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Synthesis and properties of pyrazolino[60]fullerene-donor systems

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Abstract—A series of pyrazolino[60]fullerenes has been prepared in one pot by 1,3-dipolar cycloaddition to C_{60} of the corresponding nitrile imine, which was generated in situ from the corresponding hydrazone. A range of donors and acceptors were introduced as substituents. Electrochemical and photophysical studies have revealed weak ground-state interactions between the organic addends and the fullerene sphere. Steady-state fluorescence has shown that, in both toluene and benzonitrile solutions, an efficient electron transfer process takes place when a strong donor is attached to the pyrazolino[60]fullerene system.

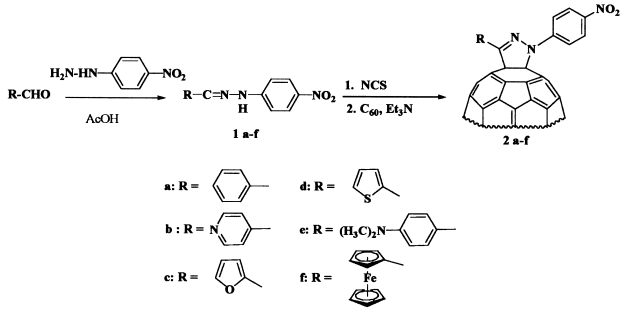
1. Introduction

The photophysical properties of [60]fullerene derivatives[1] and the inter- and intramolecular electron transfer reactions[2] of these interesting molecules have been the focus of several research groups in recent years. The reason for this interest is the combination of the strong electron-accepting properties of fullerenes[3] and the incorporation of donor moieties onto the C_{60} core through a bridge.[4] Therefore, a variety of C_{60}-bridge-donor dyads have been synthesized in the search for systems with improved charge separation properties.[5]

Although 1,3-dipolar cycloaddition reactions have been widely used to prepare fullerene derivatives, the functionalization of C_{60} with 1,3-nitrile imines to give pyrazolino[60]fullerenes has scarcely been exploited.[6] In this respect, we recently described the facile synthesis of several pyrazolylpyrazolino[60]fullerenes by 1,3-dipolar cycloaddition between nitrile imines and C_{60}.[7] The nitrile imine was generated in situ from the corresponding hydrazone and NBS under microwave irradiation, a source of energy that has proven useful when applied in fullerene chemistry.[8] Interestingly, the pyrazolylpyrazolino[60]fullerenes prepared in this way show first and second reduction potentials that are anodically shifted (~150 mV) relative to other 1,2-dihydrofullerenes (such as pyrrolidino[60]fullerenes) and are better than the C_{60} itself.[9] We attributed this shift to the electronegative character of the nitrogen atom linked to the C_{60} core. In this paper we report the synthesis, electrochemistry and photophysical properties of a series of pyrazolino[60]fullerene derivatives **2a**–**f** bearing different functional groups as substituents. Other pyrazolino[60]-fullerene derivatives have shown similar electrochemical behaviour.[10]

2. Results and discussion

Synthesis. Compounds **2a**–**f** were synthesized in two steps from the corresponding aldehydes as shown in Scheme 1. Hydrazones **1a**–**f** were prepared in good yields by reaction of the corresponding aldehyde with 4-nitrophenylhydrazine in the presence of acetic acid using ethanol as the solvent. Cycloadducts **2a**–**f** were prepared by a modification of our previously described procedure.[7] This modification avoids the use of microwave irradiation and the reaction can now be carried out at room temperature. The corresponding hydrazone was treated with *N*-chlorosuccinimide (NCS) in the presence of pyridine using chloroform as the solvent; the resulting chloro-derivative was reacted with Et_3N and C_{60}



Scheme 1.

Keywords: fullerene; electron transfer; electrochemistry.

