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C_{60}-Based Triads with Improved Electron-Acceptor Properties: Pyrazolylpyrazolino[60]fullerenes[†]

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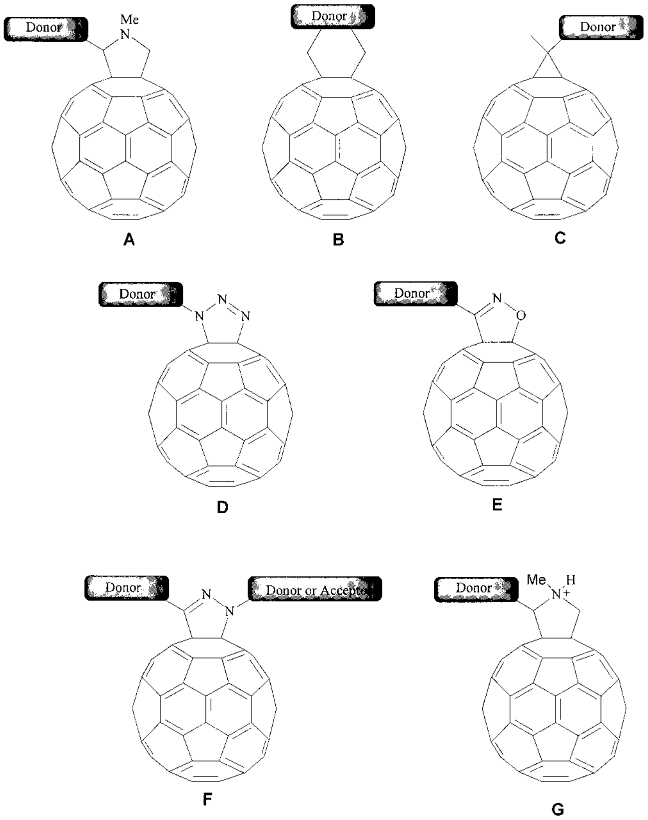
A series of triad pyrazolylpyrazolino[60]fullerenes has been prepared in one pot from suitably functionalized hydrazones by 1,3-dipolar cycloaddition reactions under microwave irradiation. The electrochemical properties of the compounds obtained were investigated by cyclic voltammmetry, and they show better electron acceptor character than the parent C_{60} in all cases. Fluorescence experiments and time-resolved transition spectroscopy indicate the existence of photoinduced charge-transfer processes with the C_{60} triplet acting as the acceptor.

Introduction

In recent years, different approaches have been used to prepare covalently linked donor-C_{60} dyads,[1] and in some cases, intramolecular photoinduced charge separation has been observed.[2] Nevertheless, derivatization of C_{60} through some of these spacers [fulleropyrrolidines (**A**), Diels−Alder cycloadducts (**B**), and methanofullerenes (**C**)] decreases the electron affinity of the C_{60} sphere and causes a displacement of reduction potentials to more negative values by about 100 mV (Chart 1).[3] Some research has been undertaken aimed at increasing the electron acceptor capacity of C_{60} and, consequently, giving rise to more efficient behavior of the C_{60} sphere in charge-transfer processes.[4] In this respect, a simple procedure to prepare donor−C_{60} dyads with similar, or even improved, electron affinity in comparison to the parent C_{60} is a goal of great interest. One immediate approach to achieve this goal is the use of fullerene derivatives incorporating electronegative or electron-deficient carbon atoms directly connected to the C_{60} core, as shown in Chart 1 (**D**−**F**). Fulleropyrrolydinium salts (**G**) have also

Chart 1



[†] Dedicated to Professor José Luis Soto on the occasion of his retirement.

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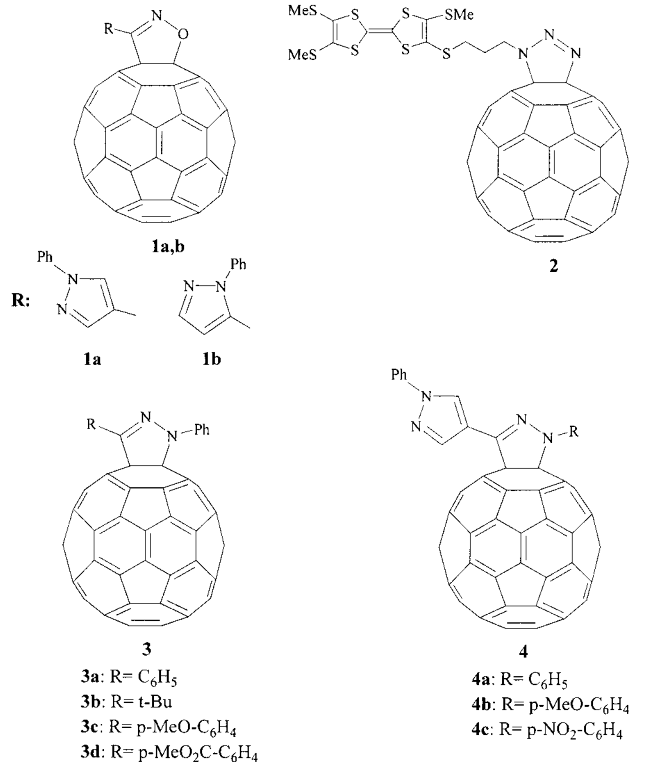
Chart 2



been used to prepare acceptors that are markedly better than the parent C_{60}.[4e]

1,3-Dipolar cycloadditions represent a powerful tool to prepare fullerene derivatives. Azomethine ylides,[5,6] diazoalkanes,[7] azides,[8] or nitrile oxides[9] all afford fulleroheterocycles. In this context, we have recently described the preparation of 3′-(*N*-phenylpyrazolyl)isoxazolo[60]fullerene dyads **1a** and **1b** along with triazolino[60]fullerene **2** (Chart 2). These compounds were all shown to be better acceptor systems than the parent C_{60} as their cyclic voltammetry measurements exhibited an anodic shift of 50−70 mV (**1a**,**b**) and 30 mV (**2**) in comparison to C_{60}.[10] This behavior can be attributed to the combined effect of the electronegativity of the oxygen atom linked to the C_{60} core and, to a lesser extent, to the electron-deficient character of C3 of the isoxazoline ring in **1a**,**b** and to the combined effect of both nitrogen atoms directly connected to the C_{60} sphere in **2**. We[11,12] and others[13] later found that other substituted isoxazolo[60]fullerenes show a similar enhanced acceptor ability in comparison to the parent C_{60}.

Nevertheless, the functionalization of C_{60} with 1,3-nitrile imine dipoles to give pyrazolino[60]fullerenes is a method that has hardly been used.[14] Interestingly, some evidence for intramolecular charge-transfer interactions was found in 1,3-diphenyl-2-pyrazoline fused to C_{60} **3a** (Chart 2). This perception was based on a remarkable low-field shift for the ortho protons with respect to the corresponding nonfused C_{60} pyrazoline as well as the observation in the UV spectra of a CT band at around 470 nm, which was shifted toward longer wavelengths upon increasing the polarizability of the solvent.[14b]

We recently described preliminary results on the facile synthesis of pyrazolino[60]fullerenes[15] **4a**−**c** from the corresponding hydrazones under microwave irradiation,[16] a technique that is particularly useful in cycloaddition reactions.[17] The ^{1}H NMR signals for compounds **4a**−**c** showed a shift to lower field by 0.51−1.18 ppm in both the pyrazole and phenyl rings, an effect that is similar to that described for the *N*-phenyl ring in **3a**. It is worth noting the remarkable advantage of the pyrazolino[60]fullerenes over the isoxazolino[60]fullerenes to obtain electroactive compounds. This is due to the possibility of preparing donor−donor−C_{60} or donor−acceptor−C_{60} triads[18] (Chart 1) by modification of the nature of the substituent linked to the sp^3 nitrogen atom.

