Synthesis and Properties of Isoxazolo[60]fullerene−Donor Dyads[†]

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A series of isoxazolo[60]fullerenes has been prepared in one pot from aldoximes under microwave irradiation. Several donors and acceptors were used as substituents. The absorption and emission spectra of these compounds in polar solvents suggest a weak charge-transfer interaction between the oxygen atom of the isoxazoline moiety and the C_{60} cage, as well as a stronger interaction between the donor and the fullerene cage when the attached groups are *p-N,N*-dimethylaniline or ferrocene. The electrochemical properties of the compounds were investigated and they show the same or better acceptor character than C_{60} in all cases. Theoretical calculations support the results obtained. Solvent effects in the ^{1}H NMR spectra have been determined and provide useful information concerning the polarization of dyads.

Introduction

The structure and reactivity of fullerenes have attracted considerable attention in a variety of research areas.[1] The photophysical and photochemical properties of fullerenes have been the subject of numerous studies because fullerene cages are ideal building blocks for donor−acceptor-type three-dimensional redox molecular systems. A number of potential technological applications exist for these materials,[2] particularly in the construction of solar energy conversion systems that mimic the primary electron-transfer events in photosynthesis.[3] This objective is a consequence of the remarkable acceptor properties of C_{60}, which allow the design and preparation of fullerene−donor dyads. However, most C_{60} derivatives have a lower electronegativity than C_{60} itself,[4] and only a few examples that exhibit better reduction potentials than the parent system have been described.[5] Thus, the design and synthesis of novel organofullerenes with improved electron affinity is still a desirable goal for the development of specific optical and electronic applications.[6]

The dipolar cycloaddition of nitrile oxides to C_{60} is a widely used procedure to prepare fullerene derivatives,[7] and a variety of isoxazolofullerenes have been synthesized since the first days of fullerene chemistry. The lack of available electrochemical data for this family of compounds up to 1999 is surprising; in only one case[7c] (R = CO_2Et) has a cyclic voltammetry (CV) study been performed, although no experimental data were reported and a brief comment indicated that the reduction potential is very similar to that of C_{60}. Recently, we described[8] the one-pot preparation of 3-(*N*-phenyl-4-pyrazolyl)- (**1a**) and 3-(*N*-phenyl-5-pyrazolyl)isoxazolo[60]fullerene (**1b**) from the corresponding aldoxime and C_{60}; the CV measurements were carried out and revealed that both compounds have a better acceptor ability than C_{60}. During the preparation of this manuscript, Irngartinger et al.[9] described the redox properties of several isox-

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Chart 1
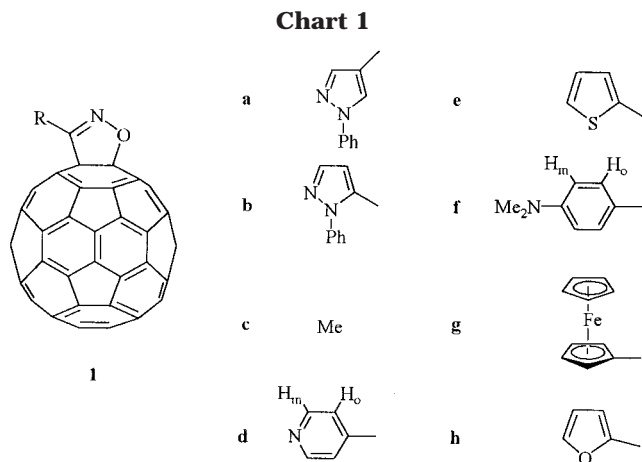
azolofullerenes showing similar behavior. In this paper, we describe the electrochemical and photophysical behavior of isoxazolo[60]fullerenes **1a**−**h** with the aim of determining the influence of π-acceptor and a π-donor moieties on the properties of the molecule. All of the compounds were prepared from the corresponding aldoxime, NBS or NCS and C_{60} under microwave irradiation.[10] The effect of solvent polarity on the ^{1}H NMR spectra is also described.

Results and Discussion

Although the most common way to generate nitrile oxides involves the use of hydroxymoyl chlorides or nitroalkanes as starting materials, in our case the corresponding oxime **2a**−**h** was treated with NBS or NCS in the presence of Et_3N. The resulting product was reacted in situ with C_{60} under focused microwave irradiation, which has proven to be a useful technique in fullerene chemistry.[11,12] Under these conditions, adducts **1a**−**h** (Chart 1) were obtained in moderate yields (16−36%) after isolation by flash chromatography on silica gel followed by centrifugation in hexane, methanol, and diethyl ether. The new compounds were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, and UV−vis spectroscopy as well as by FAB-MS. The FAB mass spectra of adducts **1a**−**h** show the MH^+ peaks together with several fragmentation peaks. The ^{1}H NMR spectra of these compounds show the signals corresponding to the organic addend. The chemical shifts of these signals are at remarkably low field in comparison to the corresponding starting oxime (see Table 3). These shifts have been attributed in other fullerene derivatives to the formation of a CT complex between the organic addend and the C_{60} cage.[13] However, the electron-deficient nature of the pyridine moiety seems to rule out this possibility in **1d**, indicating that the close proximity of the C_{60} core to the
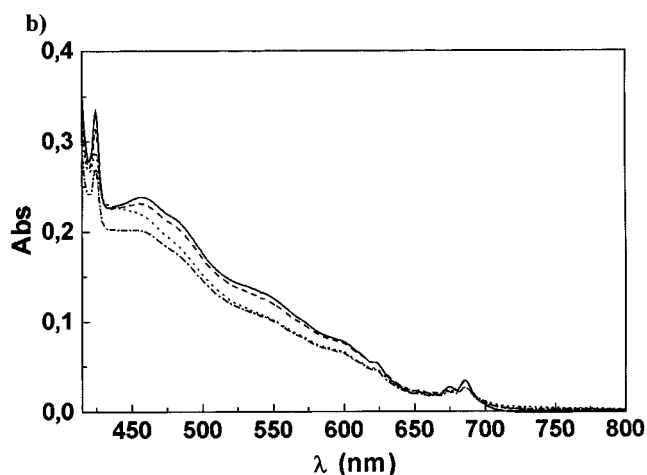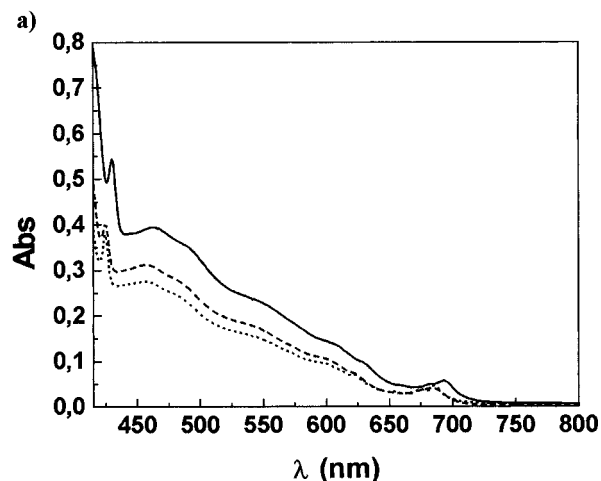
Figure 1. (a) Room-temperature UV−vis spectra of **1c** in cyclohexane (···), dichloromethane (- -), and carbon disulfide (−). (b) UV−vis spectra of **1c** in cyclohexane on addition of 98% H_2SO_4: (−) without, (- -) 1 drop, (···) 3 drops, (·-··) 5 drops.

heterocyclic substituent and also the loss of planarity of the isoxazoline ring and the heterocyclic substituent in fullerene adducts **(1)** should be responsible for this low field shift. Similar shifts have been observed in porphyrin−C_{60} derivatives.[14] Theoretical calculations confirm both the loss of planarity and the proximity of the two moieties (vide infra).

