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New pyrazolino and pyrrolidino[60]fullerenes: the introduction of the hydrazone moiety for the formation of metal complexes

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The [3 + 2] cycloaddition reaction of C_{60} with pyridine-derived hydrazones (acting as dipolar reagents) was successfully conducted resulting in fullerene derivatives 5a–b. The compounds were characterized by means of NMR, UV–Vis spectroscopy, and X-ray crystallography. The electrochemical behavior was also investigated. The fulleropyrazoline 5a exhibits anodically shifted reduction potentials of about 100 mV when compared with those for C_{60}, whereas 5b exhibits cathodic shifts relative to pristine C_{60}. The complexation reaction of 5b with metallic ions (Zn^{2+}, Cd^{2+}, and Fe^{2+}) was achieved. Job and Benesi–Hildebrand analysis confirmed the formation of complexes with a molar ratio of 1:1 and binding constants between 2.26×10^5 and $1.59 \times 10^5\ M^{-1}$. Electrochemistry of these complexes showed a marked influence of the metal ion on the reduction potentials. Copyright © 2016 John Wiley & Sons, Ltd.

Keywords: 1,3-dipolar cycloaddition; fullerene derivatives; hydrazone derivatives; pyrazolino[60]fullerene; pyrrolidino[60]fullerene

INTRODUCTION

Since the discovery of fullerenes in 1985 by Kroto, Curl, and Smalley[1] and subsequent large-scale preparation in 1990,[2] this type of molecules have attracted great interest in supramolecular chemistry.[3] Many attempts to exohedrally functionalize C_{60} with different molecules[4–7] have resulted in the preparation of supramolecular systems, which increase its solubility and expand its applications in materials science as a result of the unique electrochemical and photophysical properties of these systems.[8] One of the most widely used reactions for exohedral functionalization of C_{60} is the 1,3-dipolar cycloaddition with azomethine ylides to form fulleropyrrolidines[9]; however, a drawback is that it typically leads to mixtures of enantiomers and multiple additions; the latter can be overcome by controlled reaction conditions. Therefore, the functionalization of C_{60} with 1,3-nitrile imines, generated *in situ* from the corresponding hydrazone derivative and N-bromosuccinimide (NBS), has shown to be an effective tool for controlling the formation of stereoisomers and to obtain a wide variety of fulleropyrazolines able to exhibit unique properties.[10]

On the other hand, it is well known that hydrazones have physical and chemical properties able to be reversibly modulated in response to external stimuli such as those caused by light, heat, and pH variation.[11] In addition, hydrazone derivatives from 2-pyridincarboxaldehyde have shown to be good ligands as a result of the presence of coordination sites in their structures.[12] The latter has been specially exploited in the design of metallogrids and molecular motors.[11,13] Thereby, we report the preparation of two fullerene derivatives **5a** and **b** through the 1,3-dipolar cycloaddition between C_{60} and dipolar reagents containing hydrazone moieties. The preparation of **5a** and **b** establishes the first step in obtaining supramolecular systems, which take advantage not only of the electrochemical and photophysical properties of C_{60} but also the coordination and photochemical properties of the hydrazone derivatives. Thus, the binding study of this type of compounds with metal ions is essential in order to explore their potential use in more complex systems.

RESULTS AND DISCUSSION

Synthesis and purification of precursors

Fullerene derivatives **5a**-**b** were prepared in a multistep synthetic procedure, where the first step required the preparation of the aldehyde derivatives **2a**-**b** as depicted in Scheme 1. Partial oxidation of hydroxymethyl-pyridines **1a**-**b** with oxidizing reagents (pyridinium chlorochromate pyridinium chlorochromate, PCC, or MnO_2) [14] led to the formation of the corresponding aldehyde derivatives **2a**-**b** in acceptable yields (50–55%). Once compounds **2a**-**b** were obtained, the formation of the corresponding *E*-hydrazone derivatives **4a**-**b** was

