) M. Prato, *J. Mater. Chem.*, 1997, **7**, 1097; (*b*) F. Diederich and M. Gómez-López, *Chem. Soc. Rev.*, 1999, **28**, 263; (*c*) J. F. Nierengarten, *Chem. Eur. J.*, 2000, **6**, 3667.

3 L. Echegoyen and L. E. Echegoyen, *Acc. Chem. Res.*, 1998, **31**, 593.

4 (*a*) D. M. Guldi, *Chem. Commun.*, 2000, 321; (*b*) D. Gust, T. A. Moore and A. L. Moore, *Acc. Chem. Res.*, 2001, **34**, 40.

5 H. Imahori and Y. Sakata, *Eur. J. Org. Chem.*, 1999, 2445.

6 Q. Xie, F. Arias and L. Echegoyen, *J. Am. Chem. Soc.*, 1993, **115**, 9818.

7 (*a*) T. Da Ros, M. Prato, M. Carano, P. Ceroni, F. Paolucci and S. Bofia, *J. Am. Chem. Soc.*, 1998, **120**, 11 645; (*b*) N. Martín, L. Sánchez, B. Illescas and I. Pérez, *Chem. Rev.*, 1998, **98**, 2527; (*c*) D. M. Guldi, S. González, N. Martín, A. Antón, J. Garín and J. Orduna, *J. Org. Chem.*, 2000, **65**, 1978; (*d*) M. Prato, Q. Li, F. Wudl and V. Lucchini, *J. Am. Chem. Soc.*, 1993, **115**, 1148; (*e*) M. Keshavarz, R. González, R. G. Hicks, G. Srdanov, V. I. Srdanov, T. G. Colins, J. C. Hummelen, C. Bellavia-Lund, J. Pavlovich, F. Wudl and K. Holczer, *Nature*, 1996, **383**, 147.

8 D. M. Guldi and M. Prato, *Acc. Chem. Res.*, 2000, **33**, 695.

9 M. Prato and M. Maggini, *Acc. Chem. Res.*, 1998, **31**, 519.

10 M. Maggini, A. Karlsson, G. Scorrano, G. Sandonà, G. Farnia and M. Prato, *J. Chem. Soc., Chem. Commun.*, 1994, 589.

11 (*a*) P. de la Cruz, E. Espíldora, J. J. García, A. de la Hoz, F. Langa, N. Martín and L. Sánchez, *Tetrahedron Lett.*, 1999, **40**, 4889; (*b*) F. Langa, P. de la Cruz, E. Espíldora, A. González-Cortés, A. de la Hoz and V. López-Arza, *J. Org. Chem.*, 2000, **65**, 8675.

12 (*a*) H. Irgantingen, P. W. Fettel, T. Escher, P. Tinnefeld, S. Nord and M. Sauer, *Eur. J. Org. Chem.*, 2000, 455; (*b*) B. M. Illescas and N. Martín, *J. Org. Chem.*, 2000, **65**, 5986.

13 (*a*) Y. Matsubara, H. Tada, S. Nagase and Z. Yoshida, *J. Org. Chem.*, 1995, **60**, 5372; (*b*) Y. Matsubara, H. Muraoka, H. Tada and Z. Yoshida, *Chem. Lett.*, 1996, 373.

14 P. de la Cruz, A. Díaz-Ortiz, J. J. García, M. J. Gómez-Escalonilla, A. de la Hoz and F. Langa, *Tetrahedron Lett.*, 1999, **40**, 1587; (*b*) F. Langa, P. de la Cruz, E. Espíldora, A. De la Hoz, J. L. Bourdelande, L. Sánchez and N. Martín, *J. Org. Chem.*, 2001, **66**, 5033.

15 N. Maggini, G. Scorrano and M. Prato, *J. Am. Chem. Soc.*, 1993, **115**, 9798.

16 A. de la Hoz, A. Díaz-Ortíz, A. Moreno and F. Langa, *Eur. J. Org. Chem.*, 2000, 3659.

17 Y. P. Sun, B. Ma and C. E. Bunker, *J. Phys. Chem. A*, 1998, **102**, 7580.