Electronic Supplementary Material (ESI) for Chemical Communications.

Regioselective preparation of a bis-pyrazolinofullerene by a macrocyclization reaction

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1. General Remarks.

Experimental conditions. Buckminsterfullerene, C_{60} (+99.95%) was purchased from Materials and Electrochemical Research (MER) corporation. All solvents and reagents were purchase from Aldrich Chemicals. Chromatographic purifications were performed using silica gel 60 (particle size 0.06-0.2 mm). Analytical thin-layer chromatography was performed using ALUGRAM ® SIL G/UV_{254} silica gel 60. Nuclear magnetic resonance ^{1}H-NMR and ^{13}C-NMR were performed on BrukerInnova 400 Hz except ^{13}C-NMR and DEPT-135 NMR spectra of **4** which were performed using Bruker AVIII 700 MHz. Chemical shifts are given as δ values. Residual solvent peaks being used as the internal standard ($CHCl_3$; δ = 7.27 ppm; Acetone, δ = 2.05 ppm). ^{13}C NMR chemical shifts are reported relative to the solvent residual peaks ($CDCl_3$, δ = 77.00 ppm; THF, δ = 67.21 ppm, δ = 25.31 ppm). MALDI-TOF spectra were obtained in VOYAGER DETM STR spectrometry, using dithranol [1,8-dihydroxy-9(10H)-anthracenone] as matrix. Analytical HPLC profiles were recorded using Agilent 1100 (column: Buckyprep (4.6ID x 250 mm)), with toluene as eluent (1mL/min). Purification with HPLC was performed using preparative HPLC Agilent Technologies 1290 (column Buckyprep-M (20ID x 250 mm)), with toluene as eluent (10 mL/min). Fourier transform infrared spectrophotometer (FT-IR) Thermo Nicolet AVATAR 370 was used with KBr pellet method, in each case the most characteristic bands are indicated for each compound. Absorption spectra were performed on Shimadzu UV 3600 spectrophotometer. Solutions of different concentration were prepared in toluene, HPLC grade, with absorbance between 0.2 and 0.3 using a 1 cm UV cuvette.

Computational Details: Theoretical calculations were carried out within the density functional theory (DFT) framework by using the Gaussian 09,[1] applying density functional theory at the B3LYP level. The basis set of 6-31G+ was used in the calculations.

Electrochemical Measurements: Reduction (E_{red}) and oxidation potentials (E_{ox}) were measured by cyclic voltammetry with a potentiostat BAS CV50W in a conventional three-electrode cell equipped with a glassy carbon working electrode, a platinum wire counter electrode, and an $Ag/AgNO_3$ reference electrode at scan rate of 100 mV/s. The E_{red} and E_{ox} were expressed vs. Fc/Fc^+ used as external reference. In each case, the measurements were done in a deaerated solution containing 1 mM of a the sample compound in 0.1 M of $(n\text{-}Bu)_4NClO_4$ in *o*-DCB:Acetonitrile (4:1) as an electrolyte solution.

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1. Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam,

M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009

2. Synthesis

Synthesis of compound 2.

Compound **1** (1 eq, 4.78g) was added to a mixture of *p*-hidroxybenzaldehyde (2.1 eq, 2.36 g), potassium carbonate (2.4 eq, 3.05 g) and 18-crown-6 ether (0.15 eq, 0.36 g) on acetone (306 mL). The mixture was stirred and heated to 56^{o}C for 3 days. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, eluent: CH_2Cl_2). Isolated product was precipitated with hexane to obtain the compound **2** as a white solid (3.93 g, 70,7%). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 9.90 (s, 2H), 7.85 (d, *J* = 8.5 Hz, 4H), 7.11 (d, *J* = 8.5 Hz, 5H), 7.01 (s, 2H), 5.20 (s, 4H), 3.97 (t, *J* = 6.4 Hz, 4H), 1.81 – 1.68 (m, 4H), 1.42 (dd, *J* = 10.6, 5.1 Hz, 5H), 1.25 (s br, 32H), 0.89 (t, *J* = 6.6 Hz, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 190.75, 163.81, 150.26, 131.96, 130.02, 124.98, 115.11, 112.40, 68.97, 65.16, 31.89, 29.65, 29.62, 29.57, 29.34, 29.28, 26.10, 22.67, 14.12. FT-IR (KBr) ν/cm^{-1}: 3054, 2917, 2850, 2738, 1683, 1602, 1575, 1508, 1425.

Synthesis of compound 3.

Compound **2** (1 eq, 1.95 g) and (4-nitrophenyl)hydrazine (2 eq, 0.99 g) were dissolved on ethanol absolute (330 mL). Acetic acid glacial (0.2 mL) was added to the mixture. The reaction was stirred under argon and refluxed for 3h. The mixture was cooled at room temperature. The solid was filtrated under vacuum and washed with cold ethanol, to obtain compound **3** as an orange solid (2.2 g, 69%). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ/ppm: 10.22 (s, 2H), 8.16 (d, *J* = 8.9 Hz, 4H), 8.02 (s, 2H), 7.72 (d, *J* = 8.4 Hz, 4H), 7.25 (d, *J* = 8.8 Hz, 4H), 7.06 (d, *J* = 8.5 Hz, 4H), 4.29 (t, *J* = 6.2 Hz, 4H), 2.88 (s, 6H), 2.36 – 2.25 (m, 2H). ^{13}C NMR (100 MHz, TDF) δ/ppm: 160.89, 151.45, 151.15, 141.78, 140.18, 128.73, 128.61, 126.42, 126.36, 115.59, 113.10, 111.59, 69.45, 65.47, 32.69, 30.49, 30.43, 30.22, 30.15, 26.91, 23.38, 14.26. FT-IR (KBr) ν/cm^{-1}: 3270, 2919, 2852, 1606, 1504, 1465. UV/vis (Toluene) λ/nm (log ε): 378 (4.31).