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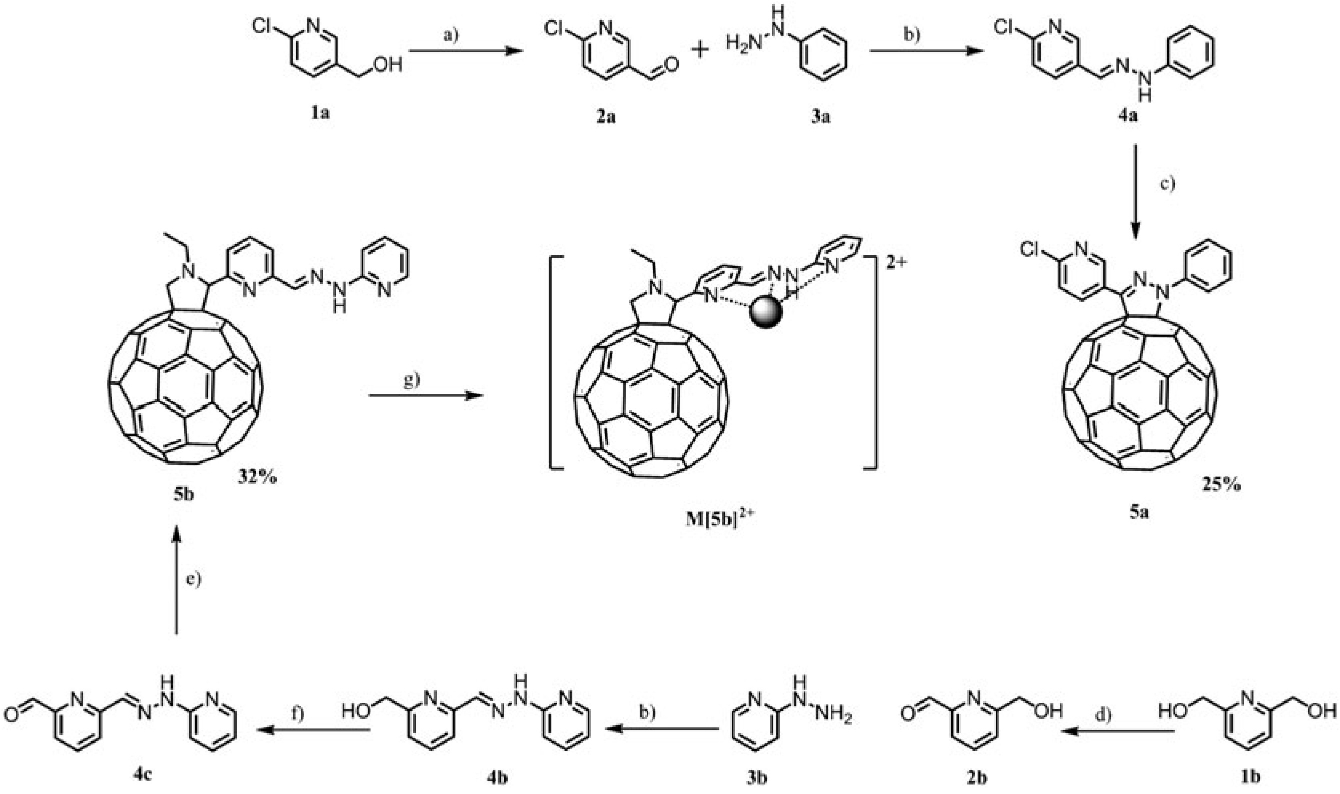

Scheme 1. Synthesis of fullerene derivatives **5a**-**b**. (a) Pyridinium chlorochromate, CH_2Cl_2, RT; (b) ethanol, reflux; (c) C_{60}, Et_3N-Pyridine, Toluene, RT; (d) MnO_2 $CHCl_3$, RT; (e) MnO_2 $CHCl_3$, reflux; (f) C_{60}, *N*-ethylglicine, reflux; g) $[M]^{2+}$ (M = Zn, Cd, Fe), methanol, reflux

performed by condensation with hydrazine derivatives **3a**-**b**, in good to very good yields (61–81%). Hydrazone **4b** was stirred with MnO_2 in $CHCl_3$ in order to synthesize **4c** (Scheme 1),[15] which was obtained in an acceptable yield (53%). All compounds were fully characterized by spectroscopic techniques such as IR and 1D- and 2D-NMR (refer to Experimental Section). The structural elucidation of these compounds was further confirmed by single crystal X-ray diffraction of the **2a** and **4a** compounds (refer to Fig. 1).

Compound **2a** crystallizes in a monoclinic space group Pc, and the molecule is almost planar, based on the maximum torsion angle $-4.3(7)°$ for C5–C4–C6–O1, between the aromatic ring and the aldehyde group (Supporting Information S2). Compound **4a** crystallizes in the orthorhombic space group P22121. The aromatic and pyridinic rings have a torsion angle of 10.96° and 1.63° for the C8–C7–N3–N2 and C3–C4–C6–N2 bonds, respectively. Weak N3–H30$\cdots$N1 intermolecular interactions with a distance of 3.403(7) Å allows the formation of chains along the [010] direction. Weak π–π interactions are also observed with a distance of 3.853(2) Å between the centroids of the aromatic rings. These interactions pack the chains along the [001] direction. Finally, very weak C3–H3$\cdots\pi$ interactions with a distance of 3.696(6) Å and an angle of 130.28(3)° give rise to the three-dimensional crystal packing shown in Fig. 2.

