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Regioselective preparation of a bis-pyrazolinofullerene by a macrocyclization reaction

V. Cuesta,[a] M. Urbani,[b,c,d] P. de la Cruz,[a] Lorena Welte,[a] J.-F. Nierengarten[b] and F. Langa[a],*

A single isomer of a pyrazolinofullerene bis-adduct was prepared by tether-directed remote functionalization. Specifically, a macrocyclization reaction between C_{60} and a bis-hydrazone reagent has been carried out to generate a regioisomerically pure fullerene bis-adduct which presents a lower LUMO than pristine C_{60}.

Solution-processed bulk-heterojunction (BHJ) photovoltaic cells are attractive systems to generate sustainable energy as these devices are light, flexible and can be produced from cheap raw materials.[1] Although most studies have concerned [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) for solution-processed devices, considerable effort has been dedicated to the search for fullerene-based acceptors with better performance than PCBM. [2] In this particular field, the use of fullerene bis-adducts in BHJ solar cells[3] is evolving very rapidly as they are effective acceptors and, in some reported examples, pure bis-adducts displayed better performance than mixtures of isomers,[4] justifying the need for developing new synthetic routes for the preparation of pure regioisomers.

When fullerene bis-adducts are prepared, up to nine regioisomers can be obtained, with the *e* and *trans-3* double bonds being the most reactive sites followed by *trans-2*, *trans-4*, *trans-1*, *cis-3* and *cis-2*, in this order. One elegant approach to prepare pure bis-adducts was described by Diederich in 1994[5] and this involved introduction of the tether-directed remote functionalization concept, as the length and structure of the tether direct the regioselective attack onto one double bond of the C_{60} cage. Most tethered bis-adducts have been prepared by double Bingel

reaction,[6] but Diels–Alder[7] or 1,3-dipolar cycloaddition of azomethine ylides[8] have also been employed. The cycloaddition reaction of nitrile imines to C_{60} affords 2-pyrazolinofullerenes.[9] This is a general procedure to prepare fullerene derivatives that have similar, or even lower, LUMO values to pristine C_{60}[10] and these monoadducts have been successfully used as acceptors in solar cells.[11] Moreover, pyrazolinofullerenes show higher thermal stability[12] than other C_{60} derivatives such as pyrrolidinofullerenes and this is of paramount importance in solar cells. Despite the interest in pyrazolinofullerenes, the preparation and properties of tethered bis-pyrazolinofullerenes remains unknown. We describe here, for the first time, the double cycloaddition to C_{60} of a tethered bis-nitrile imine to synthesize a single regioisomeric bis-adduct.

The selective formation of bis-pyrazolinofullerene **4** by cycloaddition of a bis-nitrile imine to C_{60} was achieved. The bis-adduct was fully characterized by spectroscopic and electrochemical measurements along with computational studies and AFM. Importantly, the derivative obtained had a lower LUMO than pristine C_{60} and this can be of great utility in BHJ solar cells with low LUMO donors.[13]

The synthetic route for **4** is shown in Scheme 1. The synthesis started with the alkylation of 4-hydroxybenzaldehyde (**1**) with 1,4-bis-(bromomethyl)-2,5-bis(dodecyloxy)benzene[14] to afford bis-aldehyde **2** in 70% yield. Condensation of **2** with 4-(nitrophenyl)hydrazine gave the bis-hydrazone **3** in 69% yield. Bis-adduct **4** was then prepared from **3** and C_{60} in a one-pot procedure: reaction of **3** with NBS gave the corresponding bis-brominated hydrazine, which was not isolated; direct treatment of this intermediate with trimethylamine provided the 1,3-dipole and double cycloaddition on the C_{60} scaffold gave **4**. The product of macrocyclization was isolated in 16% yield by column chromatography followed by preparative HPLC. It should be noted that a dumbbell-shaped bis-fullerene by-product was not identified by MS analysis of the crude reaction mixture. The purity of compound **4** could be verified by analytical HPLC showing a single peak with a retention time around 7.5 min (Figure S12).
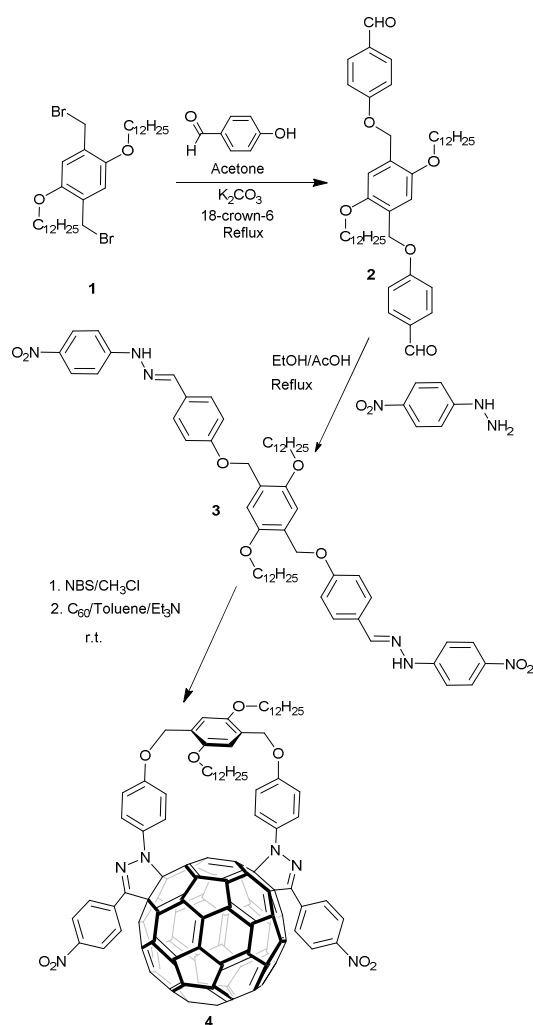
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CHO

C12H25

2

3

1. NBS/CH3Cl
2. C60/Toluene/Et3N
   r.t.

4

Scheme 1. Synthetic route for bis-pyrazolinofullerene **4**

The good solubility of compound **4** in organic solvents, such as chloroform, dichloromethane, toluene or ethyl acetate, allowed the spectroscopic characterization of this material. The structure of **4** was also confirmed by MALDI-TOF mass spectrometry, which showed a molecular ion peak at m/z 1700.40 (Figure S11 in the SI). The UV-vis absorption spectrum is similar to that of monoadducts[15] and is dominated by a broad band with a maximum at 374 nm corresponding to the N-p-nitrophenylpyrazoline moiety (Figure S15).

Full structural characterization of compound **4** required the determination of the relative positions of the two addends on the fullerene core. For this purpose, the NMR data were analyzed carefully to deduce the symmetry of the compound. As shown in Figure S7-S8, the ^1H NMR spectrum of **4** is characterized by a singlet and two AA'XX' signals in the aromatic region and this suggests a two-fold symmetrical structure. This was further confirmed by the observation of a single AB system for the two equivalent benzylic methylene units (H-A/B) and two sets of signals for the diastereotopic OCH₂ units (H-C/D). The ^{13}C NMR spectrum of **4** is also fully

consistent with a C_2-symmetrical structure (Figure S8). The 42 expected signals were observed in the typical aromatic and fullerene region (28 for the 28 pairs of equivalent fullerene sp^2 C atoms, 2 for the two different pairs of fullerene sp^3 C atoms and 12 for the non-fullerene sp^2 C atoms).

Of all the possible addition patterns of a fullerene bis-adduct, only three are C_2-symmetrical (*cis-3*, *trans-2* and *trans-4*). For the most studied fullerene bis-adducts resulting from Bingel cyclopropanations, the structural assignment is typically based on both the symmetry deduced from the NMR spectra and the comparison of the UV/vis spectrum with known reference compounds. Indeed, significant differences are observed in the UV/vis spectra of bis-Bingel adducts of C_{60} as a function of the addition pattern and the absorption spectra provide clear fingerprints to determine unambiguously the relative positions of the two addends. In the case of compound **4**, related bis-adducts are not known. This prompted us to perform theoretical calculations for all possible C_2-symmetrical regioisomers. It is also important to highlight that for each possible addition pattern, three different diastereoisomers are possible, in principle, depending on the relative orientation of the two addends on the fullerene sphere. As a result, the *p*-nitrophenyl subunits are oriented differently with respect to each other in the different diastereoisomers (*in-in*, *out-out* and *out-in* isomerism). This situation is illustrated in Figure 1 for the *trans-3* regioisomer. Two C_2-symmetrical (*in-in* and *out-out*) and one C_1 symmetrical (*out-in*) bis-adducts are in principle possible for *trans-3* bis-adducts. Given the clear steric considerations based on molecular modelling, only the *out-out* isomer is possible for the *trans-3* addition pattern. Similarly, both C_2-symmetrical *in-in* and *out-out trans-2* bis-adducts can be ruled out as the linker between the two pyrazoline moieties is too short. In contrast, the two C_2-symmetrical *cis-3* bis-adducts are in principle also possible.
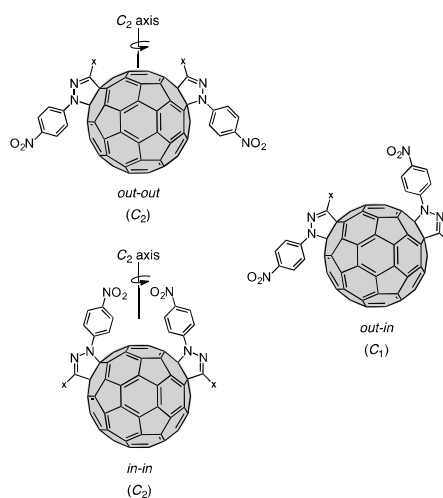
C₂ axis

out-out
(C₂)