Synthesis of compound 4.

N-Bromosuccinimide (4 eq, 180 mg) was added to a solution under argon of compound **3** (1 eq, 223 mg) on chloroform (200 mL). The mixture reaction was stirred at room temperature for 90 minutes and the solvent was removed under reduced pressure. The crude of the bromination of bishydrazone and C_{60} were dissolved on toluene (100 mL), and triethylamine (2 mL) was then added, under argon. The reaction was stirred at room temperature overnight. The solvent was remove under reduced pressure, and the crude was loaded on column chromatography (silica gel, eluent: carbon disulfide:toluene (from 1:0 to 0:1)). The isolated isomer was precipitated on pentane (x4), methanol

(x5) and diethyl ether (x3). preparative HPLC was used for purification, to obtain a brown solid (64 mg, 16%). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.54 (d, *J* = 9.2 Hz, 4H), 8.48 (t, *J* = 9.2 Hz, 4H), 8.04 (t, *J* = 8.7 Hz, 4H), 6.91 (t, *J* = 8.7 Hz, 4H), 6.64 (s, 2H), 5.43 (d, *J* = 14.9 Hz, 2H), 5.01 (d, *J* = 14.9 Hz, 2H), 3.81 – 3.74 (m, 2H), 3.70 – 3.60 (m, 2H), 1.9-0.59 (m, 46H). ^{13}C NMR (176 MHz, $CDCl_3$) δ/ppm 158.94, 150.10, 149.93, 149.88, 148.96, 148.83, 148.66, 148.63, 148.60, 147.27, 146.85, 146.83, 145.70, 145.33, 145.27, 144.94, 144.65, 144.42, 144.38, 144.09, 143.97, 143.88, 143.84, 142.43, 142.39, 142.03, 141.91, 141.53, 141.33, 139.13, 137.13, 135.06, 130.41, 125.51, 124.76, 123.57, 119.46, 114.88, 114.05, 111.68, 90.04, 81.55, 33.70, 31.93, 31.90, 30.16, 30.05, 29.70, 29.64, 29.62, 29.51, 29.44, 29.36, 29.34, 29.09, 28.97, 27.11, 26.70, 26.20, 23.18, 22.68, 19.73, 14.18, 14.12, 1.02. DEPT-135 (176 MHz, $CDCl_3$) δ/ppm: 130.43, 125.53, 119.48, 114.90, 111.70, 68.81, 62.91, 33.71, 31.91, 29.71, 29.69, 29.65, 29.63, 29.45, 29.35, 29.10, 26.21, 22.69, 14.13. UV/vis (Toluene) λ/nm (log ε): 282 (4.94). MS-MALDI TOF (*m/z*): calculated 1701.28[M^+]; found 1700.40

3. ^{1}H NMR, ^{13}C NMR, FT-IR and MALDI-TOF

a. Structural characterization of compound **2**.