[3 + 2] Cycloaddition reaction on C_{60}: synthesis and purification of adducts

The synthetic procedure to attach the hydrazone to C_{60} via a 1,3-dipolar cycloaddition is similar to those reported previously.[9,10] The synthesis of **5a** was carried out by the cycloaddition of the *in situ* generated nitrylimine to C_{60} under an inert atmosphere at room temperature. Meanwhile, **5b** was synthesized by the cycloaddition of the *in situ* generated azomethine ylide to C_{60} by heating to reflux under an inert atmosphere. Thus, two different mixtures (**4a**, NBS, and NEt_3 for **5a** and **4c** and *N*-ethylglycine for **5a**) in toluene were added under argon bubbling into a toluene solution of C_{60}, the typical 1,3-dipolar cycloaddition procedure. The color of the reaction mixtures changed from purple to brown, confirming the formation of the products. The symmetry of C_{60} allows the formation of multi-addition products; so, the reaction was constantly monitored by thin-layer chromatography thin layer chromatography (TLC) in order to avoid such subproducts, which have lower retention coefficients.[16] Once the reactions were completed, the fullerene derivatives were isolated and purified by column chromatography with yields of

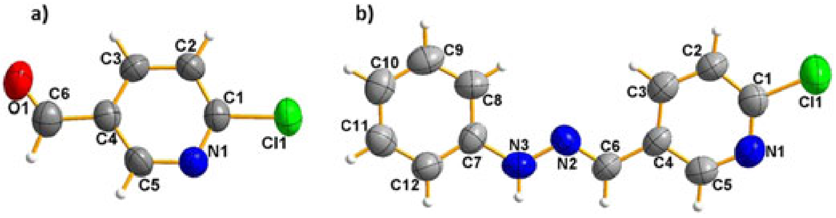

Figure 1. ORTEP drawing of the asymmetric units of (a) 2-Chloro-5-pyridinecarboxaldehyde **2a**. (b) (*E*)-2-Chloro-5-pyridinecarboxaldehyde-phenylhydrazone **4a**. Ellipsoids are displayed at the 50% probability level

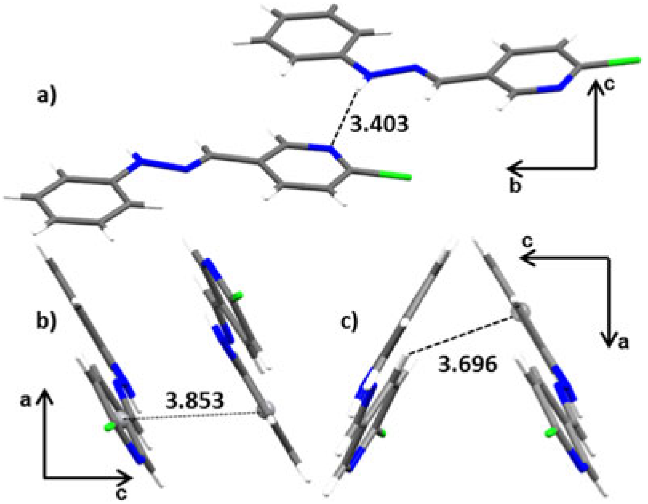

Figure 2. Representation of the (a) N3–H30···N1, (b) π–π, and (c) C3–H3···π supramolecular interactions for compound **5a**

32% for **5a** and 25% for **5b**. Details of the synthesis are shown in Scheme 1 and described in the Experimental Section.

The ^{1}H-NMR spectra revealed the formation of **5a**-**b** and the disappearance of the imine proton (signal at δ 7.89 ppm for **4a**) in the fulleropyrazoline **5a** and the formyl proton (signal at δ 9.97 ppm for **4c**) in the fulleropyrrolidine **5b**. It was possible to observe the appearance of new signals at 5.38, 5.18, and 4.28 ppm, corresponding to the protons of the pyrrolidine ring (refer to Fig. S3). The ^{13}C-NMR spectrum of **5a** showed the expected signals between 142 and 146 ppm and about 42 signals in total, where the eight signals of the pyrazoline ring were preserved. The UV–Vis spectra of both fullerene derivatives along with that for pristine C_{60} are shown in Fig. 3. The spectra of compounds **5a**-**b** show three absorptions centered at 336, 430, and 710 nm, which are typical of fullerene [6,6]-adducts.[17] Both adducts showed an hypsochromic shift of about 336 nm in comparison to C_{60} as a result of the disruption of the π system by the elimination of a double bond C = C.[18]

