

**Electroactive 3'-(*N*-Phenylpyrazolyl)isoxazoline[4',5':1,2][60]Fullerene Dyads**

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Abstract: Novel C₆₀-fused isoxazolines have been synthesized by using 1,3-dipolar cycloadditions of pyrazole nitrile oxides, generated *in situ*, to C₆₀ under thermal or focused microwave irradiation. The cyclic voltammetry measurements show a strong donor pyrazole ring and a better acceptor ability of the fullerene moiety compared to pristine C₆₀. The UV-Vis and ¹H NMR spectra suggest a weak CT interaction in the ground state. © 1999 Elsevier Science Ltd. All rights reserved.

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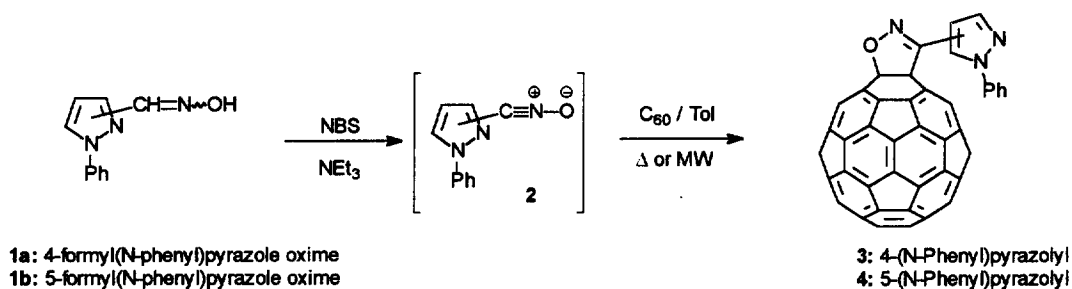
The design and synthesis of novel modified fullerenes exhibiting better electron-acceptor properties than the parent [60]fullerene is currently an active research field due to their potential applications as in optoelectronic devices.^[1] Organofullerenes show, in general, reduction potential values which are cathodically shifted in comparison to C₆₀,^[2] and only a limited number of examples with less negative potentials than C₆₀ have been reported.^[3] The presence of electronegative atoms,^[4] periconjugative effects^[5] or ammonium salts^[6] have been successfully used in the preparation of stronger acceptors than C₆₀.

Recently, we have described the synthesis of several 1-aryl-3-(1-phenylpyrazol-4-yl)-pyrazolo[4',5':1,2][60]fullerene adducts by 1,3-dipolar cycloaddition of the corresponding nitrile imines generated *in situ* from the corresponding hydrazones and NBS in the presence of Et₃N and reacted with C₆₀ under microwave irradiation.^[7] The target molecules showed an interesting low field shift in their ¹H-NMR spectra with respect to the corresponding hydrazone. Considering previous results^[8] and that the magnitude of the low field shift in the donor unit when linked to C₆₀ provides direct information for CT interactions between the donor moiety and the [60]fullerene,^[9] it was of interest to study a possible intramolecular CT interaction from the *N*-phenyl and *C*-pyrazolyl groups to C₆₀ in the ground state.

In this context and in order to get a deeper insight into the behaviour of this kind of C₆₀-donor dyad, we report herein the preparation of dyads **3** and **4**, in which a donor pyrazole unit is covalently attached to the strong isoxazolinefullerene acceptor. We have used the corresponding nitrile oxides **2** as precursors for adducts **3–4**. Although the most common way to generate nitrile oxides use hydroxymoyl chlorides as starting materials, in our case the oxime was treated with NBS in the presence of Et₃N and reacted *in situ* with C₆₀ under