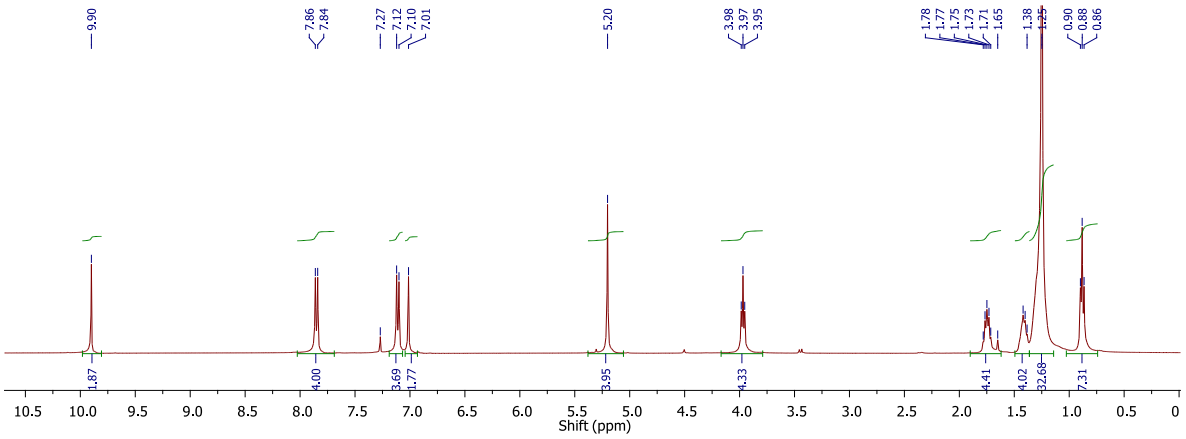


Figure S1. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **2.**

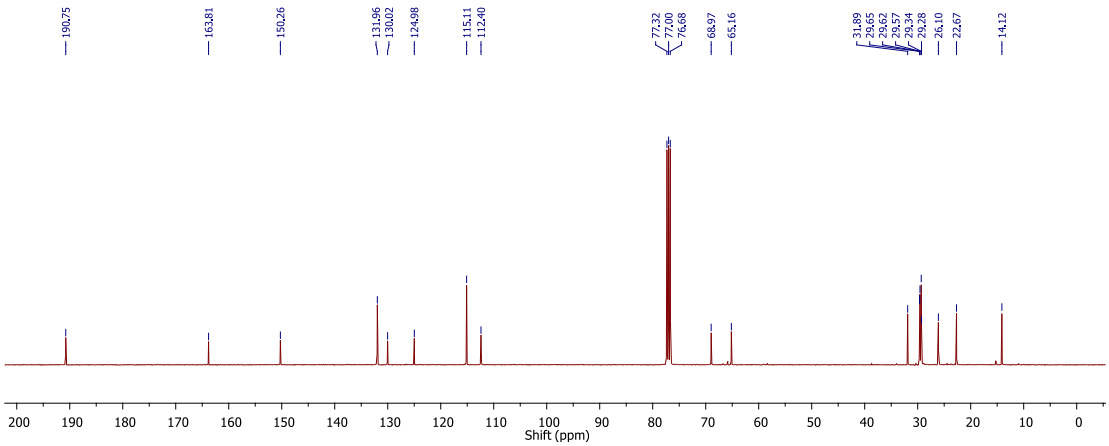


Figure S2. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of compound **2**.

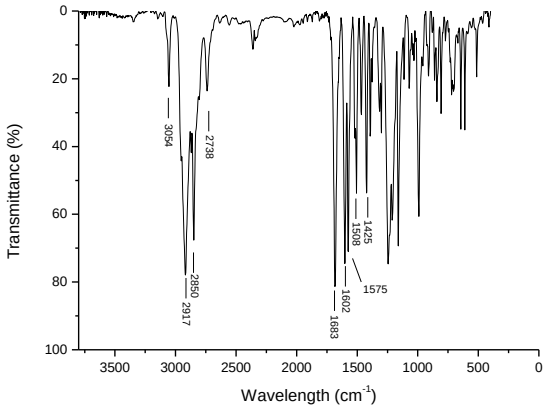


Figure S3. FT-IR of compound **2**.

b. Structural characterization of compound **3**.

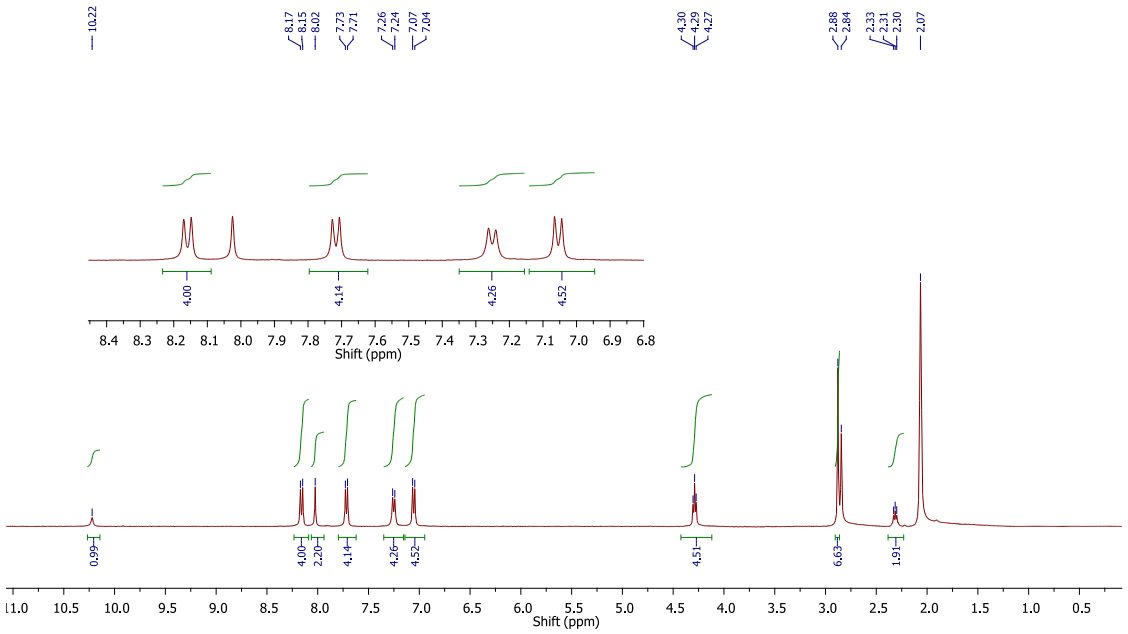


Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3**.

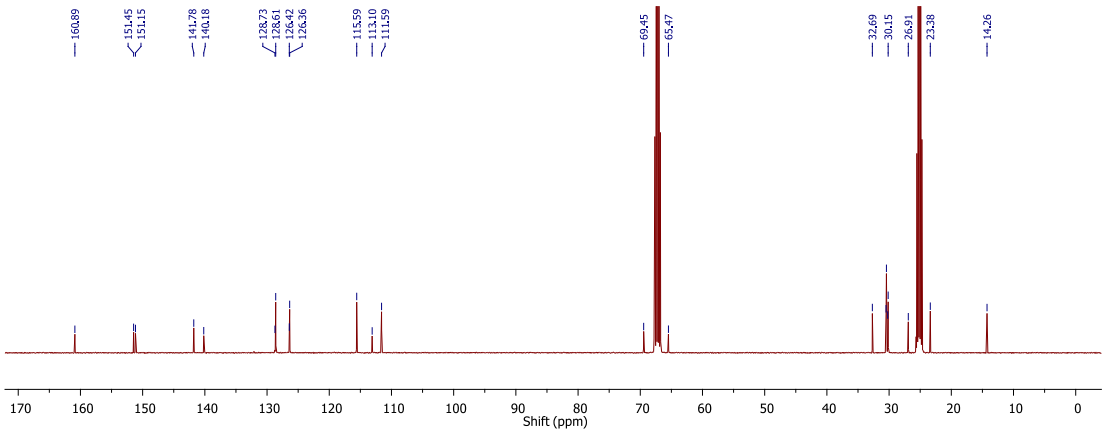


Figure S5. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3**.