We also investigated whether it would be possible to substitute the chloro atom of **5a** with hydrazine to obtain the hydrazine derivative. Unfortunately, adding the hydrazine monohydrate solution to **5a** under several conditions always resulted in reduction of the C_{60} moiety.[19]

Complexation of 5b with transition metals

Metal complexes were obtained through the reaction of **5b** with divalent transition metal salts (Zn^{II}, Cd^{II}, and Fe^{II}) in methanol (refer to Scheme 1). After precipitation, these compounds were washed with ethyl ether and methanol. As shown in Fig. 4, the complexation between the metal ions with **5b** causes a bathochromic shift of about 313 nm and a decrease of the energy of charge transfer and a decrease in the intensity in the UV–Vis and fluorescence spectra, respectively as a result of the delocalization of the lone pairs of the nitrogen atoms.[20]

The binding constants of the complexes were determined by the Benesi–Hildebrand method.[21] As shown in Fig. 5, the titration curves show the variation of the 390 nm absorbance as a function of added equivalents of M^{2+}. The absorbance increased as a result of charge transfer from the pyridine and imine nitrogen atoms to the metal ion.[20] The equilibrium constants and the change of the molar absorptivity (K and $\Delta\varepsilon$) were calculated from the plots of ΔA^{-1} versus $[M^{2+}]^{-1}$. The results showed that **5b** exhibits better affinity for metal centers with larger ionic radii (refer to Table 1), as a consequence of the low strain angle and high stability acquired by the five-membered rings formed by chelation with the larger ions.[22]

Electrochemistry of fullerene derivatives

The electrochemical properties of compounds **5a**-**b** and the respective M^{2+} (M = Fe, Zn, and Cd) complexes of **5b** were studied by cyclic voltammetry and Osteryoung square wave voltammetry. Compound **5a** exhibits five reduction peaks within the solvent window (Table 2). The reductions are anodically shifted approximately ~0.09 V when compared with C_{60}; in contrast, compound **5b** exhibits cathodic shifts for the reduction peaks.10c The latter is understood on the basis of saturation of the C = C double bond, which raises the energy of the lowest unoccupied molecular orbital, and therefore increases the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) energy gap of the compound.10e This behavior shows the effect of the exohedral moiety over the electrochemical properties of C_{60}. In that sense, the results show how the type of functionalization affects the redox potential of the derivative with respect to pristine C_{60}. Noteworthy, such ability to modulate the redox properties of fullerene derivatives can

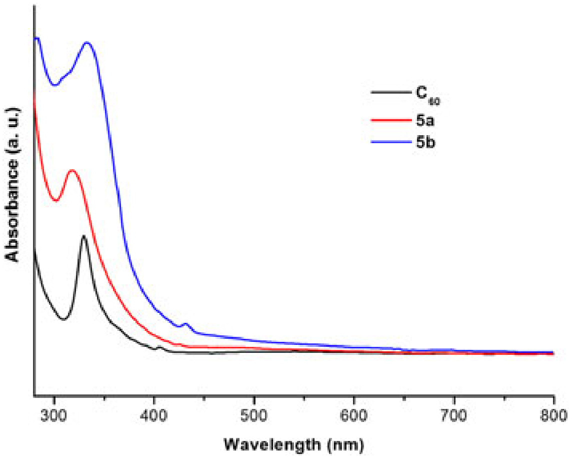

Figure 3. UV–Vis spectra of C_{60} and fullerene derivatives **5a**-**b** in chloroform (2.0×10^{-5} M)

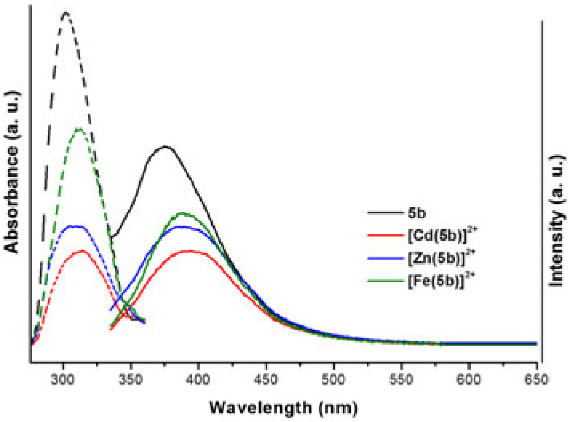

Figure 4. Absorption (dash line) and emission (solid line) spectra of **5a** and $[\mathbf{M}(\mathbf{5a})]^{2+}$ in toluene (~1.1×10^{-5} M)