We report here a new series of donor−acceptor pyrazolino[60]fullerenes (**5a**−**c**), as well as the spectroscopy and electrochemistry for donor−C_{60} dyads **4a**−**c** and **5a**−**c**. To compare the influence of the nature of the heterocycle fused to the fullerene sphere on the electrochemical behavior of the former compounds, pyrrolidino[60]fullerenes **6** and **7** (Chart 3) were also prepared and studied.

Results and Discussion

Synthesis and Characterization. The synthesis of the target structures **4a**−**c** and **5a**−**c** requires the preparation of a nitrile imine intermediate according to the route shown in Scheme 1. Hydrazones **8a**−**c** and **9a**−**c**, prepared from 4-formyl-1-phenylpyrazole[20] and 5-formyl-

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Scheme 1

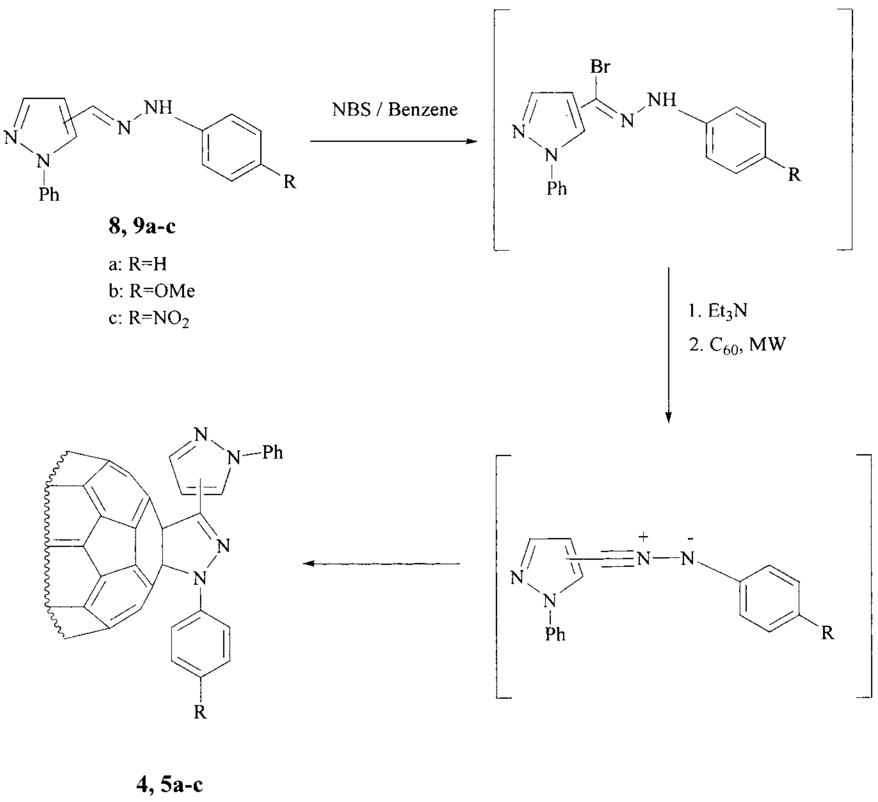
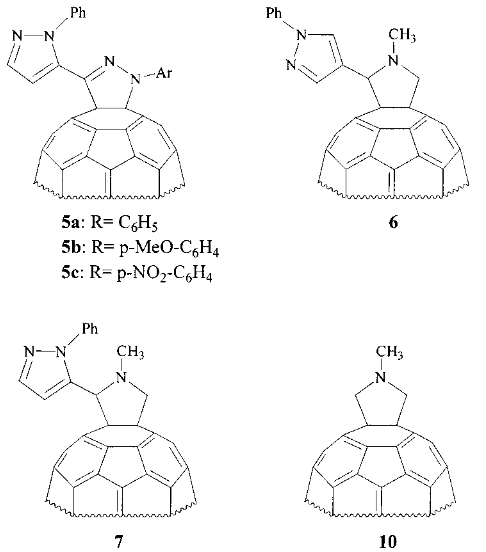


Chart 3



1-phenylpyrazole,[21] respectively, were reacted with NBS in benzene. Et_3N and C_{60} were subsequently added to the mixture, which was then irradiated in a focused microwave reactor (for irradiation power and reaction times see the Experimental Section) to afford pyrazolylpyrazolino[60]fullerenes **4a**−**c** and **5a**−**c** in moderate to good yields (22−44%). Longer reaction times than those indicated tended to decrease the yield and promote the formation of larger amounts of bisadducts. It should be mentioned that classical heating can be used as an alternative source of energy but yields are considerably lower (**4a**: 9%, **4b**: 21%, **4c**: 4%) even when longer reaction times (4−8 h) are employed.

The structures of the new compounds were confirmed by their analytical and spectroscopic data. The molecular ions were observed in the mass spectra using the FAB technique in positive ion mode: for **4a**−**c** at *m*/*z* 981 $(MH)^+$, 1011 $(MH)^+$, and 1026 $(MH)^+$ and for **5a**−**c** at *m*/*z* 981 $(MH)^+$, 1011 $(MH)^+$, and 1026 $(MH)^+$, respectively.

Pyrrolidino[60]fullerenes **6** and **7** were prepared by reaction of 4- and 5-formyl-1-phenylpyrazole and sarcosine (*N*-methylglycine) in refluxing toluene by following the procedure described by Prato et al.[7] The structures of compounds **6** and **7** were fully supported by analytical and spectroscopic data. In both cases, an ion at *m*/*z* 920 $(MH)^+$ is observed in the FAB^+ spectra and the ^1H NMR, ^{13}C NMR, UV−vis, and FT-IR data are in agreement with those previously reported for other pyrrolidino[60]fullerenes.

Redox Properties. The electrochemical properties of compounds **4a**−**c**, **5a**−**c**, **6**, and **7** were studied by cyclic voltammetry in solution in *o*-dichlorobenzene/acetonitrile (4:1) at room temperature. The data obtained in this study are collected in Table 1 along with those of [60]fullerene and compounds **1a**,**b** for the sake of comparison.

A nonreversible oxidation process corresponding to the *N*-phenylpyrazole ring and four quasi-reversible reduction waves, similar to those found for the parent [60]fullerene and corresponding to the first four reduction steps of the fullerene moiety, are observed (Table 1). In addition, another quasi-reversible reduction wave can be observed between the third and fourth reduction waves of the [60]fullerene moiety, which could be reasonably assigned to the reduction of the organic addend.