C₂ axis

out-in
(C₁)

in-in
(C₂)

Figure 1. For the C_2-symmetrical *trans-3* addition pattern, three cyclic diastereoisomers can be obtained in principle. Compound **4** is C_2-symmetrical and only the *in-in* and *out-out* isomers are possible. However, steric considerations based on molecular modelling revealed that only the *out-out* regioisomer is possible.

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In order to obtain additional information about the three reasonable isomers (*in-in cis-3*, *out-out cis-3* and *out-out trans-3*), theoretical calculations were carried out with Gaussian 09W, applying density functional theory at the B3LYP level. The 6-31G+ basis set was used in the calculations. According to the calculations, the *out-out trans-3* isomer depicted in Figure 2 is the most stable one for compound **4**.
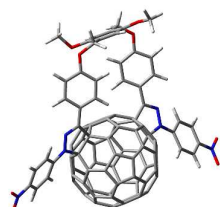

Figure 2. Calculated structure of the most stable isomer of compound **4** (the dodecyl groups were replaced by methyl groups for the calculations). The addition pattern is *trans-3* and the relative orientation of the two *p*-nitrophenyl subunits is *out-out*.

Table 1. Relative Energies of the possible C_2-symmetrical diastereoisomers of **4**.[a]

Isomer	Relative energy (Kcal/mol)
trans-3 *out-out*	0
cis-3 *out-out*	+8.94
cis-3 *in-in*	+80.79

[a] in and out refer to the relative positions of the pyrazoline ring.

The redox potentials of bis-adduct **4** and C_{60} were measured by cyclic voltammetry and OSWV to determine the LUMO levels of **4**. The results are summarized in Table 2. In the available potential window, compound **4** and C_{60} show four reversible waves corresponding to successive fullerene-centred reductions. In the case of compound **4**, the additional irreversible wave observed at ca. −1.38 V is attributed to the reduction of the *p*-nitrophenyl group.[16] Remarkably, the first reduction potential of **4**, observed at −0.92 V, is shifted by about 20 mV to less negative values when compared to pristine C_{60}. Indeed, the two electron-withdrawing addends attached to the fullerene cage confer larger electron affinity than C_{60}. Consequently, **4** has a low-LUMO level, determined as −4.50 eV (estimated using the equation: LUMO level = −(4.8 + $E_{1/2}^{red}$).[17]

Table 2. Redox potentials[a] (in V) of **4** and C_{60} measured by OSWV.

Compound	E1/2 $^{0/-}$	E1/2 $^{-1/-2}$	E1/2 $^{-2/-3}$	E LUMO (eV)
C_{60}	−0.92	−1.32	−1.78	−4.48
4	−0.90	−1.31[b]	−1.65	−4.50

[a] 3.5×10^{-4} M in ODCB/acetonitrile (4:1) versus Fc/Fc$^+$ (E_{ox} = 0.07 V) glassy carbon, Pt counter electrode, 20 °C, 0.1 M Bu$_4$NClO$_4$, scan rate = 100 mV s^{-1}. Values obtained by OSWV, in V *vs* Fc/Fc$^+$. [b] (a non-reversible shoulder at −1.38 V is observed)

It should be mentioned that little attention has been devoted to developing low-LUMO fullerenes.[18] The approach to these compounds is generally restricted to polyfluorinated fullerenes[19] or other derivatives bearing electronegative or electron-deficient

atoms directly connected to the fullerene cage.[20] However, recent work on BHJ solar cells has shown the need for low-LUMO fullerenes for appropriate band energy alignment,[21] with narrow bandgap donors, required to maximize light absorption.[17] The pyrazoline approach is a general method to synthesize low LUMO fullerene derivatives[11] and the interest in this family of compounds is clear.

Finally, in order to understand the morphology of compound **4** in films, a drop casting strategy was employed to control the organization of the compound on surfaces. Taking into account molecule-molecule, molecule-solvent and molecule-surface interactions, we were able to control the self-assembly process of the molecule into 1D or 2D features on HOPG (see Figure 3). (For more details see SI). The use of toluene as solvent and control of the concentration of the solution and the evaporation time of the drop deposited on HOPG, allowed the organization of the molecule to be tailored to give one-dimensional inhomogeneous fibres or two-dimensional single layers. These single layers were also observed on a mica surface and on using other solvents like dichloromethane but, as shown in Figure 3b, the morphology of the compound organized on HOPG deposited from toluene solutions with intermediate solvent evaporation times led to the formation of homogeneous 2D structures on the surface.
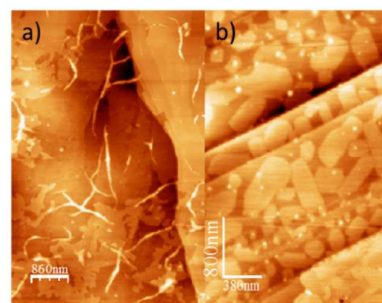

Figure 3. AFM topography of a) one-dimensional and b) two-dimensional organizations of bis-pyrazolinofullerene **4** on HOPG surface.

Conclusions

In summary, we have synthesized and fully characterized a single *trans-3* regioisomer of a macrocyclic bis-pyrazolinofullerene. Cyclization of the bis-hydrazone reagent onto the fullerene core proceeds with good regioselectivity owing to the length and rigidity of the spacer unit. Moreover, this reaction is also diastereoselective as only one out of the three possible isomeric *trans-3* bis-adducts was obtained. Electrochemical investigation revealed that the bis-pyrazolinofullerene has a LUMO at −4.50 eV. This value is lower than that of pristine C_{60} (−4.48 eV) despite the presence of two addends. This new pyrazolinofullerene derivative is therefore an appealing and soluble low-LUMO electron acceptor for applications in solution processed BHJ devices. This first example of the regioselective preparation of a bis-pyrazolinofullerene also paves the way for the synthesis of a

new family of fullerene multi-adducts by systematically modifying the structure of the linker of the bis-hydrazone reagent. In addition, control of the bis-pyrazolinofullerene **4** self-assembly on the surface into one-dimensional and two dimensional single layers is an aspect of great interest for application in bulk heterojunction organic solar cells. Work in this direction is underway in our laboratories.

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†Electronic Supplementary Information (ESI) available: [synthetic details and characterization]. See DOI: 10.1039/x0xx00000x

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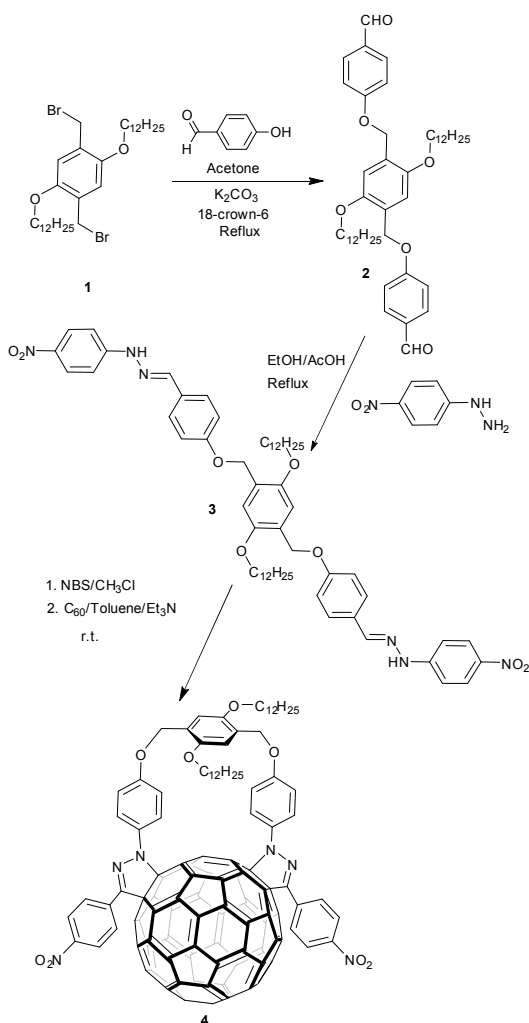
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The good solubility of compound **4** in organic solvents, such as chloroform, dichloromethane, toluene or ethyl acetate, allowed the spectroscopic characterization of this material. The structure of **4** was also confirmed by MALDI-TOF mass spectrometry, which showed a molecular ion peak at m/z 1701.51601700.40 (Figure S11 in the SI). The UV-vis absorption spectrum is similar to that of monoadducts[15] and is dominated by a broad band with a maximum at 374 nm corresponding to the N-p-nitrophenylpyrazoline moiety (Figure S15).