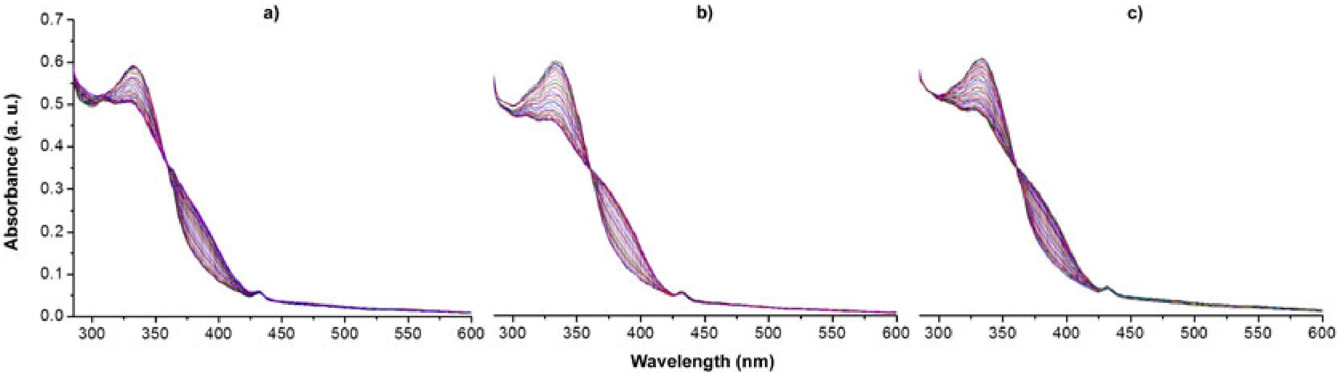

Figure 5. Titration of **5b** (1.2×10^{-5} M) with M^{2+} in Toluene : MeOH 10%. (a) $Fe(SO_4)_2 \cdot 6H_2O$; (b) $Zn(NO_3)_2 \cdot 6H_2O$; (c) $Cd(NO_3)_2 \cdot 4H_2O$. Wavelength in nanometers

Table 1. Results from linearization of graphics of $1/\Delta A$ versus $1/C_{M2+}$ ($T = 26$ °C)

M^{2+}	m (10^{-5} M)	a	R	$\Delta\varepsilon$ (M^{-1} cm^{-1})	K (10^5 M^{-1})	r_{ion} (Å)[23]
Fe^{2+}	4.21 ± 0.08	6.68 ± 0.04	0.9958	12720 ± 151	1.59 ± 0.03	0.70
Zn^{2+}	3.72 ± 0.05	8.39 ± 0.03	0.9977	10128 ± 107	2.26 ± 0.03	0.74
Cd^{2+}	2.40 ± 0.03	7.40 ± 0.02	0.9976	11477 ± 119	3.09 ± 0.04	0.95

Table 2. Redox potentials of fullerene derivatives **5a** and **b** versus ferrocene in THF (V)[1]

Compound	$E^1_{1/2Red}$	$E^2_{1/2Red}$	$E^3_{1/2Red}$	$E^4_{1/2Red}$	$E^5_{1/2Red}$
5a	−0.82	−1.31	−1.92	−2.21	−2.52
5b	−0.98	−1.49	−2.14	−2.65	
C_{60}	−0.91	−1.46	−2.01	−2.30	

[1] Working electrode: glassy carbon; counter electrode: Pt wire; pseudoreference electrode: Ag wire. Supporting electrolyte: $TBAPF_6$. Scan rate: 0.1 V s^{-1}.

be potentially used for the development of solar cells and molecular electronics.

On the other hand, complexation seems to have a strong influence on the redox properties of the studied compounds. Fe[**5b**]$^{2+}$ exhibits a first reduction potential around −0.43 V which presumably corresponds to the hydrazone moiety and four additional reduction potentials which are anodically shifted when compared with those for **5b**. In contrast, reduction potentials of Cd[**5b**]$^{2+}$ do not seem to be very different from those of **5b**, while compound Zn[**5b**]$^{2+}$ exhibits reduction potentials cathodically shifted with respect to **5b** (Table 3).

Table 3. Redox Potentials of **5b** and its metal complexes versus ferrocene in THF (V)[1]

Compound	$E^1_{1/2Red}$	$E^2_{1/2Red}$	$E^3_{1/2Red}$	$E^4_{1/2Red}$
5b	−0.98	−1.49	−2.14	−2.65
Fe[5b]$^{2+}$	−0.43	−0.85	−1.10	−2.09
Zn[5b]$^{2+}$	−1.03	−1.69	−2.46	
Cd[5b]$^{2+}$	−0.99	−1.42	−2.18	−2.61

[1] Working electrode: glassy carbon; counter electrode: Pt wire; pseudoreference electrode: Ag wire. Supporting electrolyte: $TBAPF_6$. Scan rate: 0.1 V s^{-1}.