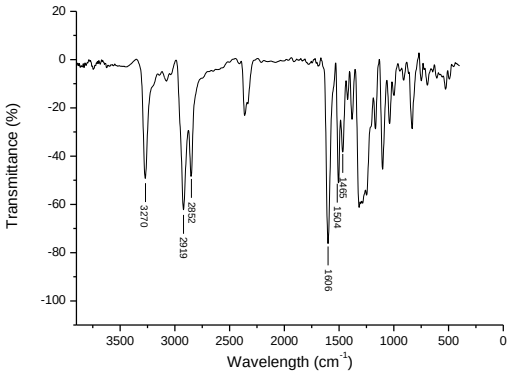


Figure S6. FT-IR of compound **3**.

c. Structural characterization of compound **4**.

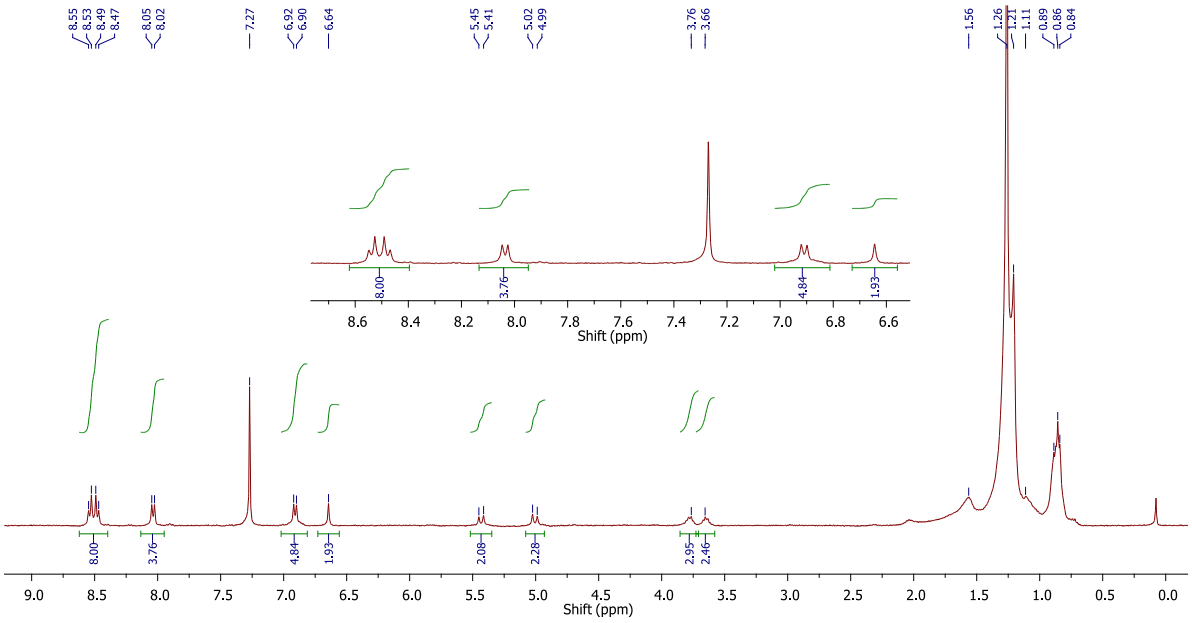


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4**.

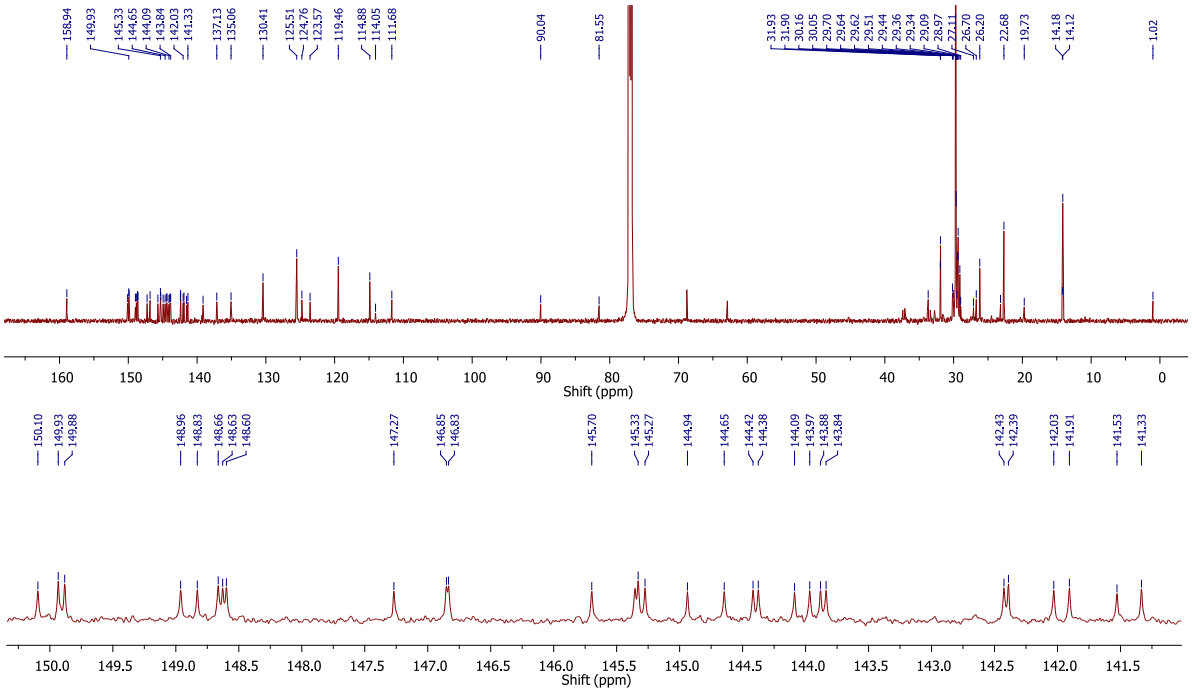


Figure S8. ^{13}C NMR spectrum (175 MHz, $CDCl_3$) of compound **4**.