Full structural characterization of compound **4** required the determination of the relative positions of the two addends on the fullerene core. For this purpose, the NMR data were analyzed carefully to deduce the symmetry of the compound. As shown in Figure S7-S8, the ^{1}H NMR spectrum of **4** is characterized by a singlet and two AA'XX' signals in the

aromatic region and this suggests a two-fold symmetrical structure. This was further confirmed by the observation of a single AB system for the two equivalent benzylic methylene units (H-A/B) and two sets of signals for the diastereotopic OCH$_2$ units (H-C/D). The ^{13}C NMR spectrum of **4** is also fully consistent with a C$_2$-symmetrical structure (Figure S8 1B and ESI). The 42 expected signals were observed in the typical aromatic and fullerene region (28 for the 28 pairs of equivalent fullerene sp^2 C atoms, 2 for the two different pairs of fullerene sp^3 C atoms and 12 for the non-fullerene sp^2 C atoms).
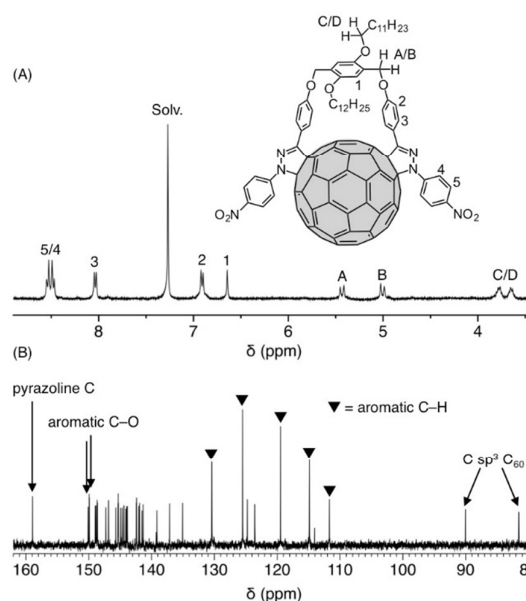

Figure 1. (A) Partial view of the ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of bis-adduct 4. (B) Partial view of the ^{13}C NMR spectrum (175 MHz, CDCl$_3$, 298 K) of bis-adduct 4, the five resonances corresponding to aromatic C–H atoms were identified based on the DEPT spectrum. The full spectra are presented in the ESI.

Of all the possible addition patterns of a fullerene bis-adduct, only three are C$_2$-symmetrical (*cis-3*, *trans-2* and *trans-4*). For the most studied fullerene bis-adducts resulting from Bingel cyclopropanations, the structural assignment is typically based on both the symmetry deduced from the NMR spectra and the comparison of the UV/vis spectrum with known reference compounds. Indeed, significant differences are observed in the UV/vis spectra of bis-Bingel adducts of C$_{60}$ as a function of the addition pattern and the absorption spectra provide clear fingerprints to determine unambiguously the relative positions of the two addends. In the case of compound **4**, related bis-adducts are not known. This prompted us to perform theoretical calculations for all possible C$_2$-symmetrical regioisomers. It is also important to highlight that for each possible addition pattern, three different diastereoisomers are possible, in principle, depending on the relative orientation of the two addends on the fullerene sphere. As a result, the *p*-nitrophenyl subunits are oriented differently with respect to each other in the different diastereoisomers (*in-in*, *out-out* and *out-in* isomerism). This situation is illustrated in Figure 2 1 for the *trans-3* regioisomer. Two C$_2$-symmetrical (*in-in* and *out-*

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out) and one C_1 symmetrical (*out-in*) bis-adducts are in principle possible for *trans-3* bis-adducts. Given the clear steric considerations based on molecular modelling, only the *out-out* isomer is possible for the *trans-3* addition pattern. Similarly, both C_2-symmetrical *in-in* and *out-out trans-2* bis-adducts can be ruled out as the linker between the two pyrazoline moieties is too short. In contrast, the two C_2-symmetrical *cis-3* bis-adducts are in principle also possible.
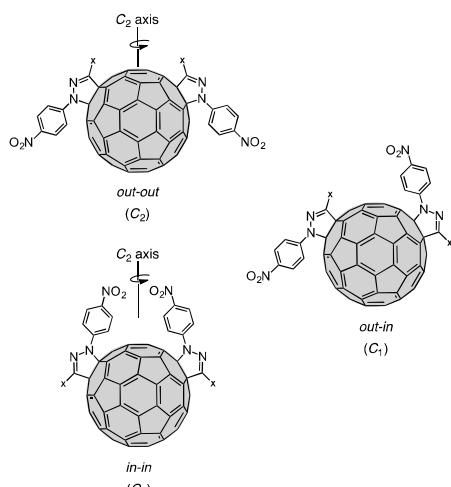
Figure 21. For the C_2-symmetrical *trans-3* addition pattern, three cyclic diastereoisomers can be obtained in principle. Compound **4** is C_2-symmetrical and only the *in-in* and *out-out* isomers are possible. However, steric considerations based on molecular modelling revealed that only the *out-out* regioisomer is possible.

In order to obtain additional information about the three reasonable isomers (*in-in cis-3*, *out-out cis-3* and *out-out trans-3*), theoretical calculations were carried out with Gaussian 09W, applying density functional theory at the B3LYP level. The 6-31G+ basis set was used in the calculations. According to the calculations, the *out-out trans-3* isomer depicted in Figure 32 is the most stable one for compound **4**.
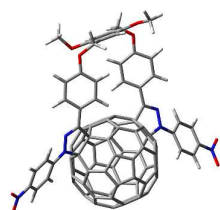

Figure 32. Calculated structure of the most stable isomer of compound **4** (the dodecyl groups were replaced by methyl groups for the calculations). The addition pattern is *trans-3* and the relative orientation of the two *p*-nitrophenyl subunits is *out-out*.

Table 1. Relative Energies of the possible C_2-symmetrical diastereoisomers of **4**.[a]

Isomer	Relative energy (Kcal/mol)
trans-3 *out-out*	0
cis-3 *out-out*	+8.94
cis-3 *in-in*	+80.79

[a] in and out refer to the relative positions of the pyrazoline ring.

The redox potentials of bis-adduct **4** and C_{60} were measured by cyclic voltammetry and OSWV to determine the LUMO levels of **4**. The results are summarized in Table 2. In the available potential window, compound **4** and C_{60} show four reversible waves corresponding to successive fullerene-centred reductions. In the case of compound **4**, the additional irreversible wave observed at ca. −1.38 V is attributed to the reduction of the *p*-nitrophenyl group.[16] Remarkably, the first reduction potential of **4**, observed at −0.92 V, is shifted by about 20 mV to less negative values when compared to pristine C_{60}. Indeed, the two electron-withdrawing addends attached to the fullerene cage confer larger electron affinity than C_{60}. Consequently, **4** has a low-LUMO level, determined as −4.50 eV (estimated using the equation: LUMO level = −(4.8 + $E_{1/2}^{red}$).[17]

Table 2. Redox potentials[a] (in V) of **4** and C_{60} measured by OSWV.

Compound	$E_{1/2}^{0/-}$	$E_{1/2}^{-1/-2}$	$E_{1/2}^{-2/-3}$	E LUMO (eV)
C_{60}	−0.92	−1.32	−1.78	−4.48
4	−0.90	−1.31[b]	−1.65	−4.50

[a] 3.5×10^{-4} M in ODCB/acetonitrile (4:1) versus Fc/Fc$^+$ (E_{ox} = 0.07 V) glassy carbon, Pt counter electrode, 20 °C, 0.1 M Bu$_4$NClO$_4$, scan rate = 100 mV s^{-1}. Values obtained by OSWV, in V *vs* Fc/Fc$^+$. [b] (a non-reversible shoulder at −1.38 V is observed)

It should be mentioned that little attention has been devoted to developing low-LUMO fullerenes.[18] The approach to these compounds is generally restricted to polyfluorinated fullerenes[19] or other derivatives bearing electronegative or electron-deficient atoms directly connected to the fullerene cage.[20] However, recent work on BHJ solar cells has shown the need for low-LUMO fullerenes for appropriate band energy alignment,[21] with narrow bandgap donors, required to maximize light absorption.[17] The pyrazoline approach is a general method to synthesize low LUMO fullerene derivatives[11] and the interest in this family of compounds is clear.