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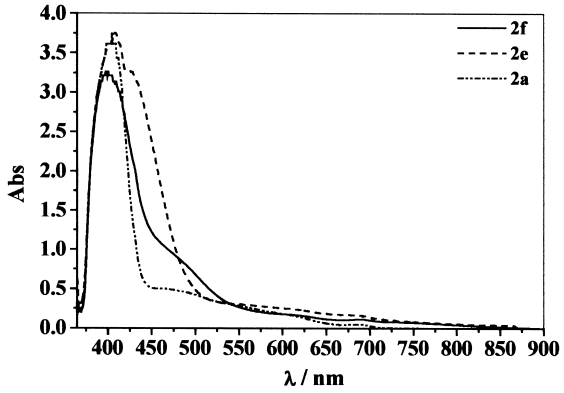

Figure 1. UV–Vis spectra of **2a** (···), **2e** (- - -) and **2f** (—) in carbon disulfide.

for 45 min. Under these conditions adducts **2a–f** were obtained in 24–43% yield (49–82% based on reacted C_{60}). The adducts were purified by column chromatography (silica gel, toluene) followed by centrifugation in hexane, methanol and diethyl ether.

The new cycloadducts **2a–f** were characterized by MALDI or FAB-MS as well as by ^{1}H, ^{13}C NMR, FT-IR and UV–Vis spectroscopy. In all cases the molecular ions were observed in the mass spectra, using MALDI or FAB techniques in positive ion mode, at *m/z* values corresponding to the MH^+ fragment (see Section 4). The ^{1}H NMR of **2a–f** show all the expected signals and the *p*-substituted phenyl groups appeared as AA′XX′ systems with $J_{AX}=J_{A'X'}$=9-10 Hz and $J_{AX'}=J_{A'X}=J_{AA'}=J_{XX'}=0$ as described in Section 4.

Absorption spectra. The UV–Vis spectra of this family of cycloadducts are similar to those described for other pyrazolino[60]fullerenes;[8] the absorption peak at 430 nm, typical of [6,6] adducts, appears as a shoulder, shaded by the *p*-nitrophenyl group. Nevertheless, some differences between the UV–Vis spectra of some adducts (**2e** and **2f**) and the superposition of the isolated components is observed. These discrepancies are indicative of weak electronic interactions between the substituent and the C_{60}

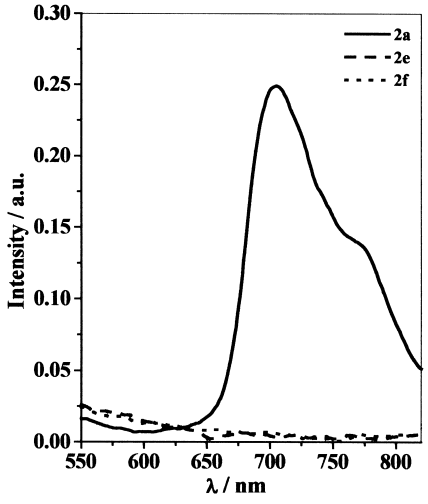

Figure 2. Fluorescence spectra of compounds **2a** (—), **2e** (- - -) and **2f** (···) in toluene.

Table 1. Fluorescence data of compounds **2a–f**

Compound	λ_{max} (nm)/intensity (a.u.)	
	Toluene	Benzonitrile
2a	705/0.249	704/0.128
	772/0.138	766/0.073
2b	631/0.068	620/0.090
	716/0.085	717/0.070
2c	719/0.108	725/0.075
2d	705/0.081	728/0.016
	725/0.083	
2e	–	–
2f	–	–

moieties in the ground state and a broad band is observed in the region 450–550 nm when CS_2 is used as the solvent (Fig. 1). This band is stronger and red-shifted with respect to those seen in CH_2Cl_2 and is consistent with the electrochemical studies detailed below. Comparable effects have been found in other donor-C_{60} systems.[11]

Fluorescence spectra. The fluorescence spectra of **2a–f** were measured in both toluene and benzonitrile upon excitation at 430 nm at room temperature. Solutions with the same absorbance were employed so that the fluorescence intensity and the quantum yields could be correlated.