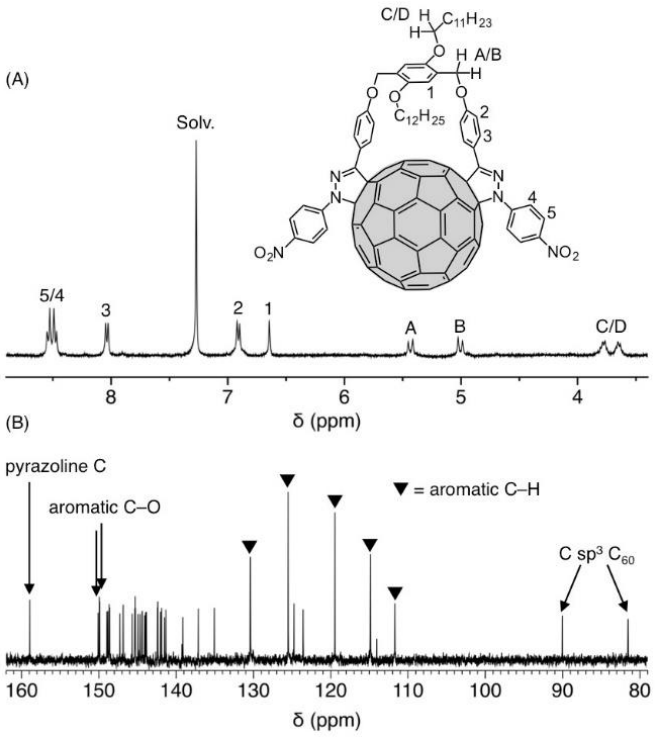


Figure S9. (A) Partial view of the ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of bis-adduct **4**. (B) Partial view of the ^{13}C NMR spectrum (175 MHz, $CDCl_3$, 298 K) of bis-adduct **4**, the five resonances corresponding to aromatic C-H atoms have been identified based on the DEPT spectrum.

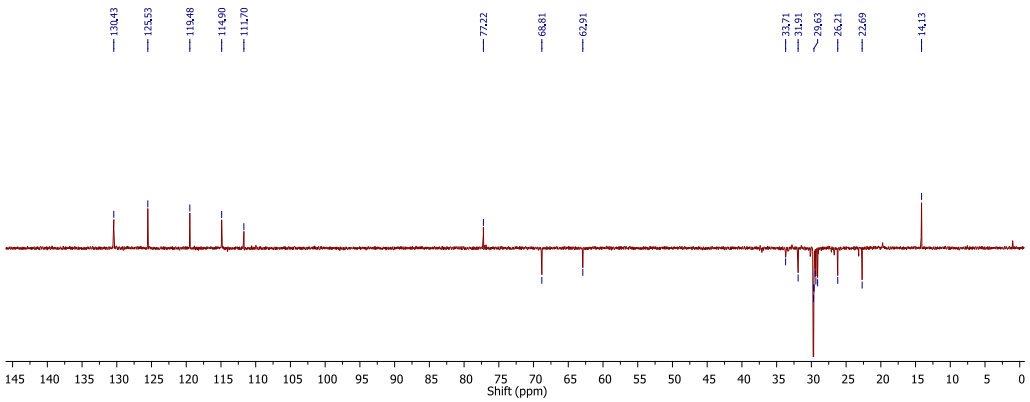


Figure S10. DEPT-135 NMR spectrum (175 MHz, $CDCl_3$) of compound **4** (the five resonances corresponding to aromatic C–H atoms were identified).

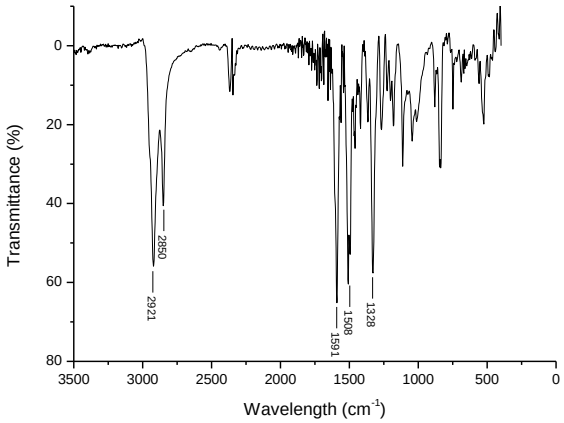


Figure S11. FT-IR (KBr) of compound **4**.