Finally, in order to understand the morphology of compound **4** in films, a drop casting strategy was employed to control the organization of the compound on surfaces. Taking into account molecule-molecule, molecule-solvent and molecule-surface interactions, we were able to control the self-assembly process of the molecule into 1D or 2D features on HOPG (see Figure 43). (For more details see SI). The use of toluene as solvent and control of the concentration of the solution and the evaporation time of the drop deposited on HOPG, allowed the organization of the molecule to be tailored to give one-dimensional inhomogeneous fibres or

two-dimensional single layers. These single layers were also observed on a mica surface and on using other solvents like dichloromethane but, as shown in Figure 4b3b, the morphology of the compound organized on HOPG deposited from toluene solutions with intermediate solvent evaporation times led to the formation of homogeneous 2D structures on the surface.
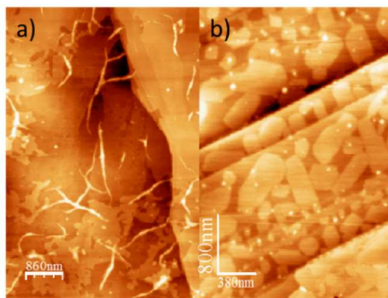

Figure 3. AFM topography of a) one-dimensional and b) two-dimensional organizations of bis-pyrazolinofullerene **4** on HOPG surface.

Conclusions

In summary, we have synthesized and fully characterized a single *trans-3* regioisomer of a macrocyclic bis-pyrazolinofullerene. Cyclization of the bis-hydrazone reagent onto the fullerene core proceeds with good regioselectivity owing to the length and rigidity of the spacer unit. Moreover, this reaction is also diastereoselective as only one out of the three possible isomeric *trans-3* bis-adducts was obtained. Electrochemical investigation revealed that the bis-pyrazolinofullerene has a LUMO at −4.50 eV. This value is lower than that of pristine C_{60} (−4.48 eV) despite the presence of two addends. This new pyrazolinofullerene derivative is therefore an appealing and soluble low-LUMO electron acceptor for applications in solution processed BHJ devices. This first example of the regioselective preparation of a bis-pyrazolinofullerene also paves the way for the synthesis of a new family of fullerene multi-adducts by systematically modifying the structure of the linker of the bis-hydrazone reagent. In addition, control of the bis-pyrazolinofullerene **4** self-assembly on the surface into one-dimensional and two dimensional single layers is an aspect of great interest for application in bulk heterojunction organic solar cells. Work in this direction is underway in our laboratories.

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Regioselective preparation of a bis-pyrazolinofullerene by a macrocyclization reaction

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A single isomer of a pyrazolinofullerene bis-adduct was prepared by tether-directed remote functionalization. Specifically, a macrocyclization reaction between C_{60} and a bis-hydrazone reagent has been carried out to generate a regioisomerically pure fullerene bis-adduct which presents a lower LUMO than pristine C_{60}.

Solution-processed bulk-heterojunction (BHJ) photovoltaic cells are attractive systems to generate sustainable energy as these devices are light, flexible and can be produced from cheap raw materials.[1] Although most studies have concerned [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) for solution-processed devices, considerable effort has been dedicated to the search for fullerene-based acceptors with better performance than PCBM.[2] In this particular field, the use of fullerene bis-adducts in BHJ solar cells[3] is evolving very rapidly as they are effective acceptors and, in some reported examples, pure bis-adducts displayed better performance than mixtures of isomers,[4] justifying the need for developing new synthetic routes for the preparation of pure regioisomers.

When fullerene bis-adducts are prepared, up to nine regioisomers can be obtained, with the *e* and *trans-3* double bonds being the most reactive sites followed by *trans-2*, *trans-4*, *trans-1*, *cis-3* and *cis-2*, in this order. One elegant approach to prepare pure bis-adducts was described by Diederich in 1994[5] and this involved introduction of the tether-directed remote functionalization concept, as the length and structure of the tether direct the regioselective attack onto one double bond of the C_{60} cage. Most tethered bis-adducts have been prepared by double Bingel reaction,[6] but Diels–Alder[7] or 1,3-dipolar

cycloaddition of azomethine ylides[8] have also been employed. The cycloaddition reaction of nitrile imines to C_{60} affords 2-pyrazolinofullerenes.[9] This is a general procedure to prepare fullerene derivatives that have similar, or even lower, LUMO values to pristine C_{60}[10] and these monoadducts have been successfully used as acceptors in solar cells.[11] Moreover, pyrazolinofullerenes show higher thermal stability[12] than other C_{60} derivatives such as pyrrolidinofullerenes and this is of paramount importance in solar cells. Despite the interest in pyrazolinofullerenes, the preparation and properties of tethered bis-pyrazolinofullerenes remains unknown. We describe here, for the first time, the double cycloaddition to C_{60} of a tethered bis-nitrile imine to synthesize a single regioisomeric bis-adduct.

The selective formation of bis-pyrazolinofullerene **4** by cycloaddition of a bis-nitrile imine to C_{60} was achieved. The bis-adduct was fully characterized by spectroscopic and electrochemical measurements along with computational studies and AFM. Importantly, the derivative obtained had a lower LUMO than pristine C_{60} and this can be of great utility in BHJ solar cells with low LUMO donors.[13]

The synthetic route for **4** is shown in Scheme 1. The synthesis started with the alkylation of 4-hydroxybenzaldehyde (**1**) with 1,4-bis-(bromomethyl)-2,5-bis(dodecyloxy)benzene[14] to afford bis-aldehyde **2** in 70% yield. Condensation of **2** with 4-(nitrophenyl)hydrazine gave the bis-hydrazone **3** in 69% yield. Bis-adduct **4** was then prepared from **3** and C_{60} in a one-pot procedure: reaction of **3** with NBS gave the corresponding bis-brominated hydrazine, which was not isolated; direct treatment of this intermediate with trimethylamine provided the 1,3-dipole and double cycloaddition on the C_{60} scaffold gave **4**. The product of macrocyclization was isolated in 16% yield by column chromatography followed by preparative HPLC. It should be noted that a dumbbell-shaped bis-fullerene by-product was not identified by MS analysis of the crude reaction mixture. The purity of compound **4** could be verified by analytical HPLC showing a single peak with a retention time around 7.5 min (Figure S12).
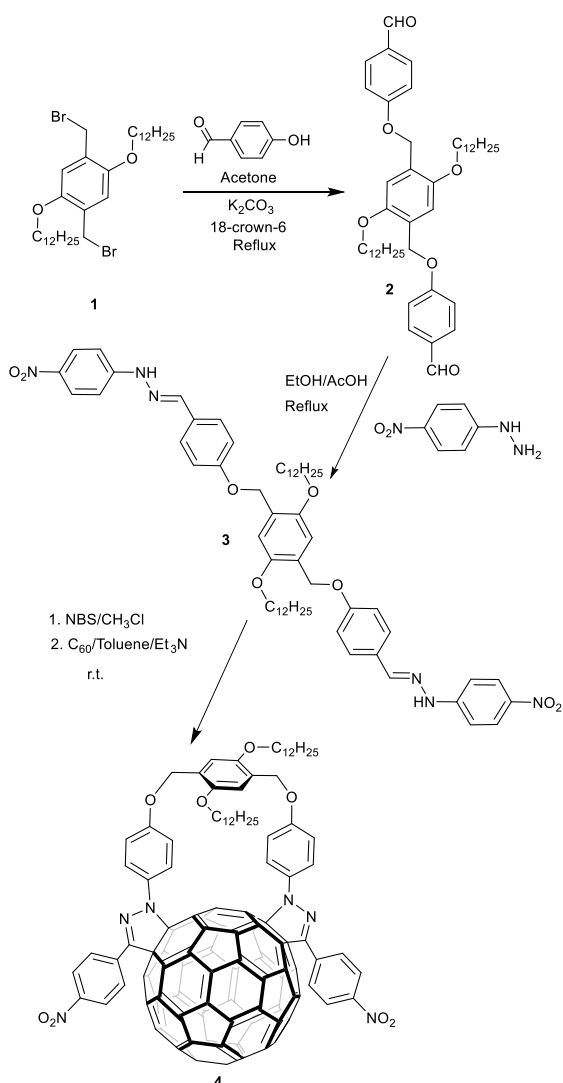
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†Electronic Supplementary Information (ESI) available: [synthetic details and characterization]. See DOI: 10.1039/x0xx00000x

Scheme 1. Synthetic route for bis-pyrazolinofullerene **4**

The good solubility of compound **4** in organic solvents, such as chloroform, dichloromethane, toluene or ethyl acetate, allowed the spectroscopic characterization of this material. The structure of **4** was also confirmed by MALDI-TOF mass spectrometry, which showed a molecular ion peak at m/z 1700.40 (Figure S11 in the SI). The UV-vis absorption spectrum is similar to that of monoadducts[15] and is dominated by a broad band with a maximum at 374 nm corresponding to the N-p-nitrophenylpyrazoline moiety (Figure S15).