On using toluene as the solvent (see Fig. 2 and Table 1), the fluorescence spectrum of pyrazolino[60]fullerene **2a** (R=Ph) is similar to those of other fullerene derivatives, showing an emission maximum at 705 nm with a shoulder at 772 nm as a consequence of the inter-system crossing into the triplet excited state.

The intensities of the emission maxima in **2b–d** are lower (see Table 1) and the maxima are red shifted (716, 719 and 725 nm, respectively) with respect to those of **2a**. This trend indicates that the excited state is partially quenched. Emission was not observed (Fig. 2) when a strong donor such as *N*,*N*-dimethylaniline (**2e**) was linked to the pyrazolino[60]fullerene system.

This quenching can be explained in terms of a photoinduced electron transfer process (PET), which is not common in non-polar solvents like toluene.

Related fulleropyrrolidines incorporating *N*,*N*-dimethylaniline and ferrocene moieties, e.g. fulleropyrrolidines **3**[12] and **4**[11b] (Chart 1), show fluorescence in non-polar solvents.

On the other hand, as shown in Table 1, the fluorescence intensity in benzonitrile was reduced (to about 1/2 that in

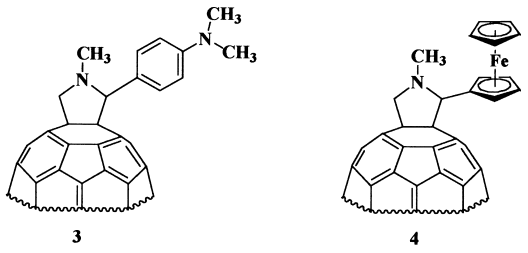

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Chart 1.

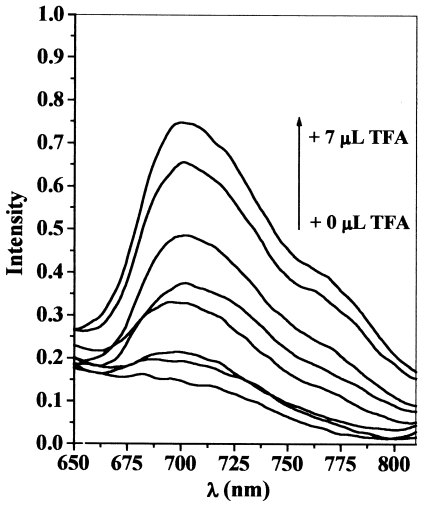

Figure 3. Fluorescence spectra of compound **2e** upon addition of increasing amounts of trifluoroacetic acid.

toluene for **2a**, to 1/1.2 for **2b**, to 1/1.5 for **2c** and to 1/20 for **2d**) with solvatochromic red-shifts of the maxima in all cases. This solvatochromic effect in benzonitrile in comparison to toluene has been assigned to a weak CT character.[13] This quenching of the fluorescence is ascribed to a weak PET interaction when the polarity of the solvent is increased and, consequently, the charge separated state should be more stable.

Addition of TFA to a benzonitrile solution of **2e** (R=*N*,*N*-dimethylaniline) causes an enhancement in the fluorescence (Fig. 3), suggesting a quenching of the PET process as the lone electron pairs of both nitrogen atoms (*N*,*N*-dimethylaniline group and pyrazoline ring) become unavailable. One of the electron pairs (or both) should be responsible for the PET process;[14] the addition of base (pyridine) again causes a quenching of the fluorescence, indicating the reversibility of the process.

Electrochemical studies. Most C_{60} monoadducts show small negative shifts (ca. 100 mV) in the reduction potential when compared with those of the parent C_{60} as a result of the partial loss of conjugation upon derivatisation.[3,15] Nevertheless, we have recently shown that several pyrazolylpyrazolino[60]fullerenes show an anodic shift (up to 80 mV for E_{red}^1) compared to C_{60}[9,10] itself, and this is due to the inductive effect of the nitrogen atom close to the C_{60} cage. Similar behaviour has also been found in isoxazolino[60]-fullerenes.[16] The redox behaviour of the newly synthesized compounds was examined using cyclic voltammetry (CV) and Osteryoung square-wave voltammetry (OSWV). These studies were carried out at room temperature in *o*-dichlorobenzene/acetonitrile (4:1) as solvent and using tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte (see Section 4). In order to investigate the influence of the substituent R^1 on the pyrazolino system we considered the first reversible reduction potential. The OSWV data of the prepared fullerene derivatives are presented in Table 2 along with those of C_{60} for comparison purposes.