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microwave irradiation.^[10] Under these conditions, adducts **3-4** were obtained in 22% in both cases after isolation by flash chromatography (silica gel, toluene). Longer reaction times afforded greater amounts of bisadducts. The same reactions were carried out under thermal conditions and similar yields were obtained (**3**: 14 %; **4**: 17%). A significant accelerating effect (10 minutes vs 24 hours) occurs under microwave irradiation without significant improvement in yield^[11] or change in selectivity.^[12] The structures of the novel compounds were supported by their spectroscopic data (UV-Vis, FTIR, ¹H-NMR and FAB mass spectra).^[13] In the ¹H-NMR spectra, the signals of the pyrazole hydrogens appeared at δ 8.52 (H₃) and 8.73 (H₅) for compound **3** and δ 7.04 (H₄) and 7.84 (H₃) for compound **4**. For dyad **3** these values show a remarkable low field shift related to the corresponding starting oxime [δ 8.03 (H₃) and 8.64 (H₅) for **1a** and δ 6.76 (H₄) and 7.66 (H₃) for **1b**]. Although these findings could be accounted for by the theoretically predicted (PM3) shorter distance of proton H-3 to the pentagonal ring of the C₆₀ surface in comparison to dyad **4**, (**3**: 2.46 Å; **4**: 2.66 Å), a specific donor/acceptor interaction can not be ruled out.



Scheme

On the basis of ¹H NMR and UV-Vis studies, an intramolecular CT-interaction between a benzene ring and C₆₀ has been previously reported by Yoshida *et al.*^[9] In our case, in addition to similar NMR observations, a weak CT band at around 460 nm which is bathochromically shifted with increasing solvent polarizability^[14] is observed in the UV-Vis spectra [**3**: cyclohexane ($n=1.4262$) 455 nm; dichloromethane ($n=1.4242$) 455 nm, CS₂ ($n=1.6275$) 460 nm; **4**: cyclohexane 458 nm; dichloromethane 458 nm; CS₂ 463 nm]. The same trend is also observed for the band at around 690 nm. The typical weak peak for the [6,6] ring junction of 1,2-dihydrofullerenes is also observed at 425 nm.

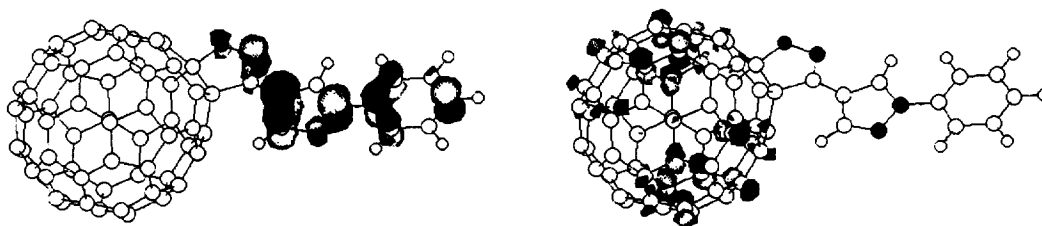


Figure 1. PM3 calculated frontier orbitals (left: HOMO, right: LUMO) of **3**.

Theoretical calculations confirm the lowest energy of the LUMO in **3** (HOMO: -9.17 eV, LUMO: -2.91 eV) and **4** (HOMO: -9.40 eV, LUMO: -3.00 eV) related to pristine C₆₀ (HOMO: -9.48 eV, LUMO: -2.88 eV). In these compounds, the HOMO is located on the organic addend and the LUMO spreads on the C₆₀ core

(Figure 1). The calculated distance between the closest C-atom of the pyrazole ring to the C₆₀ surface was found to be 3.29 Å in dyads **3**; this distance is shorter than the sum of the Van der Waals radii for C-C interaction (3.40 Å).^[15] These data suggest that a weak electronic interaction could take place between both moieties.

To support the strong donor character observed for the pyrazole ring, the redox properties of the novel compounds were determined by cyclic voltammetry measurements at room temperature (Table). Compounds **3** and **4** show a quasi-reversible electrochemical behaviour with four one-electron reduction waves corresponding to the reduction of the [60]fullerene moiety and the organic addend. Interestingly, the reduction potential values show an anodic shift (70 mV for **3** and 50 mV for **4**) in comparison to the parent C₆₀. Therefore, these new isoxazoline-fused organofullerenes present a better acceptor ability than unsubstituted C₆₀. This effect could be reasonably attributed to the combined effect of the electronegativity of the oxygen atom linked to the C₆₀ core and, in a less extent, to the electron-deficient character of C-3 of the isoxazoline ring. In this regard, it is important to note that although isoxazoline[4',5':1,2][60]fullerene are well known species,^[16] their electrochemical properties have been scarcely studied by CV and only one isoxazolinefullerene bearing an ester group was electrochemically characterized^[17] showing a first reduction potential close to that of pristine C₆₀.