The strong donor character of the *N*-phenylpyrazole ring is evidenced by the remarkably low value of the

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Table 1. Redox Potentials of Organofullerenes 1−7 and C_{60}

entry	compd	E^1_{red}	E^2_{red}	E^3_{red}	E^4_{red}	E_{oxid}
1	C_{60}	−0.59	−0.99	−1.48	−2.05	–
2	**1**	−0.52	−0.92	−1.42 (−1.73)	−1.73	0.38
3	**2**	−0.54	−0.93	−1.40 (−1.64)	−1.64	0.31
4	**4a**	−0.55	−0.97	−1.46 (−1.71)	−2.22	0.33
5	**4b**	−0.57	−0.99	−1.44 (−1.74)	−2.23	0.31
6	**4c**	−0.51	−0.91	−1.19 (−1.73)	−2.21	0.42
7	**5a**	−0.57	−0.98	−1.45 (−1.73)	−2.21	0.32
8	**5b**	−0.60	−0.99	−1.46 (−1.73)	−2.21	0.33
9	**5c**	−0.55	−0.93	−1.18 (−1.78)	−2.21	0.33
10	**6**	−0.67	−1.07	−1.61	−2.16	0.31
11	**7**	−0.68	−1.09	−1.64	−2.22	0.34

oxidation wave (Table 1), a value similar to that found for other strong donors such as TTF.[22] Interestingly, in compounds **4a**−**c** the oxidation potential value is strongly dependent on the substitution on the phenyl group attached to the nitrogen atom of the pyrazoline ring. This fact suggests some kind of electronic interaction between the two moieties [0.31 V for cycloadduct **4b** (with a donor group) and 0.42 V for compound **4c** (with an electron-withdrawing group)]. By contrast, this trend is not observed in triads **5**, where the three new compounds present similar oxidation potentials (0.32−0.33 V), and this again highlights the remarkable difference in behavior between the two families of compounds. As expected, the same values for the oxidation potentials of the pyrazole ring were found for pyrrolidino[60]fullerenes **6** and **7** (0.31 and 0.34 V, respectively).

On the reduction side, cycloadducts **4a**−**c** show an anodic shift up to 80 mV relative to the parent C_{60} and up to 170 mV (in the case of **4c**) with respect to the corresponding pyrrolidino[60]fullerenes **6** and **7**. These differences become less pronounced as the *N*-phenyl group attached to the nitrogen atom of pyrazoline ring becomes more electron rich (Table 1). The same trend is observed in dyads **5a**−**c** (see Table 1), although the magnitude of the anodic shift is slightly smaller in these cases. The inductive effect of substituents has been shown to be one of the most important factors in determining the redox properties of organofullerenes.[4a]

We also studied the electrochemical properties of pyrrolidino[60]fullerenes **6** and **7**, which show remarkably more negative values for the first reduction potentials (−0.67 and −0.68 V, respectively). The *N*-phenylpyrazole ring does not exert any influence in these dyads, as shown by the fact that the value of the reduction potential is similar to those found for other pyrrolidino[60]fullerenes.[1b,23]

Absorption Spectra. The UV−vis spectra of pyrazolo[60]fullerenes **4a**−**c** and **5a**−**c** in dichloromethane at room temperature are shown in Figure 1. Both families of compounds show similar absorption properties. While **4a**,**b** and **5a**,**b** share common absorption bands, the absorption peak at 425 nm, characteristic of [6,6]-bridged monoadducts, appears only as a shoulder in the spectra of nitrocompounds **4c** and **5c**. A band at around 685−690 nm, assigned to the 0−0 transition, is also observed. Another weak, broad absorption is observed in the region 450−650 nm, and this is stronger in dyads with an electron-donating substituent on the nitrogen atom of the pyrazoline ring (i.e., **4b** and **5a**,**b**) but is almost absent in **4a**, **4c**, and **5c**. Similar broad bands have been attributed to weak electronic interactions between donor and acceptor moieties and have been reported for intramolecular CT in other C_{60}-based dyads[14b,24−26] or intermolecular CT interactions with other donors.[27]

The broad absorptions of these compounds are red-shifted with increasing solvent polarizability[28] (Table S-1, Supporting Information; Figure 2), suggesting the formation of weak CT complexes in the ground state in those dyads in which this band is present. The weaker intensity of this band in cyclohexane as opposed to dichloromethane (in spectra taken at the same concentration) is shown by the ϵ values and supports the formation of the CT complex in more polar or polarizable solvents. This band is not observed in those derivatives bearing an electron-withdrawing substituent on the nitrogen atom of the pyrazoline ring (**4c** and **5c**), a situation that would inhibit charge transfer in these derivatives.

Fluorescence Spectra. In donor−spacer−acceptor systems, the fluorescence of the donor and/or acceptor chromophores is strongly quenched[29] due to electron transfer. In general, the CT character of the emissive state is reflected by a strong dependence of the emission wavelength on solvent polarity.[30] The fluorescence spectra of pyrazolo derivatives **4a**−**c** and **5a**−**c**, pyrrolidinofullerenes **6** and **7**, and, for the sake of comparison, the model *N*-methylpyrrolidino[60]fullerene **10**[5] were measured at room temperature in cyclohexane, toluene, and benzonitrile with 430 nm excitation. At this excitation wavelength, only the C_{60} moiety can be excited. Salient results are presented in Table 2.

The spectra of pyrrolidinofullerenes **6** and **7** in cyclohexane are similar to that of the unsubstituted compound **10**[5] and, as expected, are independent of the excitation wavelength. These spectra show maxima at 708−710 nm and a shoulder at 781 nm (in **7**), indicating that these compounds do not undergo photoinduced charge transfer in nonpolar solvents. On using solutions with the same absorbance, the fluorescence intensities were also found to be similar, indicating that the quantum yields should be almost equal.

Solvent effects on the fluorescence spectral profile were examined in toluene and benzonitrile. Previous studies on the photochemical properties of *N*-methylpyrrolidino[60]fullerenes indicated that the pyrrolidine ring nitrogen is not involved in charge transfer,[31] and indeed, compound **10** shows a similar emission pattern in cyclohexane and benzonitrile. Nevertheless, in benzonitrile the

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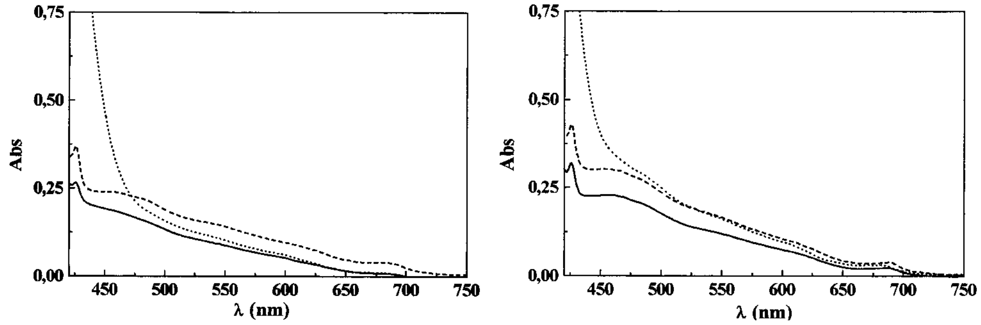

Figure 1. (Left): room-temperature UV–vis spectra of **4a** (—), **4b** (- - -), and **4c** (···) in dichloromethane. (Right): room-temperature UV–vis spectra of **5a** (—), **5b** (- - -), and **5c** (···) in dichloromethane.