Absorption Spectra. The UV−vis spectra of this family of cycloadducts exhibit the typical absorption band at around 430 nm, which is characteristic of [6,6] bridged monoadducts, and a weak 0−0 absorption band with maxima at around 690 nm. In all cases, as depicted in Figure 1 for **1c**, a broad band is observed in the region 440−650 nm, which is red-shifted on increasing the solvent polarizability (see Table 1).[15]

This solvent-shifted band has been attributed to the formation of CT complexes[16] in C_{60} dyads with donors. In some of the molecules reported in this work there are no strong donors in the organic addend, and so it can be suggested that CT complexes can only be formed between

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Chart 2

3   4
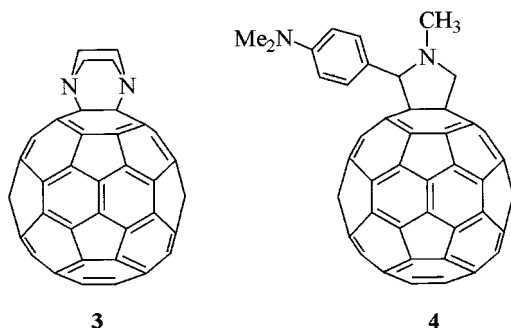
the lone pairs of the oxygen atom and the C_{60} cage due to the proximity of these two moieties. Sun et al. demonstrated that amino derivative **3** (Chart 2) shows an intramolecular $n \rightarrow \pi^*$ electron transfer[17] due to the short nitrogen−cage distance. Consequently, a similar situation can be expected in isoxazolo[60]fullerenes where the disposition of the oxygen atom is similar. To investigate this possibility, sulfuric acid was added to a solution of **1c** (Figure 1b), and a hypochromic shift was observed in this broad band, which possibly indicates the inhibition of the charge-transfer interaction by protonation.[18]

When a strong donor moiety, such as an *N,N*-dimethylaniline group, is incorporated into the molecule, e.g., dyad **1f**, a new broad band in the region of 550−650 nm appears (Figure 2a); this band is particularly intense in the more polarizable solvent carbon disulfide, indicating the possibility of electron transfer from the nitrogen lone pair. The addition of TFA causes the disappearance of this band, as one would expect, due to the lack of freedom of the nitrogen lone pair. The electron transfer from the aniline group to the fullerene cage has already been reported to occur in polar solvents by Williams and Verhoeven in pyrrolidinofullerene derivative **4** (Chart 2).[19] The difference in our case is the much better electron acceptor ability of the C_{60} cage (vide infra) for the isoxazolo[60]fullerene in comparison to the pyrrolidino-[60]fullerene (about 150 mV), which should facilitate the electron transfer in less polar solvents, as indeed is seen in the UV−vis and fluorescence spectroscopy. A similar situation is observed in ferrocene dyad **1g**.

Fluorescence Measurements. The fluorescence spectra of isoxazolo[60]fullerene derivatives **1a−h** were measured at room temperature in cyclohexane upon excitation at 430 nm. At this excitation wavelength only the C_{60} moiety can be excited. With the exceptions of *N,N*-dimethylanilino (**1f**) and ferrocene (**1g**) cycloadducts, all compounds show similar spectra that are comparable to other fullerene derivatives. The spectra each contain a maximum at about 690 nm and a shoulder at around 760 nm. As expected, the spectra are independent of the excitation wavelength (Figure 3 and Table 2). Solutions with the same absorbance were employed and so the fluorescence intensity can be correlated with the quantum yields. These results suggest that even in nonpolar solvents such as cyclohexane **1f** and, in particular, **1g** could show electron transfer, as indicated by the absorption spectra studies.
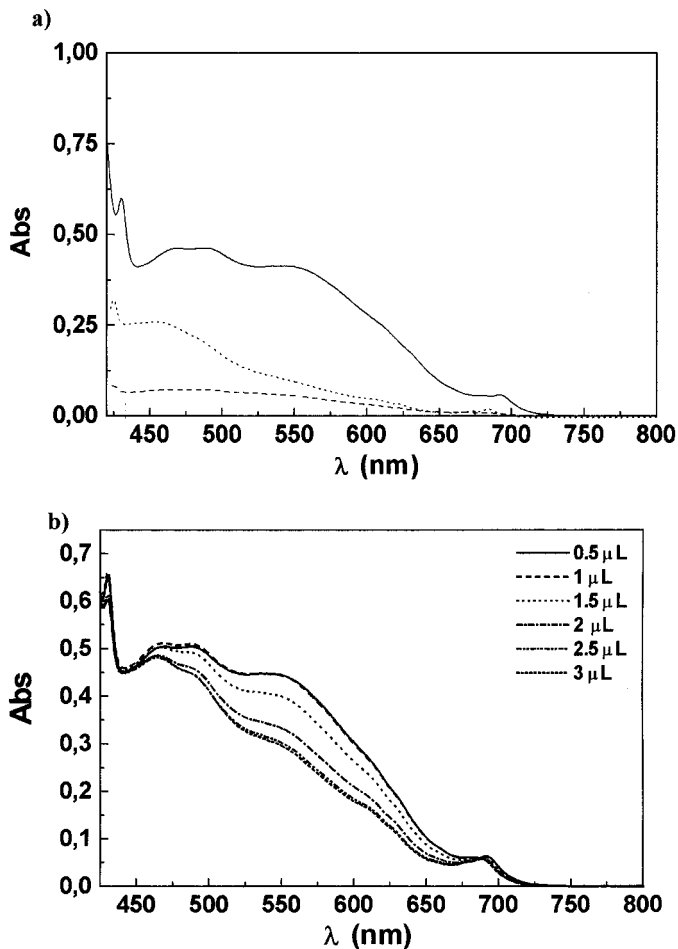
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a)

b)

Figure 2. (a) Room-temperature UV−vis spectra of **1f** in cyclohexane (···), dichloromethane (- -), and carbon disulfide (−). (b) UV−vis spectra of **1f** in cyclohexane on addition of TFA.
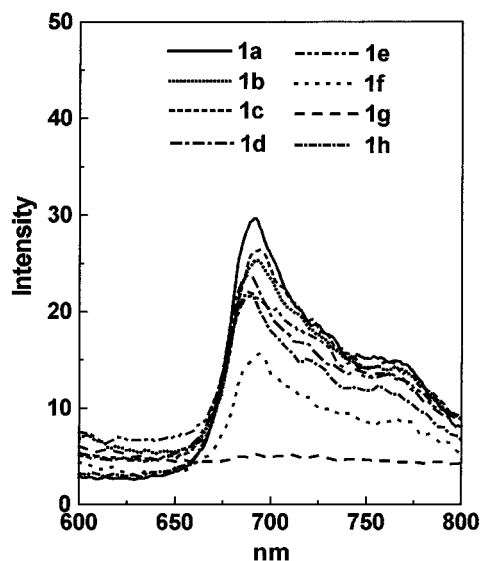

Figure 3. Fluorescence spectra of compounds **1a−h** in cyclohexane as solvent.