Table. Redox Potentials of Compounds **1a,b**, **3**, **4** and C₆₀.

Compound ^a	E ¹ _{red}	E ² _{red}	E ³ _{red}	E _{red} ^{org. addend}	E _{ox}
1a	—	—	—	—	0.37
1b	—	—	—	—	0.37
3	-0.52	-0.92	-1.42	-1.73	0.38
4	-0.54	-0.93	-1.40	-1.64	0.31
C ₆₀	-0.59	-0.99	-1.48	—	—

^aExperimental Conditions: V vs SCE; GCE as working electrode; Bu₄N⁺ClO₄⁻ 0.1 M as supporting electrolyte; ODCB:MeCN (4:1) as solvent; scan rate 200 mV/s.

An irreversible oxidation wave, at around 0.35 V, corresponding to the oxidation of the pyrazole moiety, is also observed (Figure 2). This oxidation potential of the *N*-phenylpyrazole unit is quite remarkable being lower than that observed for *N,N*-dimethylaniline^[18] which forms intermolecular CT-complexes in solution with C₆₀ showing low equilibrium constants.^[19] Therefore, organofullerenes **3** and **4** could behave like C₆₀-σ-donor dyads in which a certain electronic interaction can take place to some extent.

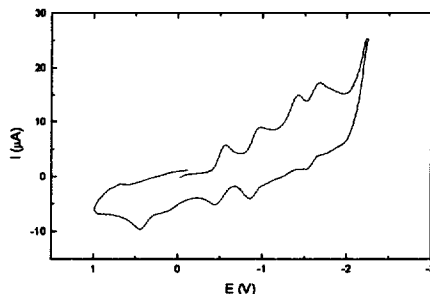


Figure 2. Cyclic voltammogram of compound **4** at 200 mV/s

In summary, we have prepared novel isoxazoline-fused [60]fullerene derivatives by using 1,3-dipolar cycloadditions of nitrile oxides to [60]fullerene under thermal and focused microwave irradiation. The resulting compounds show an enhanced acceptor ability in comparison to the parent C₆₀. The electrochemical

measurements show an oxidation wave at low positive values which indicates the presence of a strong electron-donor *N*-phenylpyrazole unit. The UV-Vis and ^1H NMR spectroscopic data could support a weak donor-acceptor interaction in the ground state. These systems are promising candidates for further photophysical studies. Work is in progress in that way.

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- [13] Selected spectroscopic data. **3**: 22 % yield (55 % yield based on recovered C_{60}); ^1H NMR (CDCl_3 , 200 MHz) δ (ppm): 8.73 (s, 1H), 8.52 (s, 1H), 7.74 (d, 2H, $J=8.0$ Hz), 7.51 (dd, 2H, $J=7.3$ Hz, $J=8.0$ Hz), 7.37 (t, 1H, $J=7.3$ Hz); FAB-MS m/z : 906 (MH^+), 720 (C_{60}); IRFT (KBr) ν : 2932, 1652, 1646, 1635, 1627, 1464, 1458, 1376, 803, 587 cm^{-1} ; UV-Vis (C_6H_{12}) λ_{max} (log ϵ) 317 (6.30), 425 (5.06), 455 (4.85), 684 (4.11) nm. **4**: 22 % yield (65 % yield based on recovered C_{60}); ^1H NMR (CDCl_3 , 200 MHz) δ (ppm): 7.84 (d, 1H, $J=2.0$ Hz), 7.65 (d, 2H, $J=6.2$ Hz), 7.51 (m, 3H), 7.04 (d, 1H, $J=2.0$ Hz); FAB-MS m/z : 906 (MH^+), 720 (C_{60}); IR-FT (KBr) ν : 1514, 1498, 1385, 1330, 1103, 759, 852, 769, 526 cm^{-1} . UV-Vis (C_6H_{12}) λ_{max} (log ϵ) 317 (6.56), 426 (5.29), 458 (5.18), 675 (4.25), 685 (4.34) nm
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