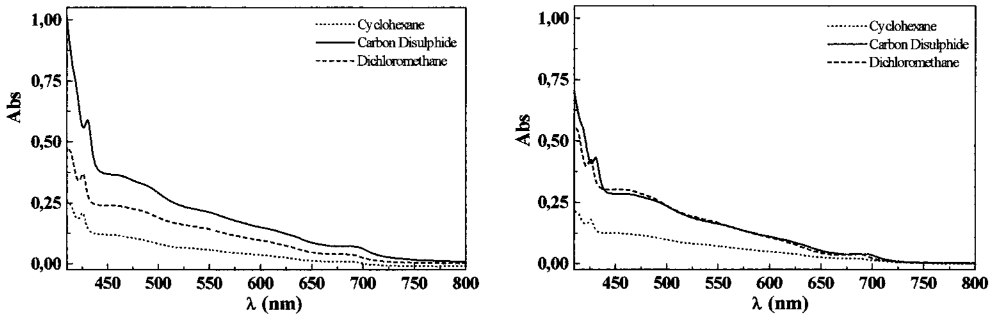

Figure 2. (Left): room-temperature UV–vis spectra of **4b** in cyclohexane (···), dichloromethane (- - -), and carbon disulfide (—). (Right): room-temperature UV–vis spectra of **5b** in cyclohexane (···), dichloromethane (- - -), and carbon disulfide (—).

Table 2. Fluorescence Data of Compounds 4a–c, 5a–c, 6, 7, and 10

	maxima (nm)/I (au)							
compd	cyclohexane		toluene			benzonitrile		
4a			662	684	732	703	734	
			2.610	2.149	2.337	1.665	1.679	
4b			722	731		739		
			1.623	1.518		4.454		
4c			714			715		
			10.146			2.661		
5a	727		676	734		713	732	
	8.772		2.348	5.352		3.677	3.775	
5b	724		723			719	747	
	7.878		2.684			4.137	3.604	
5c	688	714	702	709		709	725	762
	5.900	8.311	13.931	14.554		10.246	8.763	5.049
6	708		715			721		
	36.168		25.620			23.686		
7	710	7.81	718			719		
	0.298	0.098	0.245			0.205		
10	706	713	717			719	723	
	0.284	0.293	0.258			0.217	0.221	

fluorescence intensities in compounds **6** and **7** were reduced to 82% and 67%, respectively, of that in cyclohexane (Figure 3). An intermediate situation was observed in toluene in accordance with its intermediate polarity. This quenching of the fluorescence is ascribed to a weak charge-transfer interaction in the excited state between the C_{60} moiety and the pyrazole ring (a strong donor, as indicated by the electrochemical studies), which should be stronger in dyad **7** than in **6**. Compounds **6** and **7** show solvatochromic red-shifts with maxima at 721 and 719 nm in benzonitrile. This red-shift in benzonitrile, in contrast with the situation in cyclohexane, has been assigned to a weak CT character.[32]

On the other hand, the profile of the emission spectra of compounds **4a–c** and **5a–c** in toluene is quite different (due to the low solubility, the emission spectra of **4a–c** in cyclohexane could not be recorded). These compounds exhibit a weak fluorescence compared to the former fulleropyrrolidines, and the fluorescence becomes weaker as the electronic richness of the substituent is increased and reaches a point where it is not possible to measure a maximum for **4b** and **5b** (Figure 4).

The effect of solvent polarity on the profile of the fluorescence spectra was examined by measuring fluorescence spectra of **4c** and **5c** in toluene and benzonitrile solutions (Figure 5). In both cases, the fluorescence was more quenched as the polarity of the solvent increased.

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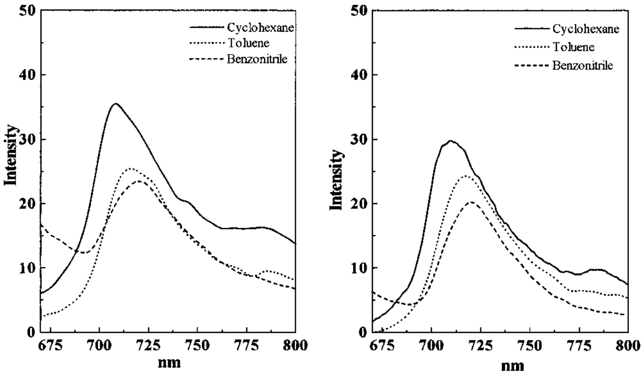

Figure 3. (Left): fluorescence spectra of compound **6** in cyclohexane (—), toluene (···), and benzonitrile (- - -) as solvents. (Right): fluorescence spectra of compound **7** in cyclohexane (—), toluene (···), and benzonitrile (- - -) as solvents.

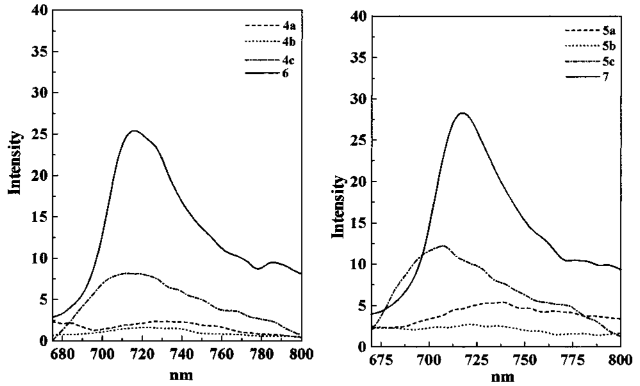

Figure 4. (Left): fluorescence spectra of compounds **4a**−**c** and **6** in cyclohexane as solvent. (Right): fluorescence spectra of compounds **5a**−**c** and **7** in cyclohexane as solvent.

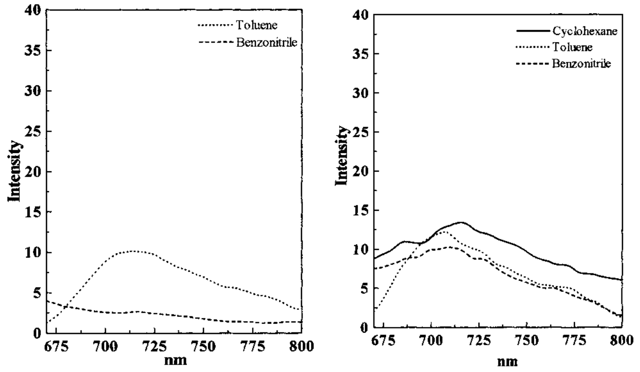

Figure 5. (Left): fluorescence spectra of compound **4c** in toluene (···) and benzonitrile (- - -) as solvents. (Right): fluorescence spectra of compound **5c** in cyclohexane (—), toluene (···), and benzonitrile (- - -) as solvents.

Thus, the fluorescence quenching of these compounds, particularly in polar solvents, is ascribed to an intramolecular pyrazolino unit-to-C_{60} electron-transfer process similar to that described for some aminofullerenes.[31a]

In conclusion, the steady-state fluorescence experiments show an efficient deactivation of the fullerene singlet excited state in pyrazolinofullerene derivatives **4a**−**c** and **5a**−**c**, as compared to pyrrolidinofullerenes **6** and **7**, even in nonpolar solvents such as cyclohexane. The dependence of the fluorescence quenching on solvent polarity in nitroderivatives **4c** and **5c** indicates a variation of the free energy associated with electron transfer.