The effect of solvent on the profile of the fluorescence spectra was examined by measuring fluorescence spectra in benzonitrile solutions and, in some cases, toluene. All compounds show solvatochromic red-shifts with maximum about 700 nm. This red shift in benzonitrile as compared to cyclohexane has been assigned in other

Table 1. Absorption Data for Compounds 1a–h in Different Solvents

	λ_{max} (nm) (log ϵ)		
compd	CS$_2$	CH$_2$Cl$_2$	C$_6$H$_{12}$
1a	430 (5.45), 462 (5.29), 493 5.17), 547 (4.97),681 (4.21), 691 (4.26)	424 (5.34), 450 (5.19), 487 (5.09), 543 (4.90), 682 (5.18)	425 (5.04), 448 (4.89), 484 (4.89), 541 (5.69), 673 (3.89), 684 (3.95)
1b	430 (5.10), 463 (4.99), 487 (4.94), 543 (4.73), 682 (4.00), 691 (4.06)	425 (4.55), 458 (4.47), 482 (4.69), 544 (4.46), 681 (3.61)	425 (5.29), 448 (5.18), 477 (4.39), 540 (4.12), 674 (4.25), 685 (4.34)
1c	430 (5.43), 462 (5.29), 551 (5.05), 684 (4.40), 693 (4.45)	424 (5.30), 456 (5.19), 541 (4.95), 683 (4.31)	425 (5.28), 455 (4.14), 539 (4.90), 674 (4.29), 685 (4.36)
1d	430 (5.45), 463 (5.34), 542 (5.09), 679 (4.36), 689 (4.42)	426 (5.33), 454 (5.25), 523 (5.02), 680 (4.32)	425 (5.29), 452 (5.19), 518 (4.98), 671 (4.24), 682 (4.32)
1e	428 (5.45), 461 (5.30), 554 (4.95), 690 (4.19)	424 (5.16), 449 (5.07), 539 (4.82), 674 (4.27)	425 (4.96), 445 (4.83), 539 (4.40), 684 (3.47)
1f	430 (3.43), 455 (3.34), 468 (3.36), 487 (3.36), 543 (3.31), 692 (2.46), 845 (2.46)	425 (3.43), 464 (3.37), 547 (3.25), 684 (2.50)	425 (3.20), 454 (3.11), 478 (3.05), 543 (2.71), 684 (1.98)
1g	430 (3.64), 455 (3.49), 486 (3.41), 549 (3.21), 691 (2.89), 847 (1.30)	425 (3.39), 455 (3.28), 486 (3.20), 543 (3.05), 675 (2.66)	425 (3.24), 455 (3.13), 484 (3.08), 549 (2.95), 684 (2.69), 847 (1.74)
1h	430 (3.43), 450 (3.31), 544 (2.95), 689 (2.19), 834 (1.00)	424 (3.31), 450 (3.20), 544 (2.87), 679 (2.23)	424 (3.13), 455 (3.04), 544 (2.75), 680 (2.30), 852 (1.30)

Table 2. Fluorescence Data of Compounds 1a–h

	maxima (nm)	
compd	cyclohexane	benzonitrile
1a	692 (29.645), 723 (18.687), 754 (15.310)	698 (22.809)
1b	692 (25.394), 766 (14.106)	698 (20.509), 764 (11.453)
1c	693 (25.940), 761 (14.625)	702 (19.633)
1d	688 (23.846), 717 (16.806), 745 (14.006), 760 (13.524)	703 (18.313)
1e	691 (21.397), 758 (13.559)	698 (19.623)
1f	693 (15.140), 766 (8.651)	693 (2.684), 722 (2.421), 763 (1.858)
1g	693 (5.047), 707 (5.039), 745 (4.652)	0
1h	688 (21.758), 719 (14.940), 757 (12.118)	704 (10.950), 764 (6.102)

Table 3. Chemical Shifts for Dyads 1a–g and Oximes 2a–g in C$_6$D$_6$ (E^N_T: 0.111);[15] CDCl$_3$ (E^N_T: 0.259);[15] and CD$_2$Cl$_2$ (E^N_T: 0.309)[15]

		1				**2**			
compd	solvent	C$_6$D$_6$	CDCl$_3$	CD$_2$Cl$_2$	slope	C$_6$D$_6$	CDCl$_3$	CD$_2$Cl$_2$	slope
a	H$_3$	8.65	8.74	8.76	0.56	8.22	8.63	8.66	2.34
	H$_5$	8.46	8.52	8.50	0.25	7.81	8.01	8.05	1.20
b	H$_3$	7.66	7.84	7.86	1.05	7.67	7.68	7.65	−0.06
	H$_4$	6.79	7.04	7.12	1.67	6.81	6.81	6.80	−0.04
c	Me	2.18	2.75	2.74	3.06	1.54	1.83	1.87	1.73
d	H$_o$	7.83	8.12	8.58	3.37	6.95	7.51	7.56	3.42
	H$_m$	8.52	8.79	8.87	1.78	8.37	8.64	8.64	1.46
e	H$_3$	7.98	8.05	8.12	0.65	6.92	7.55	7.63	3.74
	H$_4$	6.59	7.17	7.22	3.35	6.57	7.08	7.14	3.00
	H$_5$	6.81	7.55	7.64	4.37	6.77	7.38	7.37	3.28
f	H$_o$	8.36	8.14	8.21	−0.92	7.47	7.43	7.44	−0.18
	H$_m$	6.43	6.82	7.23	3.72	6.34	6.67	6.71	1.95
	Me	2.33	3.04	3.10	4.09	2.32	2.98	3.00	3.67
g	H$_2$	5.26	5.21	5.25	−0.11	4.34	4.51	4.53	1.00
	H$_3$	4.12	4.53	4.60	2.50	4.25	4.35	4.38	0.66
	H$_{Cp'}$	4.00	4.18	4.24	1.21	3.87	4.21	4.24	1.96

fullerene–donor dyads to CT character.[20] In all cases in which benzonitrile was used as the solvent, the fluorescence was quenched in comparison to cyclohexane solutions (Figure 4). This quenching is more marked when a donor is incorporated into the molecule, such as in **1f** where the fluorescence in toluene is very weak and becomes negligible in benzonitrile (Figure 5). Thus, the partial quenching of the fluorescence in dyads **1a–e** and **1h** can be ascribed to a weak charge-transfer interaction in the excited state between the C$_{60}$ moiety and one of the oxygen lone pairs. Such an interaction should be stronger in those systems that contain a strong donor as a substituent.