Table 2. Redox potentials (OSWV) of organofullerenes **2a**–**f**, and C_{60}

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

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

The cyclic voltammogram (CV) of all the pyrazolino[60]-fullerenes (**2a**–**f**) show four quasi-reversible reduction waves for the fullerene moiety, which is similar to the situation found for the parent C_{60}. In addition, another non-reversible reduction wave (between the second and the third fullerene reduction waves) is observed and this can be reasonably assigned to the *p*-nitrophenyl moiety, as suggested by comparison with the reduction potential of nitrobenzene. The influence of strong electron donors, such as ferrocene or *N*,*N*-dimethylaniline, and electron acceptors, such as pyridine, was studied. Clearly, the introduction of an electron acceptor like pyridine (**2b**) results in the most positive first reduction potential in this series (−0.91 V) and the molecule has a better electron affinity than the parent C_{60} (−0.95 V). On the other hand, electron donors like furan (**1c**) or *N*,*N*-dimethylaniline (**1e**) afford the most negative value (−0.95 V) in this series and the first reduction potential is similar to that of C_{60} (−0.95 V). It is not clear whether this influence of the nature of the substituent on the electron affinity of the fullerene derivative can be explained in terms of through-bond or through-space interactions between the substituent and the fullerene surface.

Comparison of the reduction potentials of the *p*-nitrophenyl moiety in this series shows a shift to more negative values as the electron–donor ability of the substituent on the other side of the molecule (see Scheme 1 and Table 2) is increased. This reduction potential is shifted by 60 mV when a strong electron-donor, such as *N*,*N*-dimethylaniline (**2e**) or ferrocene (**2f**), is linked to the pyrazoline ring, thus demonstrating the electronic communication between the *C*-substituent and the sp^3 nitrogen atom of the pyrazoline ring; consequently, the electron transfer process from this nitrogen atom should be favoured when an electron donor is incorporated within the molecule as a C-substituent.

3. Summary

Pyrazolino[60]fullerene derivatives functionalized with different substituents have been synthesized in one pot by 1,3-dipolar cycloaddition between C_{60} and the corresponding nitrile imine generated in situ from the appropriate hydrazone. In contrast with other families of fullerene derivatives, systems based on pyrazolino[60]fullerene present a similar electron affinity to pristine C_{60} as a consequence of the inductive effect of the nitrogen atom close to the fullerene cage. Both electrochemical and photophysical studies revealed that there are small ground-state interactions between the organic addend and the fullerene

sphere. Steady-state fluorescence indicates that an efficient photoinduced electron transfer process occurs in these systems in benzonitrile solutions. When a strong donor, such as ferrocene or *N*,*N*-dimethylaniline, is linked to the pyrazoline ring, fluorescence is not observed in toluene solutions, indicating the efficiency of the photoinduced electron transfer process for this kind of system even in non-polar solvents.

4. Experimental

4.1. General remarks

All cycloaddition reactions were performed under Argon. C_{60} was purchased from MER Corporation (Tucson, AZ); the corresponding starting materials were purchased from ACROS. TLC using Merck silica gel 60-F254 was used to monitor cycloaddition reactions. ^{1}H 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 using KBr disks. Fluorescence spectra were obtained on a JASCO FP-750 spectrophotometer.

FAB mass spectra were obtained on a VG AutoSpec spectrometer, using *m*-nitrobenzyl alcohol as a matrix, and MALDI-TOF mass spectra were obtained on a Bruker ReflexIII spectrometer. Cyclic voltammetry measurements were carried out on an Autolab PGSTAT 30 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 6.1247.000 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 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. Scan rate: 100 mV s^{-1}.