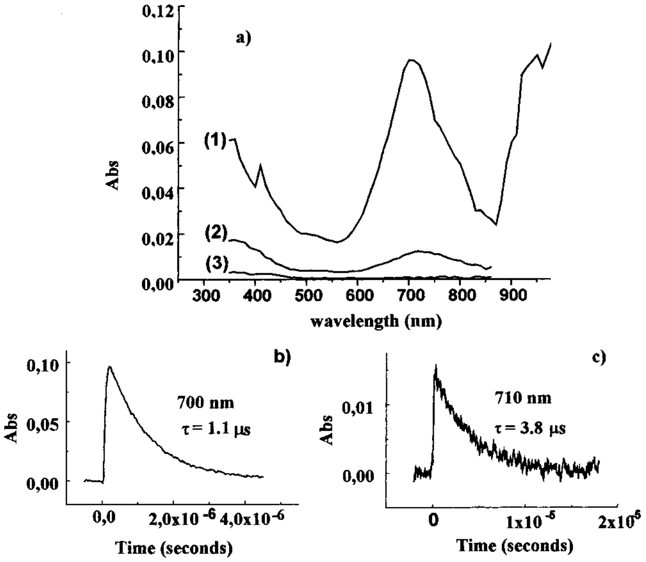

Figure 6. (a) Transient absorption spectra of nitrogen-purged benzonitrile solutions of **1a** (A_{532} = 0.091) at 0.250 E−6 s after the laser flash (1); **4c** (A_{532} = 0.19) at 1.00 E-6 s after the laser flash (2), and 18.00 E-6 s after the laser flash (3); (b) decay trace at 700 nm for **1a**; (c) decay trace at 710 nm for **4c**.

Transient Absorption Spectra. We have examined the photophysical processes of compounds **1a** and **4c** using a nanosecond laser flash photolysis equipment. Figure 6a (1) shows the difference transient absorption spectrum recorded after the excitation of dyad **1a** with a short laser pulse at 532 nm. This spectrum maximizes at 360 nm, 700 nm (assigned to the transient absorption of the C_{60} fullerene triplet),[33] and >980 nm (characteristic of the fullerene radical anion).[34] Transient decay at 700 nm (Figure 6b) is monoexponential ($k_{700} = 9.0 \times 10^5$ s^{-1}) being the deduced lifetime, $\tau = 1.1$ μs, much shorter than the lifetime of the parent C_{60} fullerene triplet (>40 μs depending on the solvent);[35] that indicates the occurrence of an efficient deactivating pathway such as an electron transfer from the donor moiety to the excited triplet fullerene. Deactivation at 960 nm also follows a monoexponential decay, with a rate constant $k_{960} = 6.5 \times 10^5$ s^{-1} ($\tau = 1.5$ μs). These decays are assigned to the fullerene triplet and the fullerene radical anion. Radical anion and radical cation are usually formed from the fullerene singlet and recombine on the subnanosecond time scale.[36] However, some electron transfer from or to triplet states and recombinations in the nanosecond time scales have been described.[24b,37]

The transient behavior of dyad **4c** is shown in Figure 6a (2). We observe the transient occurrence of a fullerene triplet (maxima at 360 and 710 nm) as well as the transient formation of the radical cation in the donor moiety of the dyad **4c**, related to the strong absorption

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in the range 350−450 nm, even present 18.00 E−6 s after the laser flash, Figure 6a (3). The lifetime deduced for the triplet fullerene moiety from the monoexponential decay at 710 nm, shown in Figure 6c, is $\tau = 3.8\ \mu$s ($k_{710} = 2.6 \times 10^5$ s^{-1}). The deactivation trace at 360 nm indicates a double exponential decay: $k_{360(1)} = 2.5 \times 10^5$ s^{-1} and $k_{360(2)} = 5.0 \times 10^4$ s^{-1}. The fast component corresponds to the decay of the triplet C_{60} moiety, while the slow one (lifetime, $\tau = 20\ \mu$s) is assigned to the radical cation of the donor moiety. Once again electron transfer to the fullerene triplet reduces its lifetime to 3.8 μs. In conclusion, the transient behavior of the two samples **1a** and **4c** supports the occurrence of intramolecular electron transfer from the donor moiety of the dyad to the C_{60} fullerene triplet.

Summary and Conclusions

Several new pyrazolylpyrazolino[60]fullerenes have been prepared in one pot from hydrazones on a time scale of minutes under microwave irradiation. All of the pyrazolino[60]fullerenes synthesized possess better electron affinity than the corresponding pyrrolidino[60]-fullerene (by up to 170 mV), and all except one present an anodically shifted first reduction potential (up to 80 mV) in comparison to the parent C_{60}. Consequently, the use of pyrazolino[60]fullerenes as acceptors for novel donor−acceptor arrays clearly has advantages over other fullerene derivatives. Moreover, the possibility of introducing two electroactive groups in the system opens the possibility of preparing donor−C_{60}−acceptor or donor−C_{60}−donor triads by an easy synthetic procedure, which represents an improvement over isoxazolino[60]fullerenes.

Steady-state fluorescence and transient absorption spectra indicate that an efficient photoinduced electron transfer process, giving rise to a charge-separated state, occurs in these systems, particularly when a polar solvent such as benzonitrile is used.

Experimental Section

General Procedures. All the cycloaddition reactions were performed under argon. Reactions under microwaves were carried out in a focused reactor (Maxidigest MX-350) obtained from Prolabo and 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 commercial starting materials 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 spectrophotometer on KBr disks. Fluorescence spectra were obtained on a JASCO FP-750 spectrophotometer. Laser Flash Photolysis experiments were performed using an LKS50 instrument from Applied Photophysics. The second harmonic (532 nm) of a Q-switched Nd:YAG laser (Spectron Laser Systems, UK; pulse width ca. 9 ns, 35.1 mJ/pulse) was used for laser flash excitation.

FAB mass spectra were obtained on a VGAutoSpec spectrometer, using *m*-nitrobenzyl alcohol as a matrix. Cyclic voltammetry measurements were obtained using a Versastat PAR EG & G potentiostat with analytical electrochemical software (Mod. 250). These measurements were made in a double-walled cell (Metrohm EA 876-20). A glassy carbon working electrode (Metrohm 6.0804.010) was used after being polished with alumina (0.3 μ) for 1 min, and platinum wire was used as counter electrode. A saturated calomel solution, used as a reference electrode, was separated from the solution by a solution of tetrabutylammonium perchlorate, which was used as the supporting electrolyte, in toluene/acetonitrile (4:1). The samples were purged with argon prior to measurement.

Preparation of Hydrazones 8a−c and 9a−c. General Procedure. Method A. A solution of 1-phenyl-4-formylpyrazole[20] or 1-phenyl-5-formylpyrazole[21] (0.5 g, 3 mmol) in 15 mL of ethanol was added to a solution of phenylhydrazine hydrochloride or *p*-methoxyphenylhydrazine (3 mmol) and sodium acetate trihydrate (0.8 g) in 10 mL of water. The reaction mixture was heated under reflux for 15 min. The mixture was cooled and the product filtered off and purified by recrystallization from ethanol.