Effect of Solvent on ^{1}H NMR Spectra. Solvent-dependent NMR studies were undertaken to show that the ground-state structure of push–pull polyenes can be significantly affected by solvent polarity. Previous ex-

perimental NMR studies have shown that the electronic structure of merocyanine[21] dyes can be modulated by solvent polarity and the results are consistent with the stabilization of the zwitterionic form by polar solvents. Polar compounds are orientated and/or polarized by surrounding solvent molecules, thus creating an electric reaction field. For polar molecules in polar solvents, significant reaction fields can be attained and these, in turn, can polarize the solute molecules. The magnitude of this effect is related to the polarizability of the molecule and it can be used to study the effect of solvent polarity on ground-state structures in support for NLO properties.[22,23]

The evolution of the chemical shifts of cycloadducts **1a–g**, as well as the corresponding oximes **2a–g**, with the solvent polarity was measured and the results are presented in Table 3 together with the E_T^N values as

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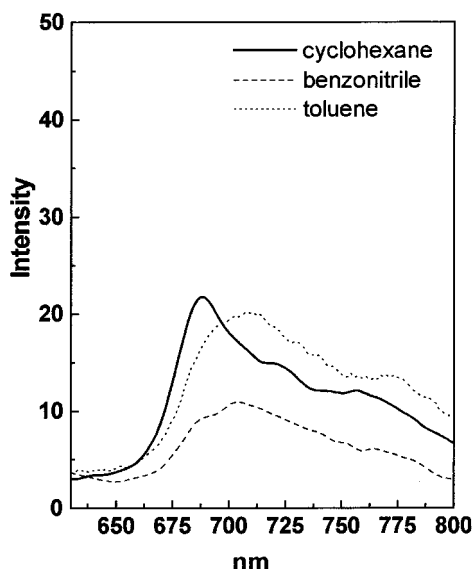
Figure 4. Fluorescence spectra of compound **1h** in cyclohexane (−), toluene (···), and benzonitrile (----) as solvents.
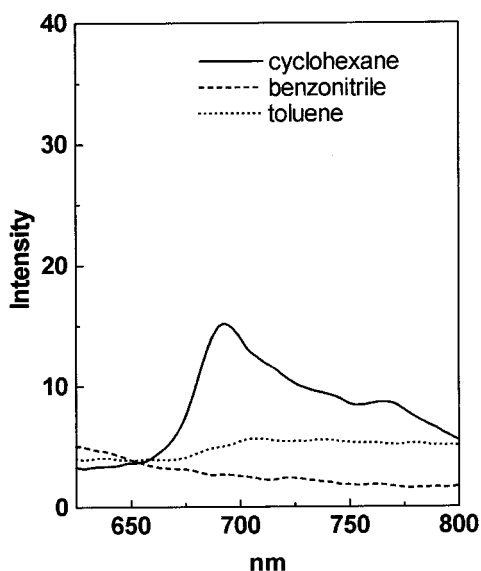

Figure 5. Fluorescence spectra of compound **1f** in cyclohexane (−), toluene (···), and benzonitrile (----) as solvents.

empirical parameters of solvent polarity. A very good linear correlation was found in all cases.

Both series, i.e., cycloadducts **1** and oximes **2**, show a low-field shift upon increasing the solvent polarity, with the exception of certain protons. This fact indicates that the compounds in both series are polar.

A comparison of the slopes of the linear plots for the oximes and cycloadducts leads to interesting conclusions about the nature of the compounds, the substitution, and especially the influence of the fullerene moiety. In these plots, a higher slope is indicative of a higher polarization. From the data in Table 3 it can be deduced that cycloadducts **1** are more polar than oximes **2** apart from the dyad **1a** and possibly **1d**. This effect, as well as the magnitude of the difference, depends on the nature of the substituent at the isoxazoline ring. The presence of

electron-withdrawing substituents (series **a** and **d**) gives rise to smaller slopes in the isoxazoline (Figures 6a and 6d), while electron donating substituents give rise to higher slopes in the isoxazoline. The difference increases with the increasing donating character of the substituent, being higher in the series **f** and **g**, which contain the strongly donating substituents *p-N,N*-dimethylanilino and ferrocenyl (Figure 6, parts e and f, respectively).

The influence of the fullerene moiety is evident and this effect is enhanced with increasing electron-donating character of the substituent. Considering the electron-acceptor character of the fullerene, this higher deshielding effect is indicative of a charge-transfer process from the substituted isoxazoline to the fullerene moiety in the ground state.

The deshielding effect and the higher slope in the cycloadducts are especially evident in protons close to the donor part of the molecule. Consequently, from the data displayed in Table 3, it can be deduced that the charge transfer is produced from the isoxazoline ring in **1b** and **1c** and from the substituent in **1e**−**g**. A higher degree of deshielding (with respect to the corresponding oxime) is observed for H3, which is close to the isoxazoline ring, in **1b** and for the methyl group, which is directly attached to the isoxazoline ring, in **1c**. The NMR data of compounds **1e**−**g** show that in compound **1e** the higher deshielding is observed for H5, the proton closest to the thiophene sulfur, and, to a lesser extent, for H4. In **1f**, H3 and the *N*-methyl group are deshielded in comparison to the corresponding protons in **2f**. Finally, in **1g** a greater degree of deshielding is observed for H3 and the cyclopentadiene ring.

One question arises from this study: why is charge transfer observed in **1b** and not in the isomeric compound **1a**? ^{13}C NMR spectroscopy and theoretical calculations shed light on this question. In 4-substituted pyrazoles conjugation of the pyrazole ring with the phenyl group is extensive, as indicated by the difference $\delta_{m-C} - \delta_{o-C} = 10.04$[24] in **1a** and the PM3-calculated dihedral angles phenyl-pyrazole (9.76°) and isoxazoline−pyrazole (32.02°). In these cases, the electron density of the π-excedent pyrazole ring is directed to the phenyl group. The high electron density at the phenyl group is shown by the strong shielding of the *o*-C, as indicated by the low chemical shift for this signal ($\delta = 117.71$). However, in 5-substituted pyrazoles, the conjugation of the pyrazole ring with the phenyl group is hindered, as indicated by the difference $\delta_{m-C} - \delta_{o-C} = 3.76$[24] in **1b** and the calculated dihedral angles phenyl−pyrazole (88.09°) and isoxazoline−pyrazole (11.98°). The higher chemical shift of the *o*-C ($\delta = 124.12$) in **1b** confirms that the electron density is not directed to the phenyl group. In this case, the electron density of the π-excedent pyrazole ring should be directed toward the isoxazoline ring, thus favoring the charge-transfer process toward the fullerene moiety (Figure 7).

In conclusion, NMR spectroscopy is a good and reliable method to obtain information about charge-transfer processes in the ground state in donor−acceptor systems.

Electrochemical Study. The redox properties of compounds **1a**−**h** were investigated by cyclic voltammetry at room temperature in *o*-dichlorobenzene/acetonitrile