4.2. Preparation of hydrazones. General procedure

A solution of the corresponding aldehyde (3.3 mmol), 4-nitrophenylhydrazine (3.3 mmol) and two drops of acetic acid in 15 mL of ethanol was heated under reflux for 10 min. The mixture was cooled to room temperature, filtered and the solid was recrystallized from ethanol.

4.2.1. Benzaldehyde 4-nitrophenylhydrazone (1a). Yield: 85%; mp: 189–190°C; FT-IR (KBr) ν (cm^{-1}) 3257.5, 1593.4, 1547.0, 1295.2, 1155.8, 1096.1, 990.1, 930.4, 837.6, 744.7, 671.8, 526.4, 479.6; ^{1}H NMR ($CDCl_3$) δ 7.14 (d, 2H, *J*=9 Hz), 7.38 (dd, 1H, *J*=3, 4 Hz), 7.41 (dd, 2H, *J*=4, 6 Hz), 7.70 (dd, 2H, *J*=3, 6 Hz), 7.81 (s, 1H), 8.04 (s, 1H), 8.20 (d, 2H, *J*=9 Hz); ^{13}C NMR ($CDCl_3$) δ 112.0, 126.5, 127.0, 129.1, 130.0, 134.3, 141.5, 144.1, 152.6; Anal. calcd for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.75; H, 4.72; N, 17.44.

4.2.2. 4-Pyridinecarboxaldehyde 4-nitrophenylhydrazone (1b). Yield: 64%; mp: 263–265°C; FT-IR (KBr) ν (cm^{-1}) 3199.4, 1600.0, 1540.3, 1493.9, 1341.4, 1215.5, 1129.3, 990.1, 917.1, 835.6, 744.8, 691.8, 552.5, 489.9; ^{1}H NMR ($CDCl_3$) δ 7.19 (d, 2H, *J*=9 Hz), 7.55 (d, 2H, *J*=6 Hz), 8.23 (d, 2H, *J*=9 Hz), 8.66 (d, 2H, *J*=6 Hz); ^{13}C NMR ($CDCl_3$) δ 150.7, 139.1, 138.1, 126.4, 126.2, 120.8, 112.8, 112.5; Anal. calcd for $C_{12}H_{10}N_4O_2$: C, 59.50; H, 4.16; N, 23.13. Found: C, 59.23; H, 3.89; N, 22.86.

4.2.3. 2-Furaldehyde 4-nitrophenylhydrazone (1c). Yield: 66%; mp: 152–153°C; FT-IR (KBr) ν (cm^{-1}) 3254.9, 1585.2, 1496.5, 1489.0, 1297.2, 1272.9, 1172.1, 1169.1, 1172.1, 1070.2, 1015.8, 939.2, 883.5, 842.1, 823.2, 748.3, 694.0, 593.3, 493.3, 416.6; ^{1}H NMR ($CDCl_3$) δ 6.47 (dd, 1H, *J*=2, 4 Hz), 6.66 (d, 1H, *J*=4 Hz), 7.08 (d, 2H, *J*=9 Hz), 7.55 (d, 1H, *J*=2 Hz), 7.67 (s, 1H), 7.96 (s, 1H), 8.16 (d, 2H, *J*=9 Hz); ^{13}C NMR ($CDCl_3$) δ 149.7, 149.5, 144.4, 140.6, 131.5, 126.4, 112.2, 112.0, 111.9; Anal. calcd for $C_{11}H_9N_3O_3$: C, 57.14; H, 3.92; N, 18.17. Found: C, 56.94; H, 3.87; N, 17.85.