Method B. A solution of 1-phenyl-4-formylpyrazole or 1-phenyl-5-formylpyrazole (0.5 g, 3 mmol) and *p*-nitrophenylhydrazine (0.46 g, 3 mmol) in 15 mL of ethanol and 0.5 mL of acetic acid was heated under reflux for 10 min. The mixture was cooled to room temperature and the product filtered off and purified by recrystallization from ethanol.

8a. By method A: yield 77%; mp 170−171 °C; FT-IR (Kbr) ν/cm^{-1} 3299, 1938, 1845, 1719, 1623, 1601, 1563, 1501, 1447; ^{1}H NMR (CDCl$_3$) δ 8.22 (s, 1H), 8.20 (d, J = 9.1 Hz, 2H), 8.03 (s, 1H), 7.95 (s, 1H), 7.83 (s, 1H), 7.74 (d, J = 8.1 Hz, 2H), 7.50 (t, J = 8.1 Hz, J = 7.7 Hz, 2H), 7.37 (t, J = 7.7 Hz, 1H), 7.10 (d, J = 9.1 Hz, 2H); ^{13}C NMR (DMSO-d_6) δ 150.6, 139.1, 137.9, 134.8, 129.6, 126.8, 126.6, 126.2, 120.3, 118.3, 110.9. Anal. Calcd for $C_{16}H_{14}N_4$, C, 73.26; H, 5.38; N, 21.36. Found: C, 73.40; H, 5.41; N, 21.30.

8b. By method A: yield 73%; mp 148−149 °C; FT-IR (Kbr) ν/cm^{-1} 3304, 2838, 1864, 1617, 1596, 1548, 1518, 1503, 1250; ^{1}H NMR (CDCl$_3$) δ 8.09 (s, 1H), 7.93 (s, 1H), 7.67 (d, J = 8.0 Hz, 2H), 7.63 (s, 1H), 7.43 (t, J = 8.0 Hz, 2H), 7.31 (s, 1H), 7.25 (t, J = 8.0 Hz, 1H), 7.01 (d, J = 9.0 Hz, 2H), 6.83 (d, J = 9.0 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 152.3, 139.6, 139.4, 138.5, 129.5, 128.1, 126.2, 125.0, 121.5, 118.1, 114.5, 112.7, 55.2. Anal. Calcd for $C_{17}H_{16}N_4O$, C, 69.85; H, 5.52; N 19.17. Found: C,70.01; H, 5.68; N, 19.12.

8c. By method B: yield 66%; mp 232−234 °C; FT-IR (KBr) ν/cm^{-1} 3253, 1621, 1613, 1597, 1560, 1497, 1317, 1298, 1276; ^{1}H NMR (CDCl$_3$) δ 8.22 (s, 1H), 8.20 (d, J = 9.1 Hz, 2H), 8.03 (s, 1H), 7.94 (s, 1H), 7.83 (s, 1H), 7.74 (d, J = 8.1 Hz, 2H), 7.50 (t, J = 8.1 Hz, J = 7.7 Hz, 2H), 7.37 (t, J = 7.7 Hz, 1H), 7.10 (d, J = 9.1 Hz, 2H); ^{13}C NMR (DMSO-d_6) δ 150.6, 139.1, 137.9, 134.8, 129.6, 126.8, 126.6, 126.2, 120.3, 118.3, 110.9. Anal. Calcd for $C_{16}H_{13}N_5O_2$, C, 62.53; H, 4.26; N, 22.79. Found: C, 62.71; H, 4.28; N, 22.66.

9a. By method A: yield 79%; mp 145−146 °C; FT-IR (Kbr) ν/cm^{-1} 3257, 1601, 1589, 1579, 1573, 1494, 1482, 1452; ^{1}H NMR (DMSO-d_6) δ 10.45 (s, 1H), 7.75 (s, 1H), 7.63 (d, J = 2.0 Hz, 1H), 7.51 (m, 5H), 7.14 (t, J = 7.3 Hz, 2H), 6.88 (d, J = 7.3 Hz, 2H), 6.85 (d, J = 2.0 Hz, 1H), 6.68 (t, J = 7.3 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ 143.5, 139.1, 138.3, 138.1, 128.2, 128.02, 127.04, 124.6, 124.4, 118.1, 110.8, 103.04. Anal. Calcd for $C_{16}H_{14}N_4$, C, 73.26; H, 5.38; N, 21.36. Found: C, 73.35; H, 5.44; N, 21.28.

9b. By method A: yield 65%; mp 145−146 °C; FT-IR (Kbr) ν/cm^{-1} 3351, 1699, 1683, 1652, 1617, 1586, 1453, 1441, 1347, 1282; ^{1}H NMR (DMSO-d_6) δ 10.26 (s, 1H), 7.68 (s, 1H), 7.63 (d, J = 2.0 Hz, 1H), 7.50 (m, 3H), 7.48 (d, J = 9.3 Hz, 2H), 6.93 (m, 2H), 6.79 (d, J = 9.3 Hz, 2H), 6.70 (d, J = 2.0 Hz, 1H), 3.63 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 151.8, 139.1, 138.3, 137.5, 128.2, 126.9, 124.4, 123.3, 113.5, 111.9, 102.6, 54.1. Anal. Calcd for $C_{17}H_{16}N_4O$, C, 69.85; H, 5.52; N 19.17. Found: C, 69.76; H, 5.64; N, 19.10.

9c. By method B: yield 73%; mp 232−233 °C; FT-IR (KBr) ν/cm^{-1} 3368, 1618, 1613, 1602, 1590, 1497, 1397, 1326, 1299; ^{1}H NMR (DMSO-d_6) δ 11.44 (s, 1H), 8.16 (d, J = 9.1 Hz, 2H), 7.95 (s, 1H), 7.72 (d, J = 2.0 Hz, 1H), 7.51 (m, 5H), 6.98 (d, J = 9.1 Hz, 2H), 6.89 (d, J = 2.0 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ 150.1, 140.4, 139.2, 138.70, 138.16, 130.95, 129.40, 128.37, 126.06, 125.63, 111.36, 105.50. Anal. Calcd for $C_{16}H_{13}N_5O_2$, C, 62.53; H, 4.26; N, 22.79. Found: C, 62.61; H, 4.31; N, 22.71.

Synthesis of Cycloadducts 4a−c and 5a−c. General Procedure. A solution of the corresponding hydrazone (**8a−c** or **9a−c**) and NBS in 45 mL of anhydrous benzene was stirred at room temperature for 15 min. Et_3N and C_{60} were then added to the solution. The reaction mixture was then irradiated in a focused microwave reactor for the appropriate time. The solvent was removed under reduced pressure. The resulting solid was purified by silica gel flash chromatography using toluene as the eluent. Centrifuging three times with methanol and once with diethyl ether accomplished further purification of the solid.