Full structural characterization of compound **4** required the determination of the relative positions of the two addends on the fullerene core. For this purpose, the NMR data were analyzed carefully to deduce the symmetry of the compound. As shown in Figure S7-S8, the ^{1}H NMR spectrum of **4** is characterized by a singlet and two AA'XX' signals in the aromatic region and this suggests a two-fold symmetrical structure. This was further confirmed by the observation of a single AB system for the two equivalent benzylic methylene units (H-A/B) and two sets of signals for the diastereotopic OCH_2 units (H-C/D). The ^{13}C NMR spectrum of **4** is also fully consistent with a C_2-

symmetrical structure (Figure S8). The 42 expected signals were observed in the typical aromatic and fullerene region (28 for the 28 pairs of equivalent fullerene sp^2 C atoms, 2 for the two different pairs of fullerene sp^3 C atoms and 12 for the non-fullerene sp^2 C atoms).

Of all the possible addition patterns of a fullerene bis-adduct, only three are C_2-symmetrical (*cis-3*, *trans-2* and *trans-4*). For the most studied fullerene bis-adducts resulting from Bingel cyclopropanations, the structural assignment is typically based on both the symmetry deduced from the NMR spectra and the comparison of the UV/vis spectrum with known reference compounds. Indeed, significant differences are observed in the UV/vis spectra of bis-Bingel adducts of C_{60} as a function of the addition pattern and the absorption spectra provide clear fingerprints to determine unambiguously the relative positions of the two addends. In the case of compound **4**, related bis-adducts are not known. This prompted us to perform theoretical calculations for all possible C_2-symmetrical regioisomers. It is also important to highlight that for each possible addition pattern, three different diastereoisomers are possible, in principle, depending on the relative orientation of the two addends on the fullerene sphere. As a result, the p-nitrophenyl subunits are oriented differently with respect to each other in the different diastereoisomers (*in-in*, *out-out* and *out-in* isomerism). This situation is illustrated in Figure 1 for the *trans-3* regioisomer. Two C_2-symmetrical (*in-in* and *out-out*) and one C_1 symmetrical (*out-in*) bis-adducts are in principle possible for *trans-3* bis-adducts. Given the clear steric considerations based on molecular modelling, only the *out-out* isomer is possible for the *trans-3* addition pattern. Similarly, both C_2-symmetrical *in-in* and *out-out trans-2* bis-adducts can be ruled out as the linker between the two pyrazoline moieties is too short. In contrast, the two C_2-symmetrical *cis-3* bis-adducts are in principle also possible.
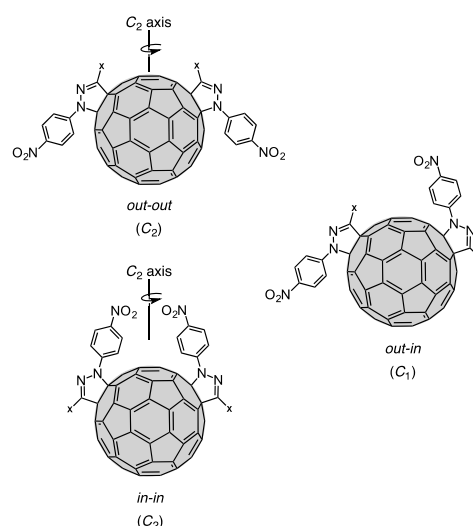

Figure 1. For the C_2-symmetrical *trans-3* addition pattern, three cyclic diastereoisomers can be obtained in principle. Compound **4** is C_2-symmetrical and only the *in-in* and *out-out* isomers are possible. However, steric considerations based on molecular modelling revealed that only the *out-out* regioisomer is possible.

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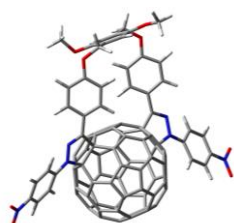

Figure 2. Calculated structure of the most stable isomer of compound **4** (the dodecyl groups were replaced by methyl groups for the calculations). The addition pattern is *trans-3* and the relative orientation of the two *p*-nitrophenyl subunits is *out-out*.

Table 1. Relative Energies of the possible C_2-symmetrical diastereoisomers of **4**.[a]

Isomer	Relative energy (Kcal/mol)
trans-3 *out-out*	0
cis-3 *out-out*	+8.94
cis-3 *in-in*	+80.79

[a] in and out refer to the relative positions of the pyrazoline ring.

The redox potentials of bis-adduct **4** and C_{60} were measured by cyclic voltammetry and OSWV to determine the LUMO levels of **4**. The results are summarized in Table 2. In the available potential window, compound **4** and C_{60} show four reversible waves corresponding to successive fullerene-centred reductions. In the case of compound **4**, the additional irreversible wave observed at ca. −1.38 V is attributed to the reduction of the *p*-nitrophenyl group.[16] Remarkably, the first reduction potential of **4**, observed at −0.92 V, is shifted by about 20 mV to less negative values when compared to pristine C_{60}. Indeed, the two electron-withdrawing addends attached to the fullerene cage confer larger electron affinity than C_{60}. Consequently, **4** has a low-LUMO level, determined as −4.50 eV (estimated using the equation: LUMO level = −(4.8 + $E_{1/2}^{red}$).[17]

Table 2. Redox potentials[a] (in V) of **4** and C_{60} measured by OSWV.

Compound	E1/2 $^{0/-}$	E1/2 $^{-1/-2}$	E1/2 $^{-2/-3}$	E LUMO (eV)
C_{60}	−0.92	−1.32	−1.78	−4.48
4	−0.90	−1.31[b]	−1.65	−4.50

[a] 3.5×10^{-4} M in ODCB/acetonitrile (4:1) versus Fc/Fc⁺ (E_{ox} = 0.07 V) glassy carbon, Pt counter electrode, 20 °C, 0.1 M Bu₄NClO₄, scan rate = 100 mV s⁻¹. Values obtained by OSWV, in V *vs* Fc/Fc⁺. [b] (a non-reversible shoulder at −1.38 V is observed)

It should be mentioned that little attention has been devoted to developing low-LUMO fullerenes.[18] The approach to these compounds is generally restricted to polyfluorinated fullerenes[19] or other derivatives bearing electronegative or electron-deficient atoms directly connected to the fullerene cage.[20] However, recent work on BHJ solar cells has shown the need for low-LUMO fullerenes for appropriate band energy alignment,[21] with narrow bandgap donors, required to maximize light absorption.[17] The pyrazoline approach is a general method to synthesize low LUMO fullerene derivatives[11] and the interest in this family of compounds is clear.

Finally, in order to understand the morphology of compound **4** in films, a drop casting strategy was employed to control the organization of the compound on surfaces. Taking into account molecule-molecule, molecule-solvent and molecule-surface interactions, we were able to control the self-assembly process of the molecule into 1D or 2D features on HOPG (see Figure 3). (For more details see SI). The use of toluene as solvent and control of the concentration of the solution and the evaporation time of the drop deposited on HOPG, allowed the organization of the molecule to be tailored to give one-dimensional inhomogeneous fibres or two-dimensional single layers. These single layers were also observed on a mica surface and on using other solvents like dichloromethane but, as shown in Figure 3b, the morphology of the compound organized on HOPG deposited from toluene solutions with intermediate solvent evaporation times led to the formation of homogeneous 2D structures on the surface.
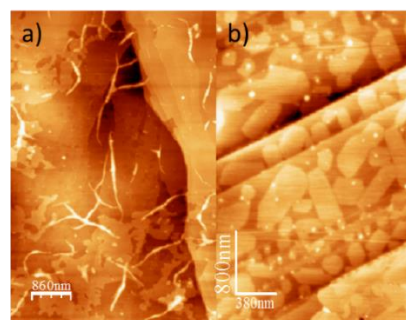

Figure 3. AFM topography of a) one-dimensional and b) two-dimensional organizations of bis-pyrazolinofullerene **4** on HOPG surface.