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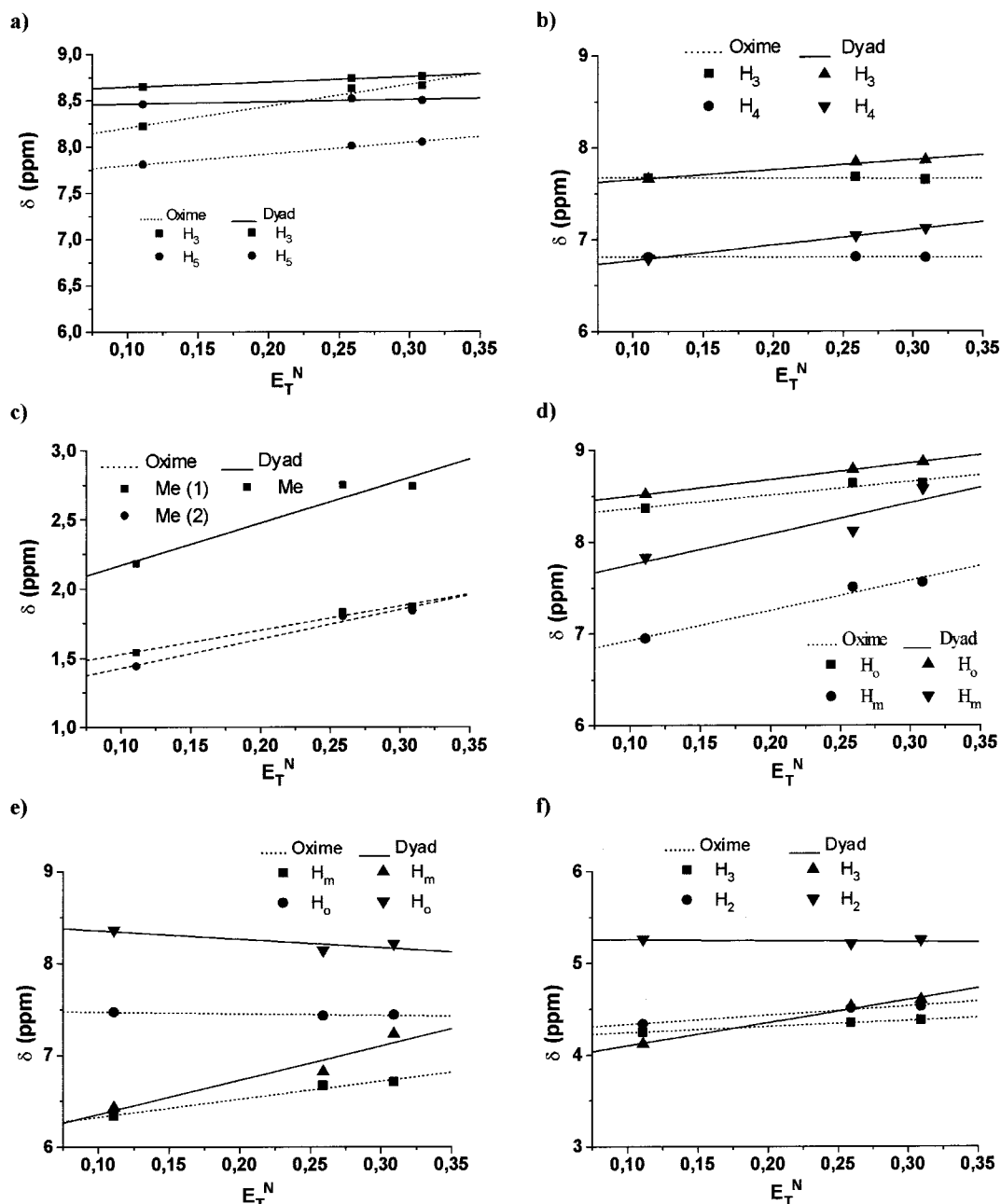
Figure 6. Evolution of chemical shifts of compounds **1a/2a** (a), **1b/2b** (b), **1c/2c** (c), **1d/2d** (d), **1f/2f** (e), and **1g/2 g** (f) vs E_T^N (empirical parameter of solvent polarity).

Table 4. Redox Potentials of 1a−h and C$_{60}$

compd	$E_{1/2}{}^1{}_{red}$	$E_{1/2}{}^2{}_{red}$	$E_{1/2}{}^3{}_{red}$	$E_{1/2}{}^4{}_{red}$
C$_{60}$	−0.65	−1.05	−1.50	−1.98
1a	−0.62	−1.02	−1.45	−1.91
1b	−0.63	−1.02	−1.46	−1.90
1c	−0.63	−1.03	−1.52	−1.92
1d	−0.62	−1.01	−1.43	−1.84
1e	−0.63	−1.03	−1.46	−1.88
1f	−0.65	−1.03	−1.51	−1.92
1g	−0.65	−1.03	−1.51	−1.92
1h	−0.65	−1.05	−1.45	−1.95

(4:1) at room temperature using tetrabutylamonium perchlorate as supporting electrolyte. The results are collected in Table 4 along with those for C$_{60}$ (for the sake of comparison). Compounds **1a−h** show quasi-reversible electrochemical behavior with four one-electron reduction waves (Table 4, Figure 8) corresponding to the first four reductions of the [60]fullerene cage found in all cases.

Compounds **1a−e** show reduction potential shifts toward more positive values (20 to 30 mV) in comparison to the parent C$_{60}$; this behavior is similar to that described recently by us[8] and Irngartinger.[9] It is worth noting that all the isoxazolo[60]fullerenes studied show better or equal acceptor character than C$_{60}$ regardless of the nature of the substituent, and as expected, cycloadducts **1a** and **1d** show the best electron affinity.

The inductive effect of substituents has been shown to be the most important factor in determining the redox properties of organofullerenes.[5a] Assuming this to be the case, the enhanced electron affinity of isoxazolo[60]-fullerenes can be explained by the presence of the oxygen atom directly attached to the C$_{60}$ cage. Moreover, electron-withdrawing substituents, as present in **1d**, enhance the electron acceptor character of the C$_{60}$ cage.

Theoretical Calculations. To gain a deeper insight into the nature of this kind of cycloadduct, we carried

a)

b)

Figure 7. Most stable conformations of **1a** (a) and **1b** (b).

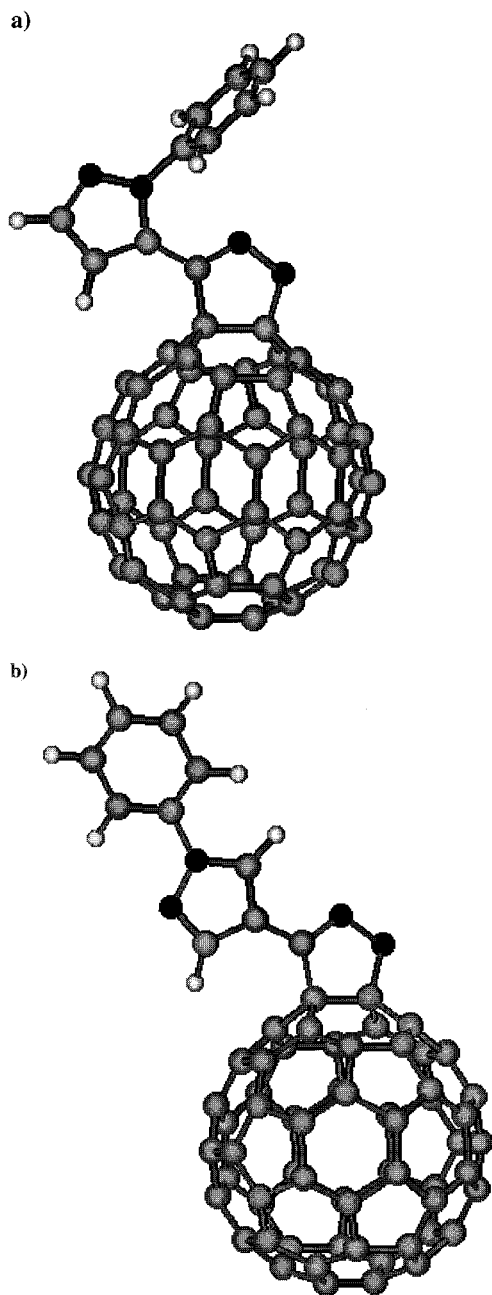**Figure 8.** Cyclic voltammogram of compound **1d**.