CONCLUSIONS

We have synthesized new fulleropyrrolidine and fulleropyrazoline derivatives via 1,3-dipolar cycloadditions to C_{60}. Additionally, metal complexes of **5b** were obtained. These compounds were fully characterized, and their electronic and electrochemical properties were studied. The binding constants of M^{2+} (M = Fe, Zn, and Cd) with **5b** were determined by Benesi–Hildebrand methods. The metal affinities are directly correlated with the ionic radii ($Fe^{2+} < Zn^{2+} < Cd^{2+}$) favoring the larger ones. On the other hand, electrochemistry of **5a**-**b** showed that reduction potentials can be either anodically or cathodically shifted by varying the exohedral moiety.

EXPERIMENTAL SECTION

All starting reagents were acquired from Sigma-Aldrich and were used without additional purification. The FT-IR, NMR (mono and bi-dimensional), UV–Vis, and fluorescence spectra were taken in Shimadzu FTIR-8400 spectrophotometer, NMR 400 MHz Bruker Ultra Shield, Pharma Spec Shimadzu UV–Vis UV-1700 spectrophotometer, and Jasco FP-8500 spectrofluorimeter, respectively. The mass spectra were obtained on a Hewlett Packard HP Engine-5989 spectrometer (equipped with a direct inlet probe) operating at 70 eV. The elemental analyses were obtained using a Thermo-Finnigan Flash EA1112 CHN (Elemental Microanalysis Ltd, Devon, UK) elemental analyzer. Cyclic voltammograms were recorded in a bipotentiostat model 700 B series electrochemical Analyzer/Workstation from CHI Instruments coupled to a computer.

2-Chloro-5-pyridinecarboxaldehyde (2a)

Pyridinium chlorochromate (2 equiv) was added to a solution of 2-chloro-5-hydroxymethyl-pyridine **1a** (1 equiv) in CH_2Cl_2, and the mixture was agitated for 6 h to room temperature. Once the reaction was finished, the mixture was filtered and washed with CH_2Cl_2 (2 × 3.0 mL). Then, the resulting filtrate was concentrated to dryness under reduced pressure, and the crude obtained was purified by column chromatography on silica gel by using $CHCl_3$ as a white solid; yield 50%. M.P. 181–182 °C; FT-IR (KBr) υ (cm^{-1}): 2970 (C–H), 2847 (=C–H), 1714 (C = O), 1603 and 1595 (C = C and C = N), 1054 (C–O). ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 10.10 (s, 1H, CHO), 8.87 (d, *J* = 2.26 Hz, 1H, H-6), 8.14 (dd, *J* = 2.26 Hz, 1H, H-4), 7.53 (d, *J* = 2.26 Hz, 1H, H-3), ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 189.97, 157.16, 152.14, 138.72, 125.680. MS (EI 70 eV) *m/z* (%): 141/143 [M^+] (42/15), 91 (100), 78 (100). Elemental analysis calcd (%) for C_6H_4ClNO: C 50.91, H 2.85, N 9.90; found: C 49.47, H 2.76, N 8.90.

6-(hydroxymethyl)-2-pyridinecarboxaldehyde (2b)

MnO_2 (5 equiv) was added to a solution of 2,6-dihydroxymethyl-pyridine **1b** (1 equiv) in $CHCl_3$ and stirred at room temperature for 6 h. Once the reaction finished, methanol (3.0 mL) was added twice, and the solid formed was removed by filtration and discarded. Then, the resulting filtrate was concentrated to dryness under reduced pressure, and the crude obtained was purified by column chromatography on silica gel by using a mixture oef $CHCl_3$:MeOH (25:1) as a yellow oil; yield 55%. FT-IR (KBr) υ (cm^{-1}): 3447 (O–H and N–H), 2921 (C–H), 2847 (=C–H), 1714 (C = O), 1603 and 1595 (C = C and C = N), 1054 (C–O). ^1H NMR (400 MHz, DMSO-d_6) δ ppm: 9.94 (s, 1H, CHO), 8.06 (t, *J* = 7.7 Hz, 1H, H-4), 7.82 (d, *J* = 7.5 Hz, 1H, H-3), 7.79 (d, *J* = 7.8 Hz, 1H, H-5), 5.67 (t, J = 5.7 Hz, 1H, O–H), 4.69 (d, J = 5.6 Hz, 2H, CH_2).^{13}C NMR (101 MHz, DMSO-d_6) δ ppm: 194.2, 163.4, 151.9, 138.7, 125.4, 120.5, 64.4. MS (EI 70 eV) *m/z* (%): 137 [M^+] (100), 120 (40), 108 (84), 91 (100), 78 (100).