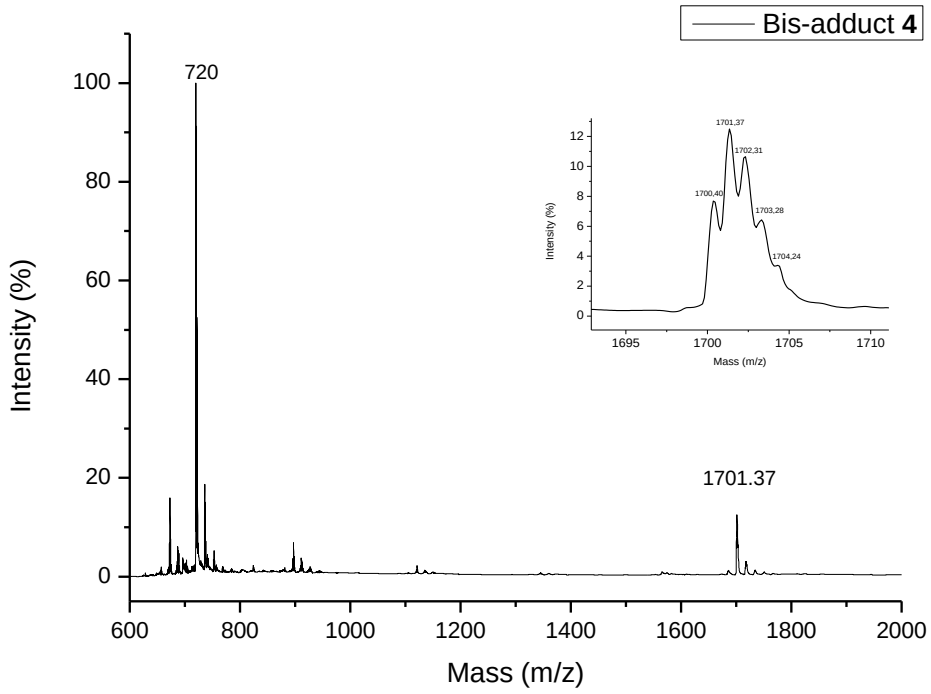


Figure S12. MALDI-TOF MS spectrum of compound **4** (Dithranol).

4. HPLC profile of compound 4.

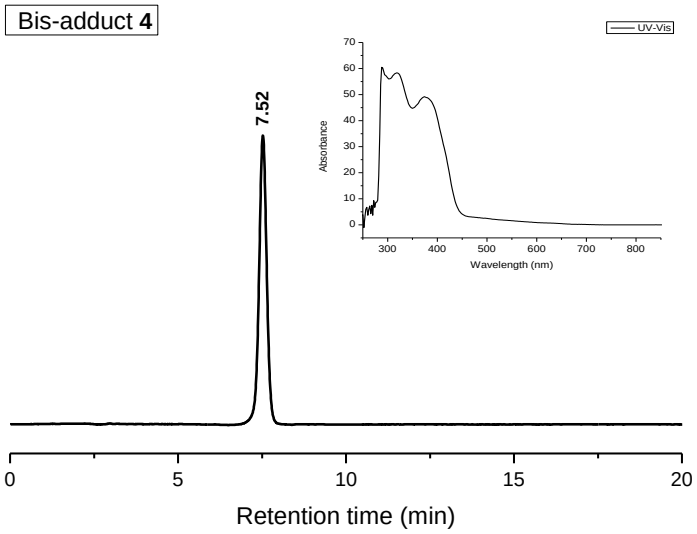


Figure S13. HPLC profile and UV-Vis of compound **4** (Conditions: Buckyprep (4.6ID x 250 mm); toluene (1mL/min) at room temperature; λ=320 nm).

5. **UV-Visible spectroscopy.**

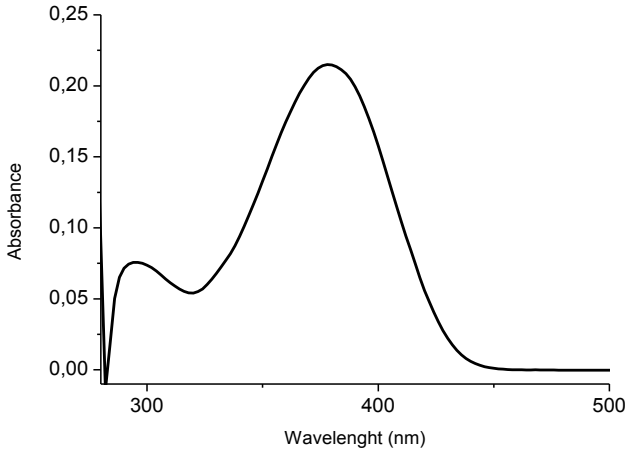


Figure S14. Absorption spectra of compound **3** in toluene.

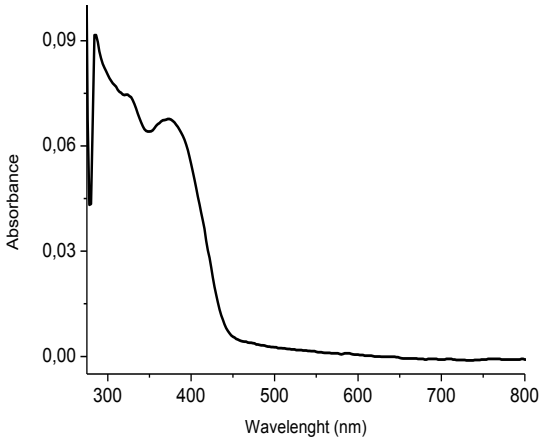


Figure S15. Absorption spectra of compound **4** in toluene.