4.2.4. 2-Thiophenecarboxaldehyde 4-nitrophenylhydrazone (1d). Yield: 60%; mp: 196–197°C; FT-IR (KBr) ν (cm^{-1}) 2406.6, 1605.8, 1591.0, 1549.7, 1493.9, 1478.8, 1462.2, 1325.8, 1295.7, 1274.8, 1233.0, 1169.5, 1105.7, 1042.2, 998.7, 929.1, 838.4, 748.7, 696.1, 657.02, 553.7, 489.6; ^{1}H NMR ($CDCl_3$) δ 7.05 (d, 1H, *J*=4 Hz), 7.09 (d, 2H, *J*=9 Hz), 7.20 (dd, 1H, *J*=4, 5 Hz), 7.36 (d, 1H, *J*=5 Hz), 8.01 (s, 1H), 8.18 (d, 2H, *J*=9 Hz); ^{13}C NMR ($CDCl_3$) δ 149.3, 140.5, 139.2, 136.1, 128.7, 127.8, 127.7, 126.3, 111.9; Anal. calcd for $C_{11}H_9N_3O_2S$: C, 53.43; H, 3.67; N, 16.99. Found: C, 53.18; H, 3.42; N, 16.74.

4.2.5. 4-(*N*,*N*-dimethylamino)benzaldehyde 4-nitrophenyl hydrazone (1e). Yield: 64%; mp: 177–178°C; FT-IR (KBr) ν (cm^{-1}) 3290.6, 2899.5, 2813.3, 1593.4, 1527.1, 1494.0, 1321.5, 1361.3, 1182.3, 1162.4, 1116.1, 990.1, 950.3, 811.1, 751.4, 685.1, 638.7, 592.3, 519.3, 479.6; ^{1}H NMR ($CDCl_3$) δ 3.02 (s, 6H), 6.71 (d, 2H, *J*=9 Hz), 7.06 (d, 2H, *J*=10 Hz), 7.56 (d, 2H, *J*=9 Hz), 8.16 (d, 2H, *J*=10 Hz); ^{13}C NMR ($CDCl_3$) δ 151.6, 150.1, 142.8, 139.8, 128.4, 126.5, 122.1, 112.2, 111.5, 40.5; Anal. calcd for $C_{15}H_{16}N_4O_2$: C, 63.37; H, 5.67; N, 19.71. Found: C, 62.92; H, 5.50; N, 19.42.

4.2.6. Ferrocenecarboxaldehyde 4-nitrophenylhydrazone (1f). Yield: 70%; mp: 183–185°C; FT-IR (KBr) ν (cm^{-1}) 3292.8, 1598.1, 1534.0, 1479.2, 1459.4, 1323.9, 1307.7, 1271.0, 1208.9, 1168.8, 1109.3, 1061.5, 1042.9, 1023.7, 999.8, 946. 8, 928.3, 836.1, 813.8, 750.4, 693.7, 544.1, 531.6, 495.5; ^{1}H NMR ($CDCl_3$) δ 4.20 (s, 5H), 4.40 (s, 2H), 4.62 (s, 2H), 7.03 (d, 2H, *J*=9 Hz), 8.17 (d, 2H, *J*=9 Hz); ^{13}C NMR ($CDCl_3$) δ 142.2, 126.5, 125.6, 113.0, 111.5, 73.5, 71.0, 70.4, 69.9, 69.3, 69.5, 69.1, 67.6; Anal. calcd for $C_{17}H_{15}FeN_3O_2$: C, 58.48; H, 4.30; N, 12.04. Found: C, 57.78; H, 4.16; N, 11.70.

4.3. Synthesis of cycloadducts. General procedure

To a solution under argon of the appropriate hydrazone (0.07 mmol) in 10 mL of dry chloroform was added pyridine (10 μL). The mixture was cooled to 0°C, 18 mg (0.014 mmol) of NCS was added and the mixture was stirred for 15 min; [60]fullerene (50 mg, 0.07 mmol) and Et_3N

(7 mg, 0.07 mmol) were then added. The solution was allowed to reach room temperature and stirred for 45 min. The solvent was removed under reduced pressure and the resulting solid was purified by silica gel flash chromatography, using toluene as eluent. Centrifugation with methanol and diethyl ether achieved further purification of the solid.