(*E*)-2′-Chloro-5′-pyridinecarboxaldehyde-phenylhydrazone (4a)

Phenylhydrazine **3a** (1 equiv) was added to a solution of 2-chloro-5-pyridinecarboxaldehyde **2a** (1 equiv) in ethanol); subjected to reflux during 3 h, the precipitate was collected by vacuum filtration and washed with cold ethanol to obtain the pure product in 61% as a yellow solid. M.P. 185–186 °C; FT-IR (KBr) υ (cm^{-1}): 3421 (O–H), 3201 (N–H), 2924 y 2851 (C–H), 1602 (C = C) 1578 (C = N), 1090 (C–O). ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 8.49 (d, *J* = 2.26 Hz, 1 H), 8.01–8.08 (m, 1 H), 7.89 (s, 1 H), 7.64 (s, 1 H), 7.27–7.36 (m, 3H), 7.13 (s, 2 H), 6.93 (t, *J* = 7.40 Hz, 1 H) ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 150.5, 147.6, 143.9, 135.0, 131.9, 130.5, 129.4, 124.4, 120.9, 112.9. 64.63. MS (70 eV) m/z (%):231/233 [M^+] (79/27), 92 (100). Elemental analysis calcd (%) for $C_{12}H_{10}ClN_3$: C 62.21, H 4.35, N 18.14; found: C 61.51, H 4.14, N 18.04.

(*E*)-6′-hydroxymethyl-2′-pyridinecarboxaldehyde-2-pyridylhydrazone (4b)

A solution of 2-hydrazinylpyridine **3b** (1 equiv) in ethanol (1 mL) was added to a solution of **2b** (1 equiv) in ethanol (1 ml) containing two drops of dilute acetic acid. The resulting precipitate was washed several times with small portions of chloroform, then it was recrystallized from absolute ethanol to afford the pure product in 82% as beige solid. M.P. 190–191 °C; FT-IR (KBr) υ (cm^{-1}): 3421 (O–H), 3201 (N–H), 2924 y 2851 (C–H), 1602 (C = C) 1578 (C = N), 1090 (C–O). ^1H NMR (400 MHz, DMSO-d_6) δ ppm: 11.13 (s, 1H, N–H), 8.13 (d, *J* = 4.9 Hz, 1H, H-6), 8.03 (s, 1H, H_{im}). 7.84–7.76 (m, 2H, H-4′ and H-5′), 7.66 (t, *J* = 7.8 Hz, 1H, H-4), 7.37 (d, *J* = 8.4 Hz, 1H, H-3′), 7.29 (d, *J* = 7.8 Hz, 1H, H-3), 6.84-6.78 (m, 1H, H-5), 5.41 (t, *J* = 5.9 Hz, 1H, O–H), 4.56 (d, *J* = 5.8 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 162.1, 157.2, 153.8, 148.3, 139.8, 138.6, 137.5, 119.8, 117.5, 116.1, 107.0, 64.6. MS (70 eV) m/z (%): 228 [M^+] (13), 120 (100). Elemental analysis calcd (%) for $C_{12}H_{12}N_4O$: C 63.15, H 5.30, N 24.55; found: C 62.77, H 5.38, N 24.32.

(*E*)-6′-carboxaldehyde-2′-pyridinecarboxaldehyde-2-pyridylhydrazone (4c)

A solution of **4b** (1 equiv) in $CHCl_3$ (2 mL) was shaken with MnO_2 (5 equiv) and heated under reflux for 4 h. Once the reaction finished, methanol (3.0 mL) was added, and the solid formed was removed by filtration and discarded. Then, the resulting filtrate was concentrate to dryness under reduced pressure, and the crude obtained was purified by column chromatography on silica gel by using a mixture $CHCl_3$:MeOH (9:1) as eluent and obtained in 53% as a yellow solid. M.P. 196–197 °C; FT-IR (KBr) υ (cm^{-1}): 3210 (N–H), 2983 (=C–H), 1759 (C = O) 1603, 1595 (C = C and C = N). ^1H NMR (400 MHz, DMSO-d_6) δ ppm: 11.36 (s, 1H, N–H), 9.97 (s, 1H, CHO), 8.24 (d, *J* = 8.0 Hz, 1H, H-5′), 8.16–8.14 (m, 2H, H_{im} and H-6), 8.03 (t, *J* = 7.8 Hz, 1H, H-4′), 7.82 (d, *J* = 7.5 Hz, 1H, H-3′), 7.69 (d, *J* = 8.7, 1H, H-4), 7.34 (d, *J* = 8.4 Hz, 1H, H-3), 6.86–6.81 (m, 1H, H-5). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 193.9, 156.9, 155.6, 152.5, 148.3, 138.6, 138.4, 138.3, 123.7, 121.3, 116.1, 107.2. MS (70 eV) m/z (%): 226 [M^+] (20), 197 (29), 120 (100). Elemental analysis calcd (%) for $C_{12}H_{10}N_4O$: C 47.68, H 3.27, N 20.22; found: C 47.14, H 3.18, N 19.84.