1′-Phenyl-3′-(1-phenylpyrazol-4-yl)pyrazolino[4′,5′:1,2]-[60]fullerene (4a). According to the general procedure, a solution of hydrazone **8a** (55 mg, 0.021 mmol) and NBS (38 mg, 0.021 mmol) in benzene was stirred at room temperature, and C_{60} (50 mg, 0.07 mmol) and Et_3N (21 mg, 0.21 mmol) were then added. The solution was irradiated for 30 min and 105 W irradiation power. The product was purified according to the general procedure, yielding 26 mg (38%, 55% based on reacted C_{60}) of **4a**: FT-IR (KBr) ν/cm^{-1} 1661, 1653, 1647, 1637, 1628, 1624, 1100, 952, 750, 526, 505, 473; ^1H NMR ($CDCl_3$) δ 8.71 (s, 1H), 8.54 (s, 1H), 7.95 (d, $J = 8.0$ Hz, 2H), 7.74 (d, $J = 7.6$ Hz, 2H), 7.49 (t, $J = 7.6$ Hz, $J = 8.0$ Hz, 3H), 7.36 (t, $J = 7.6$ Hz, $J = 8.0$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 144.3, 143.9, 143.7, 143.6, 142.7, 141.5, 141.3, 140.8, 139.2, 139.02, 138.1, 134.7, 128.1, 127.8, 127.4, 126.6, 125.6, 124.6, 123.5, 122.5, 117.9, 115.03, 109.07; UV−vis λ_{max}/nm (log ϵ) (C_6H_{12}) 686.3 (1.70), 449 (3.02), 426.0 (3.17), 311.5 (3.48); FAB-MS m/z 981 (M + 1), 720 (C_{60}).

1′-(4-Methoxyphenyl)-3′-(1-phenylpyrazol-4-yl)pyrazolino[4′,5′:1,2][60]fullerene (4b). According to the general procedure, a solution of hydrazone **8b** (61 mg, 0.21 mmol) and NBS (38 mg, 0.21 mmol) in benzene was stirred at room temperature, and C_{60} (50 mg, 0.07 mmol) and Et_3N (21 mg, 0.021 mmol) were added. The solution was irradiated for 30 min and 105 W irradiation power. The product was purified according to the general procedure, yielding 17 mg (24%, 33% based on reacted C_{60}) of **4b**: FT-IR (KBr) ν/cm^{-1} 1662, 1634, 1558, 1541, 1506, 1458, 1248, 754, 526; ^1H NMR ($CDCl_3$) δ 8.70 (s, 1H), 8.53 (s, 1H), 7.81 (d, $J = 8.9$ Hz, 2H), 7.73 (d, $J = 7.7$ Hz, 2H), 7.49 (t, $J = 7.3$ Hz, $J = 7.8$ Hz, 2H), 7.35 (t, $J = 7.3$ Hz, 1H), 7.02 (d, $J = 8.9$ Hz, 2H), 3.86 (s, 3H);^{13}C NMR ($CDCl_3/CS_2$ 1:1) δ 158.0, 147.5, 146.6, 146.5, 146.3, 146.2, 146.1, 146.0, 145.8, 145.5, 145.4, 144.6, 143.4, 143.1, 142.6, 142.5, 142.2, 141.0, 140.9, 140.2, 140.1, 140.0, 138.5, 137.4, 137.0, 136.3, 135.3, 129.8, 127.3, 126.7, 126.0, 125.4, 119.6, 117.1, 114.8, 55.7; UV−vis λ_{max}/nm (log ϵ) (C_6H_{12}) 688.6 (1.65), 447.0 (2.78), 425.5 (3.02), 318.0 (4.99); FAB-MS m/z 1011 (M + 1), 720 (C_{60}).

1′-(4-Nitrophenyl)-3′-(1-phenylpyrazol-4-yl)pyrazolino-[4′,5′:1,2][60]fullerene (4c). According to the general procedure, a solution of hydrazone **8c** (22 mg, 0.07 mmol) and NBS (13 mg, 0.07 mmol) in benzene was stirred at room temperature, and C_{60} (50 mg, 0.07 mmol) and Et_3N (7 mg, 0.07 mmol) were added. The solution was irradiated for 5 min and 210 W irradiation power. The product was purified according to the general procedure, yielding 20 mg (28%, 58% based on reacted C_{60}) of **4c**: FT-IR (KBr) ν/cm^{-1} 1903, 1588, 1546, 1496, 1428, 1314, 1112, 754, 526; ^1H NMR ($CDCl_3$) δ 8.73 (s, 1H), 8.55 (s, 1H), 8.36 (d, $J = 9.3$ Hz, 2H), 8.28 (d, $J = 9.3$ Hz, 2H), 7.75 (d, $J = 8.2$ Hz, 2H) 7.51 (t, $J = 7.3$ Hz, $J = 8.2$ Hz, 2H), 7.39 (t, $J = 7.3$ Hz, 1H); ^{13}C NMR ($CDCl_3/CS_2$ 1:1) δ 155.8, 146.4, 145.8, 144.9, 142.5, 141.1, 129.9, 126.7 125.6, 120.1, 119.7, 119.4, 116.6, 104.0; UV−vis λ_{max}/nm (log ϵ) (C_6H_{12}) 682.9 (1.90), 427.0 (3.23), 324.8 (4.29); FAB-MS m/z 1026 (M + 1), 720 (C_{60}).

1′-Phenyl-3′-(*N*-phenylpyrazol-5-yl)pyrazolino[4′,5′:1,2]-[60]fullerene (5a). According to the general procedure, a solution of hydrazone **9a** (37 mg, 0.15 mmol) and NBS (28 mg, 0.15 mmol) in benzene was stirred at room temperature and C_{60} (33 mg, 0.046 mmol) and Et_3N (15 mg, 0.15 mmol) were added. The solution was irradiated for 15 min and 195 W irradiation power. The product was purified according to the general procedure, yielding 14 mg (31%, 33% based on reacted C_{60}) of **5a**: FT-IR (KBr) ν/cm^{-1} 1595, 1492, 1384, 1339, 871, 759, 691, 526; ^1H NMR ($CDCl_3$) δ 7.76 (d, $J = 2.0$ Hz, 1H), 7.71 (d, $J = 6.7$ Hz, 2H), 7.51 (m, 5H), 7.30 (t, $J = 7.3$ Hz, 2H), 7.14 (t, $J = 7.3$ Hz, 1H), 7.05 (d, $J = 2.0$ Hz, 1H); ^{13}C NMR ($CDCl_3/CS_2$ 1:1) δ 147.9, 146.6, 146.5, 146.3, 146.2, 145.9, 145.7, 145.6, 145.3, 144.5, 144.4, 143.4, 143.1, 142.6, 142.5, 142.4, 142.3, 142.2, 141.1, 140.8, 140.5, 139.9, 136.5, 136.3, 134.9, 133.8, 132.7, 131.0, 129.5, 129.4, 129.0, 128.5, 126.4, 125.3, 123.5, 110.1, 68.2; UV−vis λ_{max}/nm (log ϵ) (C_6H_{12}) 688.5 (1.69), 449.0 (2.72), 425.5 (2.89), 313.5 (4.32); FAB-MS m/z 981 (M + 1), 720 (C_{60}).