4.3.1. 1′-(4-Nitrophenyl)-3′-phenylpyrazolino[4′,5′:1,2]-[60]fullerene (2a). Yield: 34 mg (43, 82% based on reacted C_{60}). FT-IR (KBr) ν (cm^{-1}) 3443.1, 2926.0, 1580.1, 1500.5, 1321.5, 1255.2, 1102.8, 837.6, 744.7, 671.8, 526.0; ^{1}H NMR ($CDCl_3$) δ 7.55 (dd, 1H, J=2, 6 Hz), 8.21 (dd, 2H, J=2, 6 Hz), 8.22 (dd, 2H, J=6, 6 Hz), 8.27 (d, 2H, J=10 Hz), 8.35 (d, 2H J=10 Hz); ^{13}C NMR ($CDCl_3/CS_2$ 1:1) δ 146.8, 146.4, 146.0, 145.7, 144.9, 143.3, 142.8, 142.5, 142.3, 137.3, 130.5, 129.5, 129.3, 128.6, 127.7, 127.2, 125.6, 119.5, 97.2; UV–Vis (CH_2Cl_2) λ_{max} (nm) (log ε) 617.0 (2.68), 491.0 (3.25), 375.0 (4.45), 318.5 (4.68); FAB-MS m/z: 960 (M+1), 720 (C_{60}).

4.3.2. 1′-(4-Nitrophenyl)-3′-(4-pyrimidyl)pyrazolino-[4′,5′:1,2][60]fullerene (2b). Yield: 23 mg (34, 69% based on reacted C_{60}). FT-IR (KBr) ν (cm^{-1}) 3409.8, 1730.6, 1154.8, 1508.2, 1489.4, 1328.2, 1263.8, 1244.1, 1107.4, 1040.3, 878.2, 844.9, 817.6, 746.3, 676.2, 562.8, 544.4, 526.0; ^{1}H NMR ($CDCl_3$) δ 8.21 (d, 2H, J=6 Hz), 8.26 (d, 2H, J=9 Hz), 8.37 (d, 2H, J=9 Hz), 8.81 (d, 2H, J=6 Hz); ^{13}C NMR ($CDCl_3/CS_2$ 1:1) δ 150.8, 149.3, 146.8, 146.4, 146.3, 145.8, 145.6, 144.7, 143.5, 143.3, 142.7, 142.4, 142.2, 140.8, 139.8, 139.4, 137.3, 136.7, 125.7, 122.9, 120.3; UV–Vis (CH_2Cl_2) λ_{max} (nm) (log ε) 606.0 (2.96), 488.5 (3.56), 388.0 (4.64), 318 (4.9); MALDI-TOF m/z: 961 (M+1), 720 (C_{60}).

4.3.3. 1′-(4-Nitrophenyl)-3′-(2-furanoyl)pyrazolino-[4′,5′:1,2][60]fullerene (2c). Yield: 31 mg (43, 76% based on reacted C_{60}). FT-IR (KBr) ν (cm^{-1}) 3456.3, 2922.6, 2852.2, 1618.0, 1459.8, 1323.2, 1270.8, 1209.6, 1110.2, 825.9, 745.4, 529.5, 470.3; ^{1}H NMR ($CDCl_3$) δ 6.66 (dd, 1H, J=3, 2 Hz), 7.39 (d, 1H, J=3 Hz), 7.68 (d, 1H, J=2 Hz), 8.26 (d, 1H, J=10 Hz), 8.34 (d, 1H, J=10 Hz); ^{13}C NMR ($CDCl_3/CS_2$ 1:1) δ 154.3, 149.7, 146.4, 145.5, 144.7, 143.4, 142.5, 141.5, 130.3, 125.7, 125.6, 122.3, 119.9, 113.6, 112.6, 96.7, 66.22; UV–Vis (CH_2Cl_2) λ_{max} (nm) (log ε) 611.5 (2.84), 393.5 (4.03), 320.5 (4.63); FAB-MS m/z: 950 (M+1), 720 (C_{60}).