6. Theoretical calculations

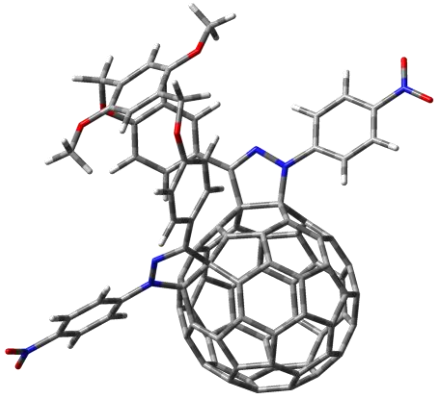
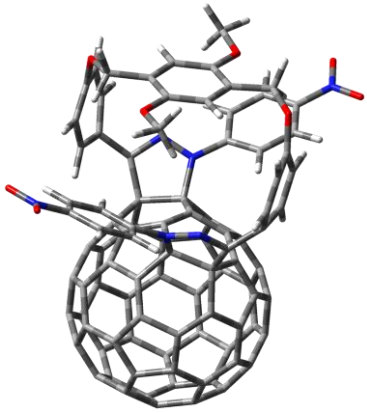
Isomer	
***cis-3* (*out-out*)**	
***cis-3* (*in-in*)**	

Figure S16. Other possible C_2-symmetrical regioisomers of compound **4**

7. Cyclic voltammetry

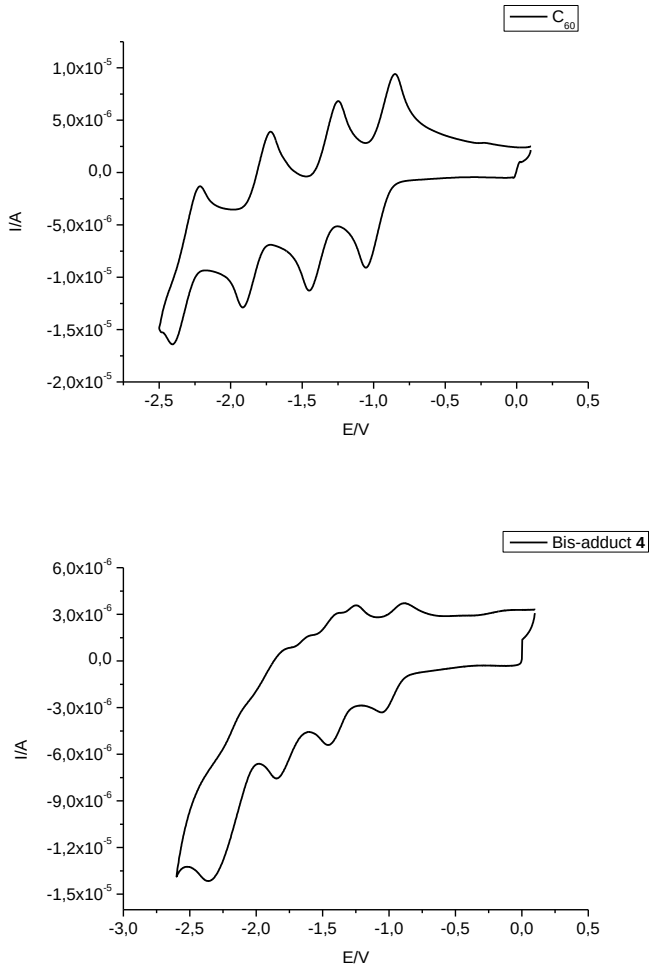


Figure S17. Cyclic voltammetry of C_{60} (up) and compound **4** (down).

AFM studies.

AFM images were recorded in tapping mode and in air conditions using a Multimode 8 system with a NanoScope V controller from Bruker. RTESP-300 Bruker cantilevers with a *resonance frequency* of *300 kHz* and a nominal force constant of 40 Nm^{-1} were used. The images were processed using WSxM (freely downloadable scanning probe microscopy software from http://www.wsxmsolutions.com/).[i]

Due to the high solubility of the molecule in different organic solvents, a strategy for the control of the molecule organization on surface based on a drop-casting deposition method was developed.

The samples investigated by AFM were prepared by drop-casting on HOPG and mica substrates of 20 µL of toluene and dichloromethane bis-pyrazolinofullerene solutions with different concentrations. This study allows us to set a range of concentrations (6 nM - 6pM) in which the organization of the compound on surface can be studied.

The topography images of the drop casted dichloromethane solutions with a 6 pM concentration show the formation of layers on mica and HOPG substrates. When the concentration of the drop casted solution is reduced to 0.06 pM a layer, with a homogeneous height of 1.5 nm is observed on HOPG. This height corresponds with a bis-pyrazolinofullerene single molecule, so it could be considered that single islands of the compound are formed on surface.

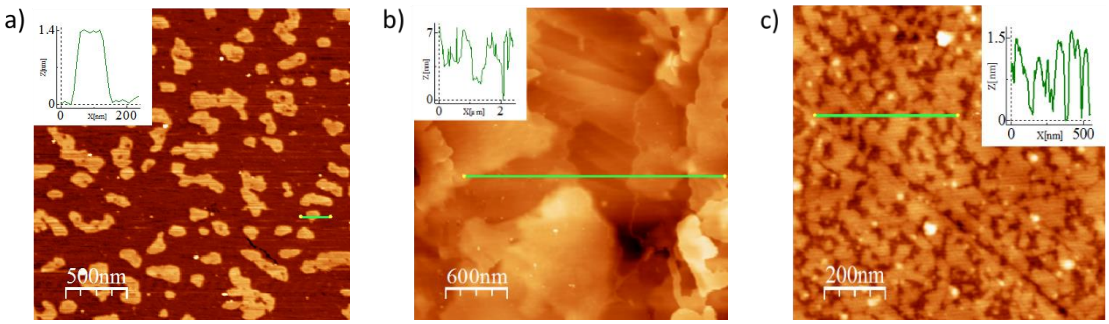


Figure S18: AFM topography images and height profile of a bis-pyrazolinofullerene 6 pM dichloromethane solution deposited on a) mica and b) HOPG. c) The deposition of 20 µL of a 0.06 pM dichloromethane solution on HOPG let the formation of single islands of the compound on surface.