Conclusions

In summary, we have synthesized and fully characterized a single *trans-3* regioisomer of a macrocyclic bis-pyrazolinofullerene. Cyclization of the bis-hydrazone reagent onto the fullerene core proceeds with good regioselectivity owing to the length and rigidity of the spacer unit. Moreover, this reaction is also diastereoselective as only one out of the three possible isomeric *trans-3* bis-adducts was obtained. Electrochemical investigation revealed that the bis-pyrazolinofullerene has a LUMO at −4.50 eV. This value is lower than that of pristine C_{60} (−4.48 eV) despite the presence of two addends. This new pyrazolinofullerene derivative is therefore an appealing and soluble low-LUMO electron acceptor for applications in solution processed BHJ devices. This first example of the regioselective preparation of a bis-pyrazolinofullerene also paves the way for the synthesis of a new family of fullerene multi-adducts by systematically modifying the structure of the linker of the bis-hydrazone

reagent. In addition, control of the bis-pyrazolinofullerene **4** self-assembly on the surface into one-dimensional and two dimensional single layers is an aspect of great interest for application in bulk heterojunction organic solar cells. Work in this direction is underway in our laboratories.

Notes and references

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Regioselective preparation of a bis-pyrazolinofullerene by a macrocyclization reaction

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Table of contents.

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 $(n$-Bu$)_4$NClO$_4$ in o-DCB:Acetonitrile (4:1) as an electrolyte solution.

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.

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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°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) v/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) v/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 ~~1701.43~~1700.40

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

a. Structural characterization of compound **2**.
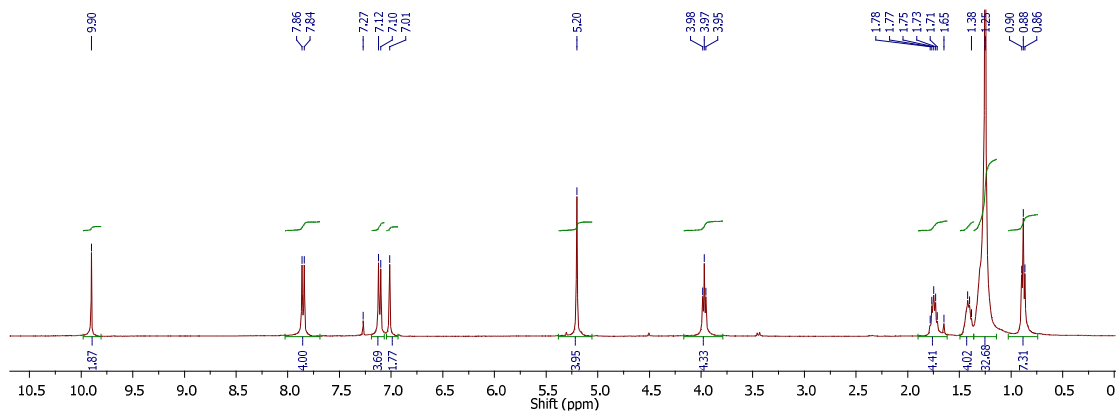
Figure S1. ^{1}H-NMR spectrum (400 MHz, CDCl$_3$) of compound **2.**
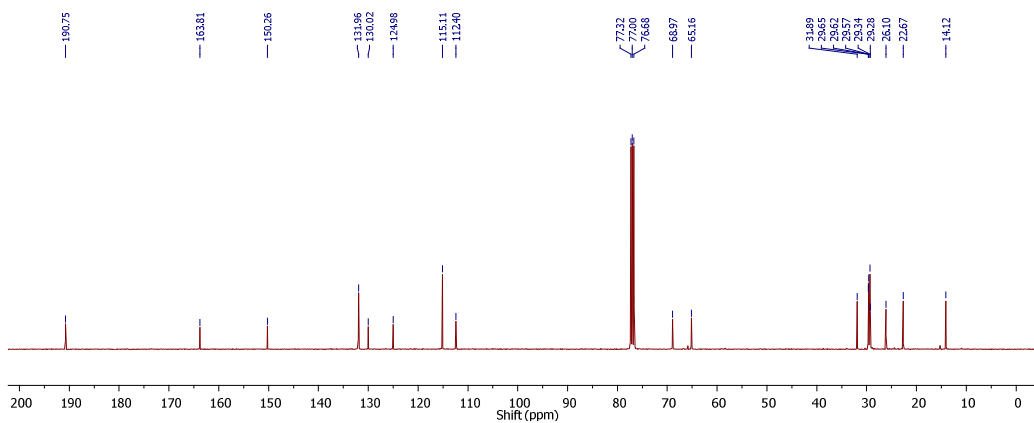
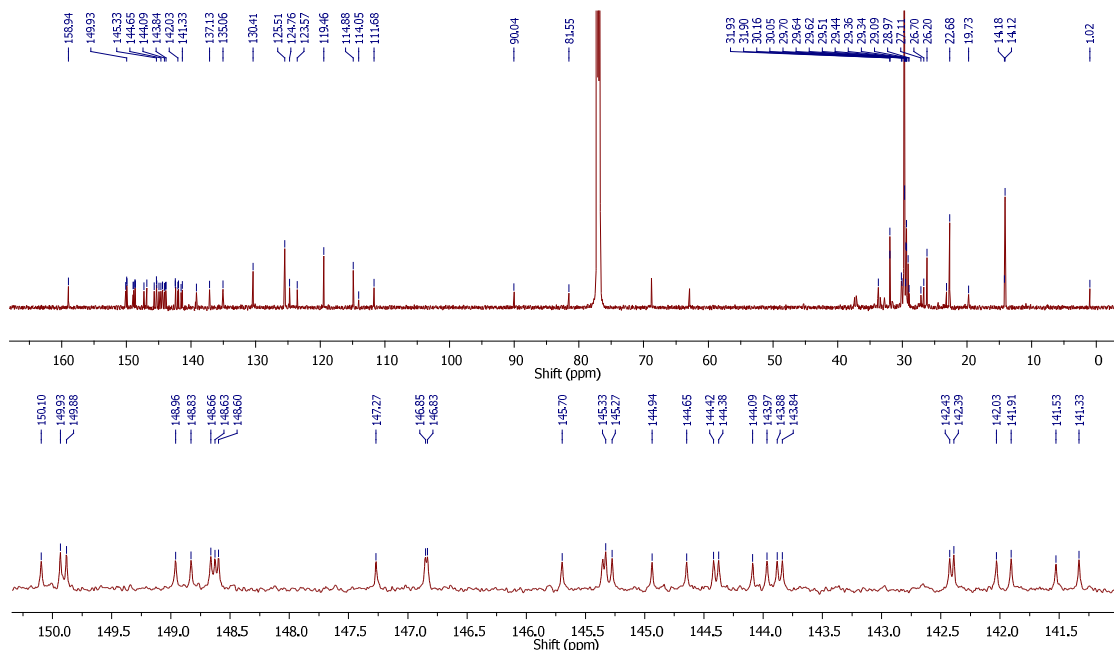**Figure S2**. ^{13}C-NMR spectrum (100 MHz, CDCl$_3$) of compound **2**.
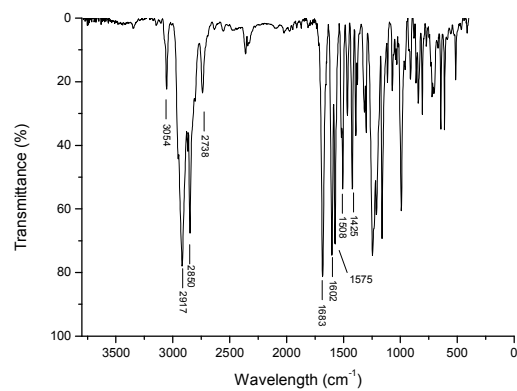
Figure S3. FT-IR of compound **2**.