4.3.4. 1′-(4-Nitrophenyl)-3′-(2-thienyl)pyrazolino-[4′,5′:1,2][60]fullerene (2d). Yield: 29 mg (43, 70% based on reacted C_{60}). FT-IR (KBr) ν (cm^{-1}) 3434.9, 1589.5, 1493.9, 1427.6, 1328.6, 1261.9, 1102.8, 845.3, 708.1, 526.5; ^{1}H NMR ($CDCl_3$) δ 7.17 (dd, J=5, 4 Hz), 7.54 (d, 1H, J=5 Hz), 8.04 (d, 1H, J=4 Hz), 8.26 (d, 2H, J=10 Hz), 8.34 (d, 2H, J=10 Hz); ^{13}C NMR ($CDCl_3/CS_2$ 1:1) δ 149.6, 146.4, 146.2, 145.5, 144.8, 144.0, 143.5, 142.7, 142.5, 140.7, 139.7, 129.2, 128.8, 128.4, 125.6, 119.8, 69.10; UV–Vis (CH_2Cl_2) λ_{max} (nm) (log ε) 672.0 (2.58), 501.0 (3.24), 398.0 (4.13), 319.5 (4.29); MALDI-TOF m/z: 966 (M+1), 720 (C_{60}).

4.3.5. 1′-(4-Nitrophenyl)-3′-(4-*N*,*N*-dimethylaminophenyl)-pyrazolino[4′,5′:1,2][60]fullerene (2e). Yield: 29 mg (42, 65% based on reacted C_{60}). FT-IR (KBr) ν (cm^{-1}) 3339.2, 1584.2, 1509.2, 1324.5, 1261.1, 1192.8, 1109.9, 1045.7, 842.2, 812.8, 746.3, 524.9, 476.2; ^{1}H NMR ($CDCl_3$) δ 3.06 (s, 6H), 6.82 (d, 2H, J=9 Hz), 8.16 (d, 2H, J=9 Hz), 8.26 (d, 2H, J=10 Hz), 8.33 (d, 2H, J=10 Hz); ^{13}C NMR ($CDCl_3/CS_2$ 1:1) δ 151.5, 150.3, 147.1, 146.7, 146.4, 146.2, 145.5, 144.9, 144.4, 144.1, 143.4, 143.2, 142.7, 142.4, 140.6, 139.6, 137.3, 136.3, 130.6, 125.7, 119.2, 112.2, 40.4; UV–Vis (CH_2Cl_2) λ_{max} (nm) (log ε) 657.5 (2.53), 486.0 (3.35), 390.5 (3.92), 319.5 (4.29); MALDI-TOF m/z: 1002 (M+1), 852 (M−150), 720 (C_{60}).

4.3.6. 1′-(4-Nitrophenyl)-3′-(ferrocenyl)pyrazolino-[4′,5′:1,2][60]fullerene (2f). Yield: 18 mg (24, 49% based on reacted C_{60}). FT-IR (KBr) ν (cm^{-1}) 2899.4, 1585.1, 1491.6, 1460.5, 1318.5, 1273.2, 1105.4, 842.6, 745.9, 525.6, 477.7; ^{1}H NMR ($CDCl_3$) δ 4.23 (s, 5H), 5.49 (t, J=2 Hz), 5.28 (t, J=2 Hz), 8.21 (d, 2H, J=10 Hz), 8.33 (d, 2H, J=10 Hz); ^{13}C NMR ($CDCl_3/CS_2$ 1:1) δ 150.5, 150.0, 147.4, 146.6, 146.4, 146.0, 145.9, 145.0, 144.7, 143.3, 142.7, 142.4, 142.2, 140.4, 139.7, 137.2, 135.6, 127.8, 125.6, 119.4, 69.5; UV–Vis (CH_2Cl_2) λ_{max} (nm) (log ε) 672.0 (2.72), 609.5 (2.91), 405.9 (4.15), 319.5 (4.29); MALDI-TOF m/z: 1067 (M+1), 917 (M−150), 720 (C_{60}).

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