1′-(4-Methoxyphenyl)-3′-(1-phenylpyrazol-5-yl)pyrazolino[4′,5′:1,2][60]fullerene (5b). According to the general procedure, a solution of hydrazone **9b** (21 mg, 0.07 mmol) and NBS (13 mg, 0.07 mmol) in benzene was stirred at room temperature and C_{60} (50 mg, 0.07 mmol) and Et_3N (7 mg, 0.07 mmol) were added. The solution was irradiated for 5 min and 210 W irradiation power. The product was purified according to the general procedure, yielding 31 mg (44%, 69% based on reacted C_{60}) of **5b**: FT-IR (KBr) ν/cm^{-1} 1718, 1700, 1637, 1508, 1104, 968, 800, 562, 526; ^1H NMR ($CDCl_3$) δ 7.80 (d, $J = 2.0$ Hz, 1H), 7.73 (d, $J = 6.7$ Hz, 2H), 7.56 (m, 3H), 7.35 (d, $J = 8.8$ Hz, 2H), 7.05 (d, $J = 2.0$ Hz, 1H), 6.84 (d, $J = 8.8$ Hz, 2H), 3.78 (s, 3H); ^{13}C NMR ($CDCl_3/CS_2$ 1:1) δ 157.8, 146.6, 146.2, 145.7, 145.6, 144.8, 144.5, 143.1, 142.5, 142.3, 140.8, 140.5, 140.1, 137.7, 136.3, 129.7, 129.5, 128.4, 126.4, 126.0, 114.6, 110.0, 55.7; UV−vis λ_{max}/nm (log ϵ) (C_6H_{12}) 677.0 (2.02), 447 (2.79), 426.0 (2.95), 312.5 (4.11); FAB-MS m/z 1011 (M + 1), 720 (C_{60}).

1′-(4-Nitrophenyl)-3′-(1-phenylpyrazol-5-yl)pyrazolino-[4′,5′:1,2][60]fullerene (5c). According to the general procedure, a solution of hydrazone **9c** (22 mg, 0.07 mmol) and NBS (13 mg, 0.07 mmol) in benzene was stirred at room temperature and C_{60} (50 mg, 0.07 mmol) and Et_3N (7 mg, 0.07 mmol) were added. The solution was irradiated for 7 min and 180 W irradiation power. The product was purified according to the general procedure, yielding 16 mg (22%, 49% based on reacted C_{60}) of **5c**: FT-IR (KBr) ν/cm^{-1} 1637, 1591, 1498, 1328, 1315, 1115, 764, 526; ^1H NMR ($CDCl_3$) δ 8.18 (d, $J = 9.3$ Hz, 2H) 7.86 (d, $J = 2.0$ Hz, 1H), 7.66 (d, $J = 9.3$ Hz, 2H), 7.64 (m, 5H), 7.14 (d, $J = 2.0$ Hz, 1H); ^{13}C NMR ($CDCl_3/CS_2$ 1:1) δ 149.4, 146.7, 145.8, 144.7, 143.3, 142.7, 142.4, 141.0, 140.7, 131.1, 129.7, 129.1, 128.8, 127.6, 126.5, 125.4, 122.4, 119.6, 110.6; UV−vis λ_{max}/nm (log ϵ) (C_6H_{12}) 682.8 (2.08), 427.4 (2.82), 325.9 (3.23); FAB-MS m/z 1026 (M + 1), 720 (C_{60}).

2′-(1-Phenylpyrazol-4-yl)pyrrolidino[3′,4′:1,2][60]-fullerene (6). A solution of C_{60} (50 mg, 0.07 mmol), 1-phenyl-4-formylpyrazole (60 mg, 0.35 mmol) and *N*-methylglycine (13 mg, 0.14 mmol) in 50 mL of toluene was heated under reflux for 2 h. The solvent was then evaporated and the crude material was purified by flash chromatography on silica gel using toluene as eluent to yield 32 mg of **6** (51%, 68% based on reacted C_{60}). Further purification of the solid was accomplished by centrifuging three times with methanol and once with diethyl ether: FT-IR (KBr) ν/cm^{-1} 1748, 1652, 1635, 1622, 1616, 1505, 782, 752, 526; ^1H NMR ($CDCl_3$) δ 8.24 (s, 1H), 8.01 (s, 1H), 7.69 (d, $J = 7.3$ Hz, 2H), 7.43 (t, $J = 7.3$ Hz, $J = 8.0$ Hz, 2H), 7.26 (t, $J = 7.43$ Hz, 1H), 4.99 (s, 1H), 4.94 (d, $J = 9.5$ Hz, 1H), 4.18 (d, $J = 9.5$ Hz, 1H), 2.85 (s, 3H); ^{13}C NMR ($CDCl_3/CS_2$ 1:1) δ 156.4, 154.0, 153.5, 147.6, 146.7, 146.6, 146.4, 146.2, 146.0, 145.8, 145.7, 145.6, 144.8, 144.6, 143.4, 143.2, 143.0, 142.8, 142.4, 142.3, 141.8, 140.4, 140.1, 137.2, 136.7, 136.0, 134.9, 129.8, 127.0, 126.9, 120.8, 119.1; UV−vis λ_{max}/nm (log ϵ) (C_6H_{12}) 689.0 (2.58), 452.0 (3.17), 430.5 (3.50), 308.5 (4.63); FAB-MS m/z 920 (M + 1), 720 (C_{60}).

2′-(1-Phenylpyrazol-5-yl)pyrrolidino[3′,4′:1,2][60]-fullerene (7). A solution of C_{60} (50 mg, 0.07 mmol), 1-phenyl-5-formylpyrazole (60 mg, 0.35 mmol) and *N*-methylglycine (13 mg, 0.14 mmol) in 50 mL of toluene was heated under reflux for 2 h. The solvent was then evaporated and the crude material was purified by flash chromatography on silica gel using toluene as eluent to yield 13 mg of **7** (20%, 78% based unconsumed C_{60}). Centrifuging three times with methanol and once with diethyl ether accomplished further purification of the solid: FT-IR (KBr) ν/cm^{-1} 1637, 1629, 1500, 1396, 1179, 1121, 1109, 782, 526; ^1H NMR ($CDCl_3$) δ 7.75 (d, $J = 1.6$ Hz, 1H), 7.41 (m, 5H), 6.86 (d, $J = 1.6$ Hz, 1H), 5.12 (s, 1H), 4.87 (d, $J = 9.7$ Hz, 1H), 4.07 (d, $J = 9.7$ Hz, 1H), 2.82 (s, 3H); ^{13}C NMR ($CDCl_3/CS_2$ 1:1) δ 155.65, 152.98, 152.74, 151.90, 147.14, 146.15, 144.45, 144.11, 142.75, 142.50, 141.90, 141.77, 140.47, 140.05, 139.8, 139.01, 138.76, 137.27, 136.61, 135.45, 129.02, 128.78, 127.16, 108.44, 71.10, 69,34, 68.73, 39.73; UV−vis λ_{max}/nm (log ϵ) (C_6H_{12}) 688.5 (3.09), 450.0 (3.55), 430.5 (3.72), 309.5 (4.68); FAB-MS *m*/*z* 920 (M + 1), 720 (C_{60}).

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Supporting Information Available: Cyclic voltammogram of compound**4c** (Figure SI-1). Absorption maxima of dyads **4a**−**c**, **5a**−**c**, **6,** and **7** in different solvents (Table SI-1). Fluorescence spectra of compounds **6**, **7**, and **10** in cyclohexane (Figure SI-2). ^{1}H NMR and MS spectra for compounds **5a**−**c**, **6**, **7,** and the corresponding starting materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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