In order to study how the solvent is involved on the self-assembly process, toluene solutions of the compound were prepared and drop casted on mica and HOPG substrates. A study of the organization in function of the solution concentration were performed in order to set a concentration range in which the organization on surface of the molecule can be studied.

When 20 µL of 6 pM bis-pyrazolinofullerene toluene solutions are drop casted on HOPG, one-dimensional structures of the compound on surface are observed. The fibers are characterized by a low length, heterogeneous height and low persistence length. In a detailed view it could be seen a discontinous morphology of the fibers structure (fig S19) and a heterogeneous height along the one-dimensional organization.

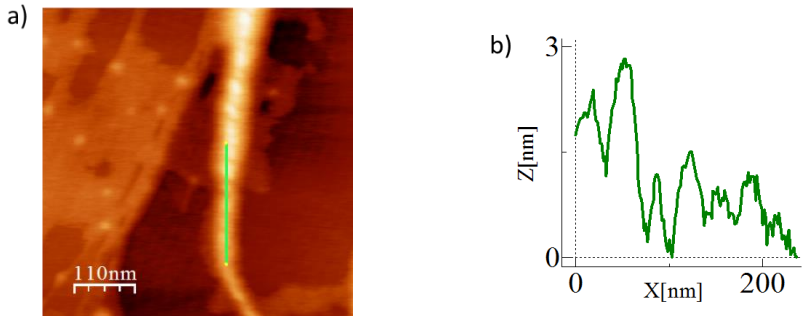


Figure S19. a) Detail of a fiber where an interrupted chain structure can be observed b) Height profile measured along the fiber showing its heterogeneous height.

In order to prove that the organization process is mediated by a surface-molecule and molecule-solvent interaction, 20 µL of the 6 pM toluene solution was drop-casted simoultaneously on mica. AFM topography images show the presence of another type of bis-pyrazolinofullerene organizations, but no one-dimensional assembling has been observed on mica surface.

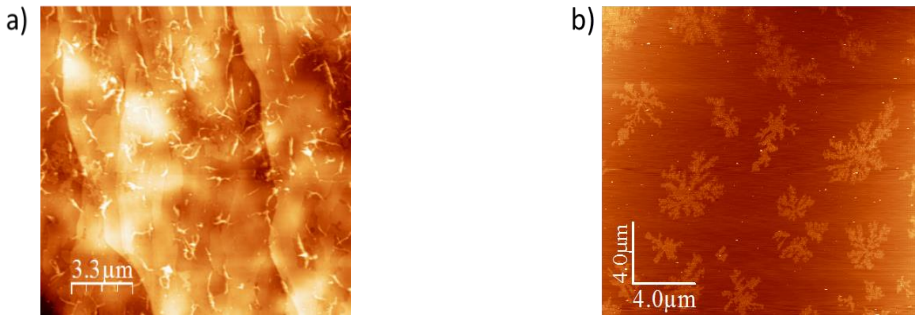


Figure S20. a) Topography image of a 6 pM bis-pyrazolinofullerene toluene solution drop casted on HOPG surface b) Topography image of a 6 pM bis-pyrazolinofullerene toluene solution drop casted on mica surface

With the aim to understand the self-assembly process, samples controlling the solvent evaporation during the drop casting deposition were prepared on HOPG.

The topography images of large solvent evaporation times show no organization of the molecule on surface. Intermediate solvent evaporation times, show the presence of well ordered 2D layers with homogeneous height and well defined morphology. One-dimensional structures with a higher length were also observed in this samples, but in this case the fiber density on surface was considerably lower. When the solvent evaporation take place at ambient conditions without any control, the formation of one-dimensional structures is promoted. There was also observed layers, but with a poor organization.

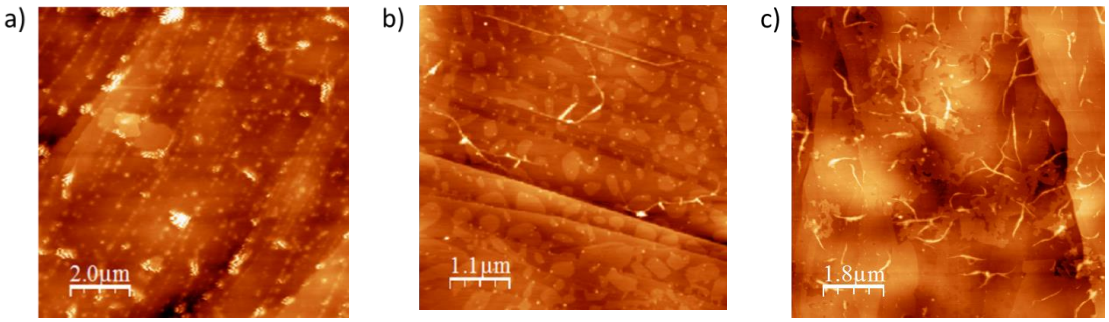


Figure S21. The control of the solvent evaporation is an important parameter involved in the bis-pyrazolinofullerene assembly on surface. a) Topography AFM image of a large solvent evaporation time. b) Topography AFM image of an intermediate solvent evaporation time. c) Solvent evaporation at ambient conditions.

The bis-pyrazolinofullerene self-assembly is a complex process mediated by intermolecular interactions that depends of several parameters like molecule-surface, solvent-surface and molecule-solvent interactions. The control of the solvent, surface, solvent evaporation process and other parameters allows the development of strategies that can guide the self-assembly preferentially to the formation of certain morphologies.

[i] I. Horcas, R. Fernandez, J.M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero and A. M. Baro*, Rev. Sci. Instrum.* 78, 013705 (2007)" and WSxM solutions website.