(6-6-(2′-Phenyl-3′-(6-chloropyridinyl))-1,9-fulleropyrazoline (5a)

A solution of **4a** (1 equiv), pyridine (2 equiv), and NBS (2 equiv) in 40 mL of toluene was cooled to 0 °C and added in 100 mL solution of C_{60} (1 equiv) and Et_3N (1 equiv) in toluene. The reaction mixture was stirred for 2 h in inert atmosphere until a color change from violet to dark brown was observed. The thin-layer chromatography showed two different spots corresponding to the pristine fullerene and desired product. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography using a mixture of toluene : hexane (3:1) as eluent and obtained in 25% as a brown solid. FT-IR (KBr) υ (cm^{-1}): 3025–2966 (=C–H), 1605 (C = N), 1431 (C = C C_{60}), 1310 (C–N), 1164 (C = C C_{60}), 581 (C = C C_{60}), 517 (C = C C_{60}) ^1H NMR (400 MHz, $CDCl_3$) δ 9.40 (d, J = 2.26 Hz, 1 H), 8.57–8.64 (m, 1 H), 7.91–8.00 (m, 2 H), 7.45–7.56 (m, H), 7.18 (d, J = 7.28 Hz, H), ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 151.82, 148.89, 147.69, 147.29, 146.43, 146.33, 146.08, 146.01, 145.92, 145.73, 145.57, 145.40, 145.34, 145.26, 145.23, 145.01, 144.61, 144.30, 144.17, 143.22, 143.13, 142.96, 142.92, 142.45, 142.42, 142.23, 142.19, 141.94, 140.52, 139.89, 139.84, 138.22, 137.90, 136.77, 136.30, 129.48, 129.07, 128.26, 127.88, 125.83, 125.33, 124.53, 124.14. Elemental analysis calcd (%) for $C_{72}H_8ClN_3$: C 91.00, H 0.85, N 4.42; found: C 90.21, H 1.04, N 4.19.

N-Ethyl-2-(6-6-((2-(pyridin-2-yl)hydrazono)methyl)pyridine)-3,4-fulleropyrrolidine (5b)

A solution of C_{60} (1 equiv), **4c** (5 equiv), and *N*-ethylglicine (5 equiv) in 70 mL of toluene was heated under reflux for 30 min in inert atmosphere. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography using mixture of toluene : ethyl acetate (9:1) as eluent and obtained in 32% as a brown solid. FT-IR (KBr) υ (cm^{-1}): 3212 (N–H), 3340-2966 (=C–H), 2905–2761 (C–H), 1605 (C = N), 1425 (C = C C_{60}), 1305 (C–N), 1178 (C = C C_{60}), 573 (C = C C_{60}), 520 (C = C C_{60}). ^1H NMR (400 MHz, CS_2-$CDCl_3$ 10:1) δ ppm: 9.88 (s, 1H, N–H), 8.06 (ddd, J = 5.1 Hz, J = 1.7 Hz, J = 0.8 Hz, 1H, H-6), 7.96 (d, J = 8.1 Hz, 2H, H-3 and H-5), 7.92 (s, 1H, H_{im}), 7.82 (t, J = 7.8 Hz, 1H, H-4), 7.63 (ddd, J = 8.9 Hz, J = 7.2 Hz, J = 1.8 Hz, 1H, H-4′), 7.38 (d, J = 8.5, 1H, H-3′), 6.80 (ddd, J = 7.2 Hz, J = 5.1 Hz, J = 1.0 Hz, 1H, H-5′), 5.38 (s, 1H, H_d), 5.18 (d, J = 9.2 Hz, 1H, H_c), 4.28 (d, J = 9.2 Hz, 1H, $H_{c'}$), 3.40 (dq, J = 7.4 Hz, J = 12.3 Hz, 1H, $H_{b'}$), 2.80 (dq, J = 7.3 Hz, J = 11.4 Hz, 1H, H_b), 1.61 (t, J = 7.2 Hz, 3H, CH_3). Elemental analysis calcd (%) for $C_{75}H_{17}N_5$: C 91.18, H 1.73, N 7.09; found: C 90.73, H 1.74, N 6.99.

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