a)

b)
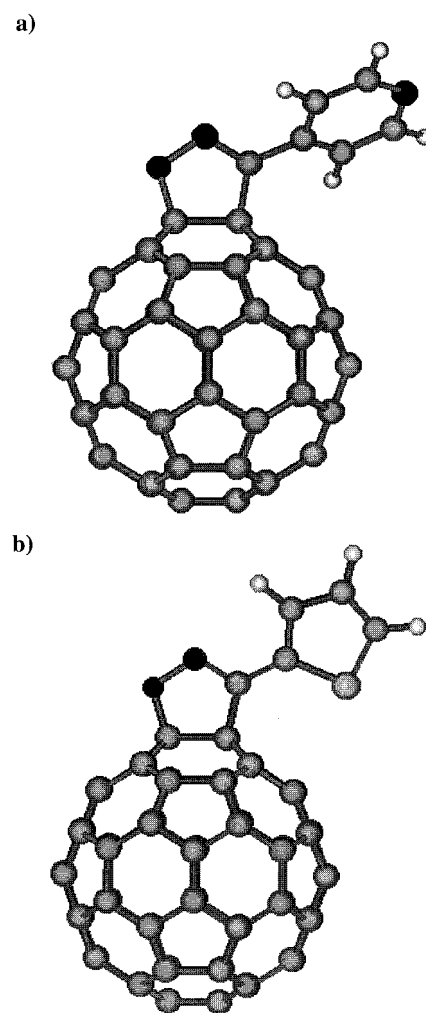
Figure 9. Most stable conformations of **1d** (a) and **1e** (b).

out semiempirical calculations (PM3/RHF) using the program package Hyper 5.1. Figure 9 shows the most stable conformation of cycloadducts **1d** (a) and **1e** (b), although other conformations that differ only slightly in energy are possible. In **1d**, the pyridine ring is twisted by 52.1° with respect to the isoxazoline ring, whereas in **1e** these two rings are almost coplanar. The LUMO energy levels of all of these systems are lower than that of C_{60} and these calculations confirm the experimentally determined first one-electron reductions in the dyads **1a**−**h**. As shown in Table 5, the calculated HOMO−LUMO energy gaps are in all cases lower than that of C_{60}. In addition, these energy gaps are all similar with the exception of dyad **1f**, which has a significantly lower value that indicates the possibility of an easier electron transfer.

Figure 10 shows the frontier orbitals of pyridino (**1d**) and *N,N*-dimethylanilino (**1f**) cycloadducts. In both cases,
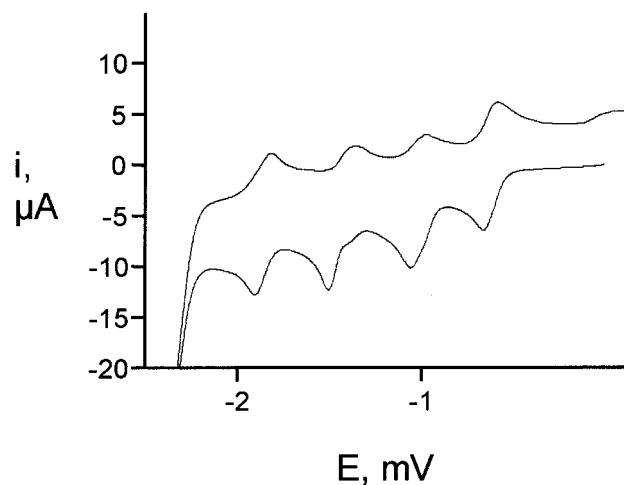
the LUMO is, as expected, fullerene-centered (Figure 10 b,d) but the distribution of the HOMO levels is quite different. While the HOMO in **1d** (Figure 10a) is centered on the fullerene cage, in **1f** it is addend-centered (Figure 10c) and is significantly higher than that of the other derivatives, a fact that may explain the different photophysical behavior of this cycloadduct.

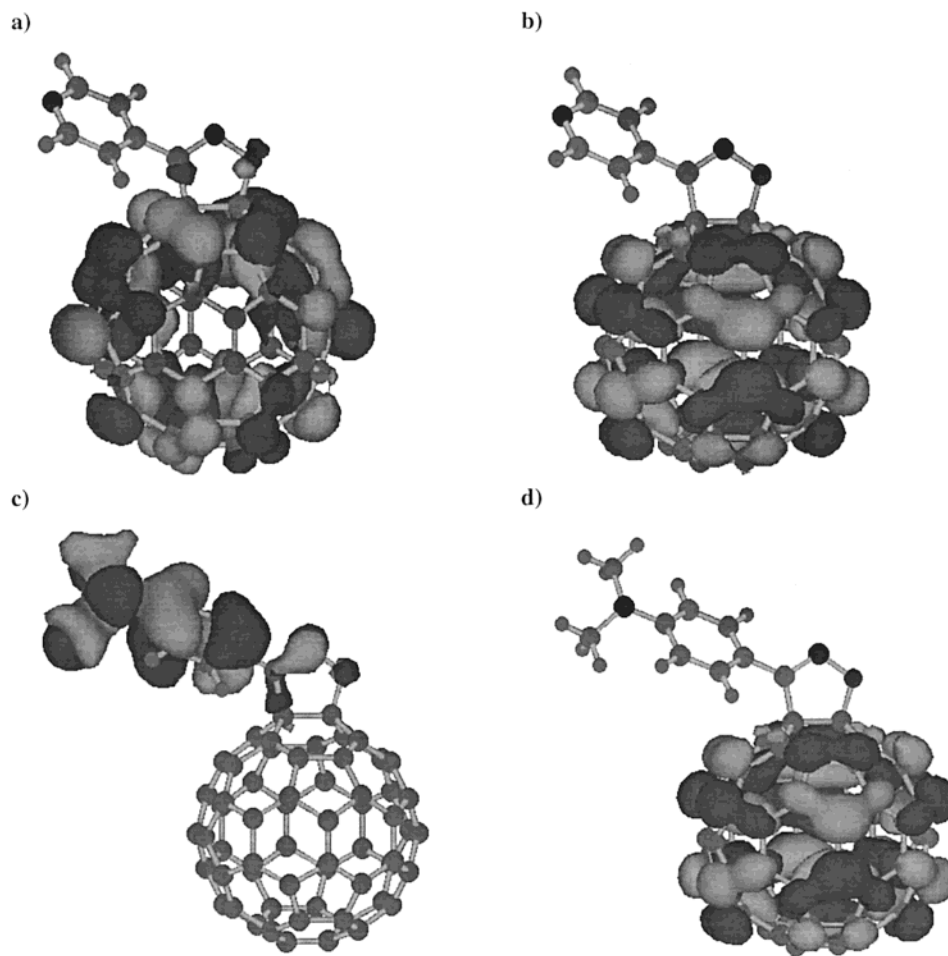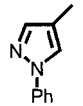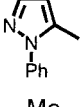Finally, we calculated the net charges (Figure 11) of the basic skeleton of isoxazolo[60]fullerene, as well as

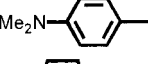a)   b)

c)   d)

Figure 10. PM3-calculated frontier orbitals of **1d** and **1f**: (a) HOMO of **1d**, (b) LUMO of **1d**, (c) HOMO of **1f**, (d) LUMO of **1f**.