b. Structural characterization of compound **3**.
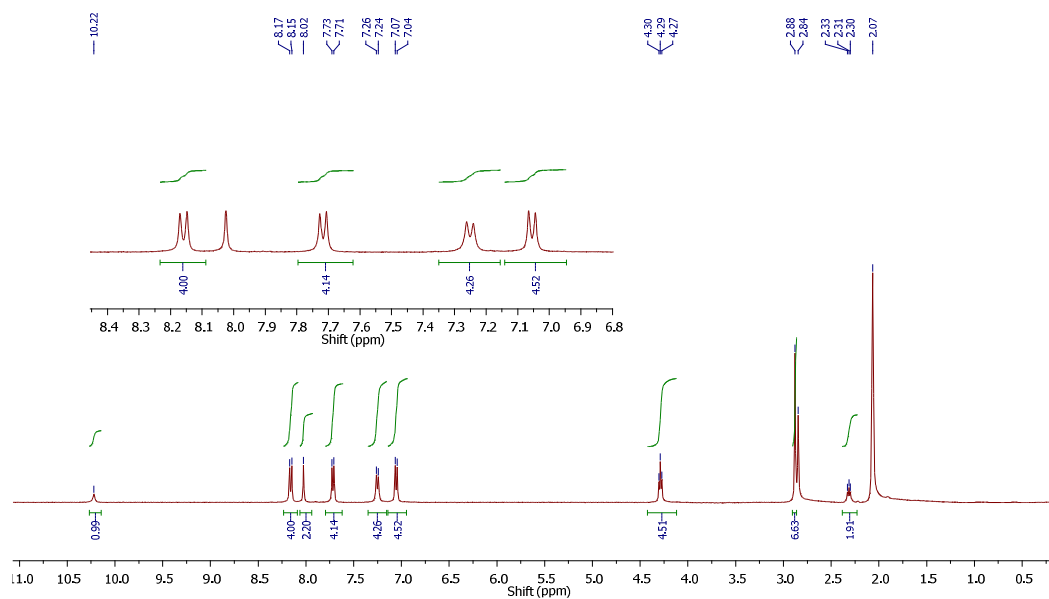
Figure S4. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound **3**.
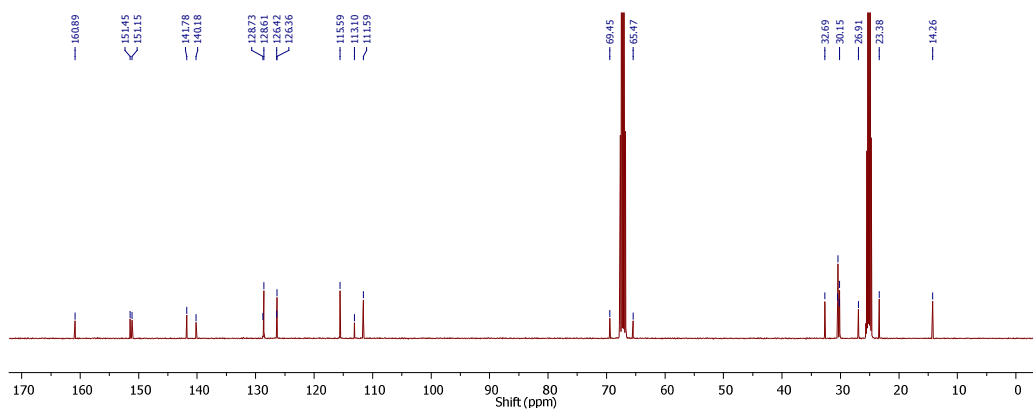
Figure S5. ^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **3**.
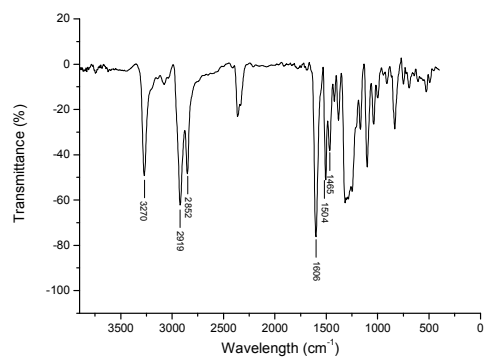
Figure S6. FT-IR of compound **3**.

c. Structural characterization of compound **4**.
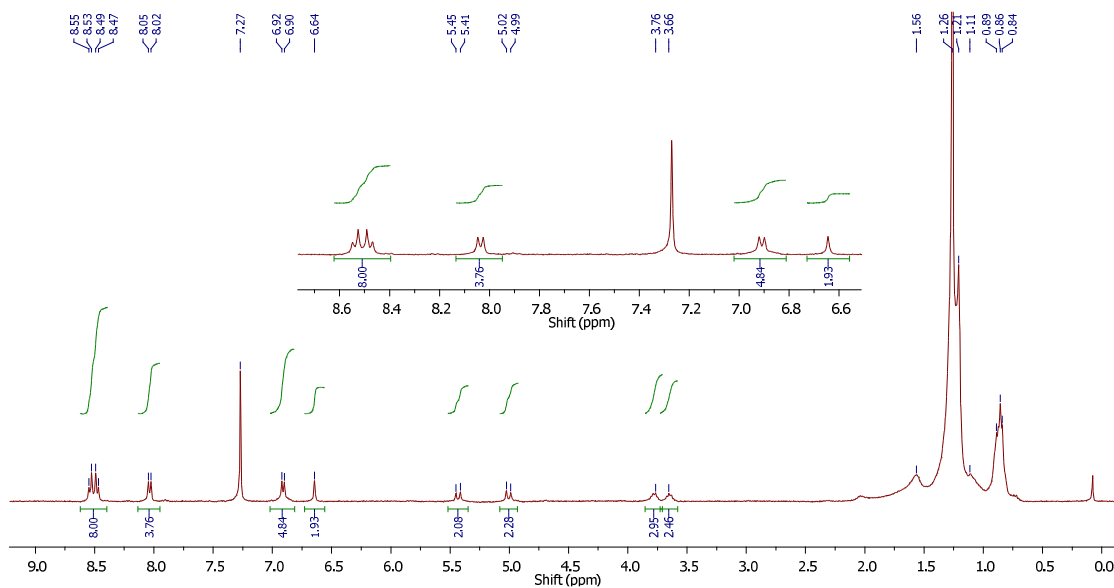
Figure S7. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound **4**.

Figure S8. ^{13}C NMR spectrum (175 MHz, CDCl$_3$) of compound **4**.
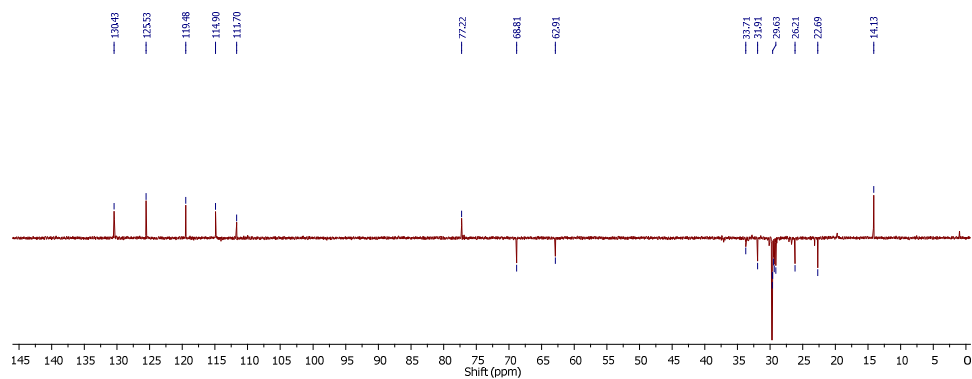
Figure S9. DEPT-135 NMR spectrum (175 MHz, CDCl$_3$) of compound **4** (the five resonances corresponding to aromatic C–H atoms were identified).
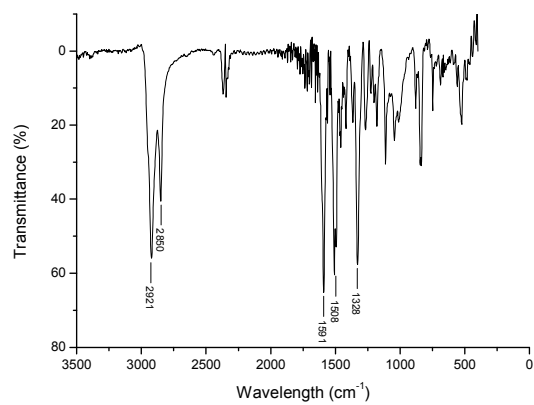
Figure S10. FT-IR (KBr) of compound **4**.
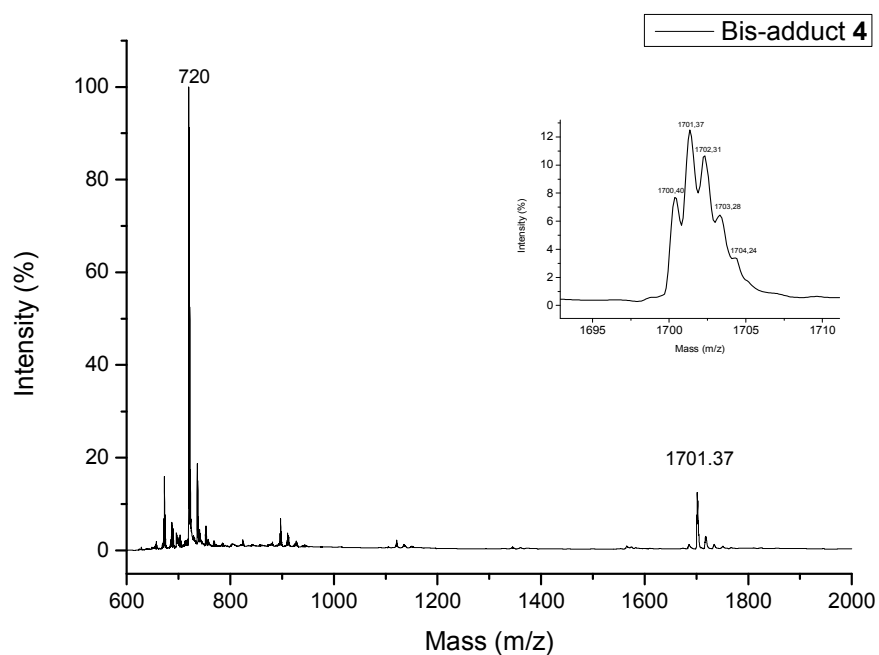
Figure S11. MALDI-TOF MS spectrum of compound **4** (Dithranol).