Table 5. Calculated HOMO and LUMO Levels of C_{60} and Dyads 1a–f,h

Compound	R	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE^a
C_{60}		−9.48	−2.88	−6.60
1a		−9.18	−2.91	−6.26
1b		−9.40	−3.00	−6.40
1c	Me	−9.36	−2.97	−6.39
1d		−9.42	−3.02	−6.40
1e		−9.32	−2.92	−6.40
1f	Me₂N	−8.86	−2.94	−5.92
1h		−9.32	−2.93	−6.39

$^a \Delta E = E_{HOMO} - E_{LUMO}$.

pyrrolidino[60]fullerene and the corresponding *o*-quinodimethane cycloadduct as representative examples of some of the most used spacers to link a donor group to [60]fullerene. Theoretical calculations show that the net charge in both sp³ atoms of the C_{60} cage support a more
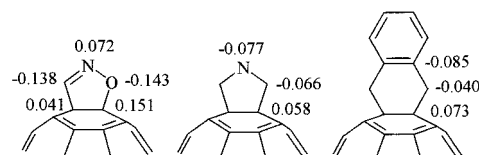
Figure 11. PM3-calculated net charges in basic skeletons of fullerene derivatives.

positive charge (+0.192) in the case of the isoxazolofullerene (Figure 11a) than in the other two cases studied (+0.116 and +0.148, respectively). Moreover, the net charge of the C_{60} cage is slightly positive (+0.048) for isoxazolo[60]fullerene, while it is negative for the two other cycloadducts [−0.112 for pyrrolidino[60]fullerene (Figure 11b) and −0.117 for the *o*-quinodimethane cycloadduct, Figure 11c]. A more positive charge on the C_{60} cage is in agreement with a better electron affinity, a situation that is consistent with the CV results obtained.

Conclusions

Several new isoxazolo[60]fullerenes have been prepared in one pot from aldoximes in 10 min under microwave irradiation. All of the compounds prepared present a better electron affinity than other fullerene derivatives; moreover, when an electron acceptor group is attached, the observed reduction potentials are slightly better than the parent C_{60}. Absorption and fluorescence spectra indicate a weak photoinduced electron transfer

from the oxygen atom to the fullerene cage in polar solvents. When strong donors are introduced into the molecule the photoinduced electron transfer is observed even in nonpolar solvents.

The influence of solvent polarity on the ^{1}H NMR spectra of dyads **1b**,**c** and **1f**,**g** indicates a higher polarization than in the precursor oximes. This polarization is enhanced with increased electron donating character of the substituent and can be attributed to charge-transfer processes from the substituted isoxazoline moiety in the ground state.

The results presented in this work suggest two main points: (1) the attachment of strong acceptor substituents to the C_{60} cage through this spacer should afford better acceptors than [60]fullerene for intermolecular CT processes, and (2) donors can be easily incorporated into the molecule by 1,3-dipolar cycloaddition of nitrile oxides, yielding cycloadducts that are of interest for intramolecular CT processes and that have improved electron affinity in comparison to other fullerene derivatives.

In conclusion, electron acceptors that are better than other C_{60} adducts are of interest in the elaboration of supramolecular machinery in which photoinduced intramolecular charge-transfer occurs. The anodic shift of such an acceptor can favor the formation of charge-transfer complexes when coupled with strong donors, as indicated by the results obtained when the *N,N*-dimethyl-anilino group or ferrocene groups are attached through this spacer to the fullerene cage. We have shown that the isoxazolo[60]fullerenes present similar acceptor ability than the parent C_{60} system regardless of the nature of the substituent. There are some indications in the absorption spectra of a possible weak charge-transfer interaction between the oxygen atom and the C_{60} cage. The fact that isoxazolo[60]fullerenes can be easily prepared in one pot from available aldoximes leads us to suggest that the introduction of strong donors as substituents through this route is an excellent way to prepare new donor−acceptor dyads with interesting behavior in CT processes. Work is currently in progress within our group in this direction.

Experimental Section

General Remarks. All cycloaddition reactions were performed under argon. Reactions under microwaves 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), acetaldoxime and the corresponding aldehydes were purchased from ACROS. Cycloaddition reactions were monitored by TLC using Merck silica gel 60-F$_{254}$. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 200 apparatus. UV−vis absorption spectra were obtained on a Shimatzu spectrophotometer. FT-IR spectra were recorded on a Nicolet Impact 410 on KBr disks. Fluorescence spectra were obtained on a JASCO FP-750 spectrophotometer.

FAB mass spectra were obtained on a VG AutoSpec, using *m*-nitrobenzyl alcohol as a matrix. Cyclic voltammetry measurements were carried out on a BAS 100 potentiostat using a BAS MF-2062 Ag/0.01 M AgNO$_3$, 0.1 M TBAP in ACN 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 a working electrode, 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 toward 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. Scan rate: 100 mV/s. Theoretical calculations were performed running the Hyperchem 5.1 program running the PM3 Hamiltonian.

General Procedure for the Synthesis of the Oximes. The synthesis was carried out according to the general method described in the literature, from the corresponding aldehydes.[25]

Pyridine-2-carbaldehyde oxime (2d):[26] yield 50%; mp 128−130 °C; ^{1}H NMR (CDCl$_3$) δ 8.65 (d, *J* = 4.5 Hz, 2H), 8.12 (s, 1H), 7.52 (d, *J* = 4.5 Hz, 2H).

Thiophene-2-carbaldehyde oxime (2e):[27] yield 70%; mp 130−133 °C; ^{1}H NMR (CDCl$_3$) δ 7.70 (s, 1H), 7.55 (d, *J* = 5.13 Hz, 1H), 7.38 (d, *J* = 3.91 Hz, 1H), 7.08 (dd, *J* = 3.91, 5.13 Hz, 1H).

4-*N,N*-Dimethylaminobenzaldoxime (2f):[28] yield 44%; mp 140−141 °C; ^{1}H NMR (CDCl$_3$) δ 8.03 (s, 1H), 7.42 (d, *J* = 8.97 Hz, 2H), 6.67 (d, *J* = 8.97 Hz, 2H), 2.98 (s, 6H).

Ferrocene-2-carbaldehyde oxime (2g):[29] yield 27%; mp 130−132 °C; ^{1}H NMR (CDCl$_3$) δ 7.95 (s, 1H), 4.51 (s, 2H), 4.35 (s, 2H), 4.19 (s, 5H).

Furan-2-carbaldehyde oxime (2h):[30] yield 45%; mp 82−84 °C; ^{1}H NMR (CDCl$_3$) δ 7.48 (s, 1H), 7.45 (d, *J* = 1.80 Hz, 1H), 7.29 (d, *J* = 3.45 Hz, 1H), 6.52 (dd, *J* = 1.80, 3.45 Hz, 1H).

General Procedure for the Synthesis of the Isoxazolo-[60]fullerenes. The synthesis was carried out according to the following methods:

Method A. This procedure is a modification of the general method for the cycloaddition of nitrile oxides to olefins.[31] To a solution of 0.070 mmol of the appropriate oxime in 10 mL of dry chloroform was added 0.005 mL of dry pyridine. The mixture was cooled to 0 °C, 19 mg (0.14 mmol, 2 equiv) of NCS was added to the solution, and the mixture was stirred for 15 min. The chlorooxime solution was added to 50 mg (0.07 mmol) of C_{60} dissolved in 50 mL of dry toluene. The mixture was treated with 0.02 mL (0.15 mmol) of triethylamine and irradiated in a focused microwave reactor at 210 W for 30 min. The corresponding cycloadducts were purified by flash chromatography on silica gel eluting with toluene.

Method B. A solution of the corresponding oxime (0.21 mmol) and NBS (0.21 mmol) in 45 mL of benzene was stirred for 15 min at room temperature. To this solution was added 150 mg of C_{60} and Et$_3$N (0.21 mmol) and the mixture was irradiated in a focused microwave reactor at 210 W for 30 min. The corresponding cycloadducts were purified by flash chromatography on silica gel eluting with toluene.

3′-Methylisoxazolo[4′,5′:1,2][60]fullerene (1c).[7a] Method A: yield 34% (99% based on recovered C_{60}). Method B: 22% (49% based on recovered C_{60}).

3′-(4-Pyridyl)isoxazolo[4′,5′:1,2][60]fullerene (1d). Method A: yield 26% (89% based on recovered C_{60}). Method B: 27% (44% based on recovered C_{60}); FT-IR (KBr) ν/cm^{-1} 3476.2, 3403.3, 2919.3, 2839.8, 1633.1, 1586.7, 1401.1, 1301.7, 1102.8, 1056.3, 990.1, 857.5, 771.3, 526.0; ^{1}H NMR (CDCl$_3$) δ 8.79 (dd, *J* = 6.23, 1.83 Hz, 2H), 8.12 (d, *J* = 6.23, 1.67 Hz); ^{13}C NMR (CDCl$_3$/CS$_2$ 1:1) δ 122.8, 127.2, 132.5, 135.4, 137.0, 137.6, 140.7, 142.0, 142.2, 142.5, 142.7, 143.2; 143.3, 143.9, 144.3, 144.7, 144.9, 145.5, 145.6, 145.7, 146.0, 146.2, 146.3, 146.6, 146.7, 147.6, 150.9, 152.3; UV−vis λ_{max}/nm (log ϵ) (CH$_2$Cl$_2$) 317 (4.63), 426 (3.33), 454 (3.25), 523 (3.02), 680 (2.32); FAB-MS *m/z* 841 (M + 1), 720 (C$_{60}$).

3′-(2-Thienyl)isoxazolo[4′,5′:1,2][60]fullerene (1e). Method A: yield 18% (65%). Method B: 15% (52% based on recovered C_{60}); FT-IR (KBr) ν/cm^{-1} 3423.2, 2972.4, 1626.5, 1600.0, 1500.5, 1407.7, 963.5, 824.3, 758.0, 685.1, 526.0; ^{1}H NMR (CDCl$_3$) δ 8.05 (dd, *J* = 1.22, 3.66 Hz, 1H), 7.55 (dd, *J* = 1.22, 5.13 Hz, 1H), 7.17 (dd, *J* = 3.66, 5.13 Hz, 1H); ^{13}C NMR (CDCl$_3$/CS$_2$

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1:1) δ 83.8, 103.8, 128.2, 129.6, 129.7, 140.5, 141.1, 142.2, 142.6, 142.8, 142.8, 143.2, 143.3, 143.4, 144.4, 144.7, 145.0, 145.5, 145.6, 146.0, 146.2, 146.3, 146.6, 146.7, 156.0; UV−vis λ_{max}/nm (log ϵ) (CH$_2$Cl$_2$) 318 (4.19), 424 (3.16), 449 (3.07), 539 (2.82), 674 (2.27); FAB-MS m/z 846 (M + 1), 720 (C$_{60}$).

3′-(4-*N,N*-Dimethylaminophenyl)isoxazolo[4′,5′:1,2][60]-fullerene (1f). Method A: yield 36% (64% based on recovered C$_{60}$); FT-IR (KBr) ν/cm^{-1} 3549.2, 3482.9, 2926.0, 2853.1, 1600.0, 1547.0, 1354.7, 1308.3, 1242.0, 1195.6, 1102.8, 1016.6, 811.1, 510.3; ^{1}H NMR (CDCl$_3$) δ 8.14 (d, J = 9.1 Hz, 2H), 6.82 (d, J = 9.1 Hz, 2H), 3.04 (s, 6H); ^{13}C NMR (CDCl$_3$/CS$_2$ 1:1) δ 85.0, 102.1, 112.2, 116.3, 130.3, 137.0, 137.2, 140.5, 142.6, 142.7, 143.1, 144.7, 145.2, 145.4, 145.8, 146.2, 146.5, 151.8; UV−vis λ_{max}/nm (log ϵ) (CH$_2$Cl$_2$) 320 (4.40), 425 (3.43), 464 (3.37), 547 (3.25), 684 (2.5); FAB-MS m/z 883 (M + 1), 720 (C$_{60}$).

3′-Ferrocenylisoxazolo[4′,5′:1,2][60]fullerene (1g). Method A: yield 20% (47% based on recovered C$_{60}$). Method B: yield 12% (32% based on recovered C$_{60}$); FT-IR (KBr) ν/cm^{-1} 3414.6, 2925.4, 1655.6, 1638.1, 1618.6, 1509.7, 1500.7, 1460.3, 1422.0, 1407.5, 1380.4, 1291.8, 1105.2, 973.5, 903.1, 839.3, 817.7, 768.3, 606.3, 563.3, 525.7, 478.6; ^{1}H NMR (CDCl$_3$) δ 5.21 (dd, J = 1.71, 1.95 Hz, 2H), 4.53 (dd, J = 1.95 Hz, 2H), 4.18 (s, 5H); ^{13}C NMR (CDCl$_3$/CS$_2$ 1:1) δ 69.1, 70.8, 70.9, 74.3, 97.2, 136.4, 140.3, 141.9, 142.6, 143.1, 144.4, 144.7, 145.2, 145.5, 145.7, 145.8, 146.2, 146.5, 147.2, 147.6, 153.2, 162.8; UV−vis λ_{max}/nm (log ϵ) (CH$_2$Cl$_2$) 317 (4.49), 425 (3.39), 455 (3.28), 486 (3.20), 543 (3.05), 675 (2.66); FAB-MS m/z 948 (M + 1), 720 (C$_{60}$).

3′-(2-Furyl)isoxazolo[4′,5′:1,2][60]fullerene (1h). Method A: yield 16% (43% based on recovered C$_{60}$); FT-IR (KBr) ν/cm^{-1} 3429.8, 2919.3, 2833.2, 2355.8, 2309.4, 1792.3, 1719.3, 1619.9, 1421.0, 1374.6, 1116.0, 976.8, 850.8, 764.6, 525.9; ^{1}H NMR (CDCl$_3$) δ 7.68 (d, J = 1.80 Hz, 1H), 7.41 (d, J = 3.66 Hz, 1H), 6.60 (dd, J = 1.80, 3.66 Hz, 1H); ^{13}C NMR (CDCl$_3$/CS$_2$ 1:1) δ 112.5, 114.5, 128.5, 128.1, 145.5; UV−vis λ_{max}/nm (log ϵ) (CH$_2$Cl$_2$) 316 (4.60), 424 (3.31), 450 (3.20), 544 (2.87), 679 (2.23); FAB-MS m/z 830 (M + 1), 720 (C$_{60}$).

Supporting Information Available: ^{1}H NMR spectra for new compounds **1d,f−h**. This material is available free of charge via the Internet at http.//pubs.acs.org.

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