4. **HPLC profile of compound 4.**
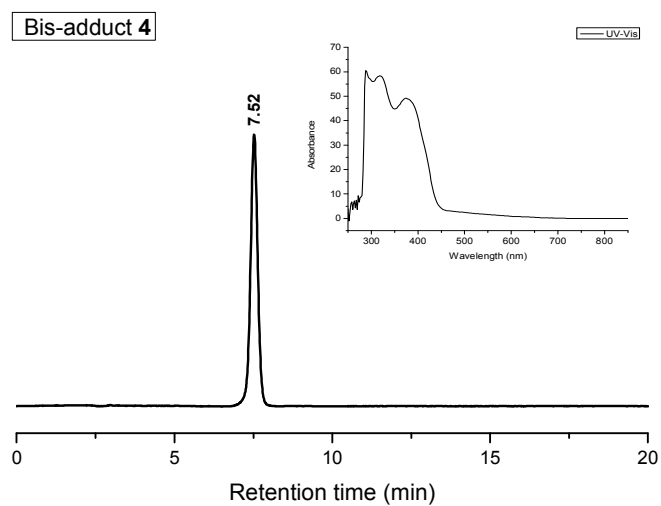
Figure S12. HPLC profile and UV-Vis of compound **4** (Conditions: Buckyprep (4.6ID x 250 mm); toluene (1mL/min) at room temperature; λ=320 nm).

5. **UV-Visible spectroscopy.**
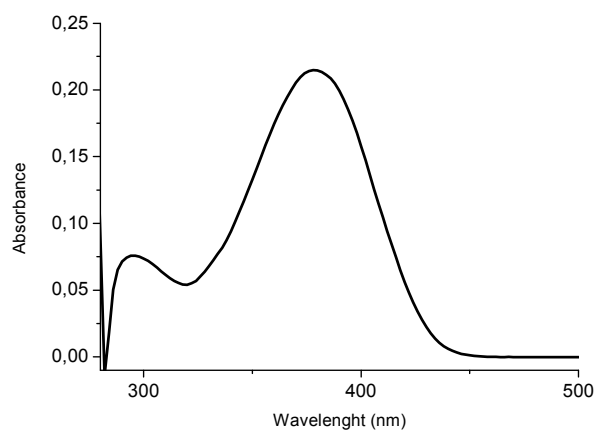
Figure S13. Absorption spectra of compound **3** in toluene.
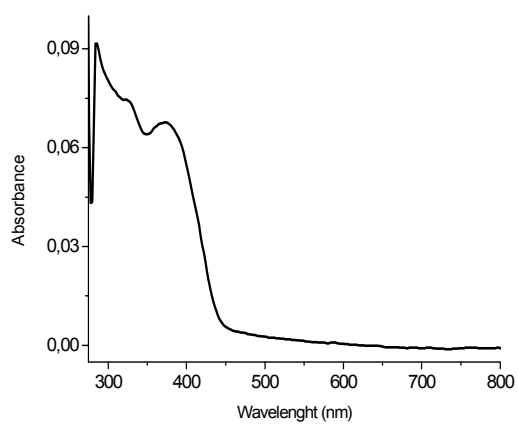
Figure S14. Absorption spectra of compound **4** in toluene.
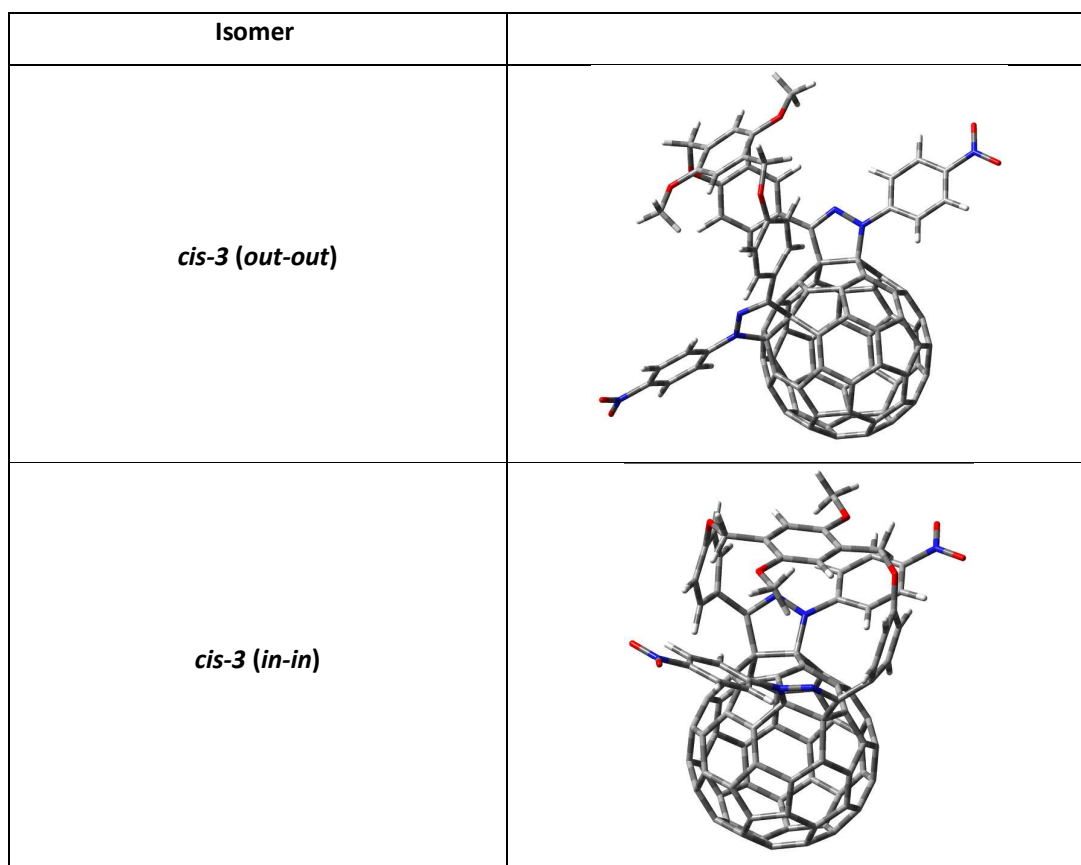
6. **Theoretical calculations**

Isomer	

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

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

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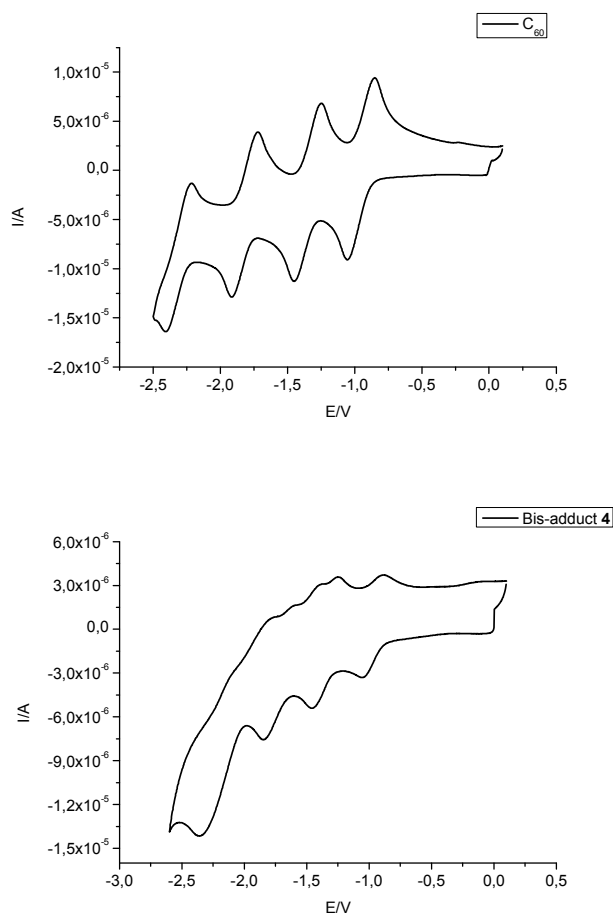
Figure S17. Cyclic voltammetry of C_{60} (up) and compound **4** (down).

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.
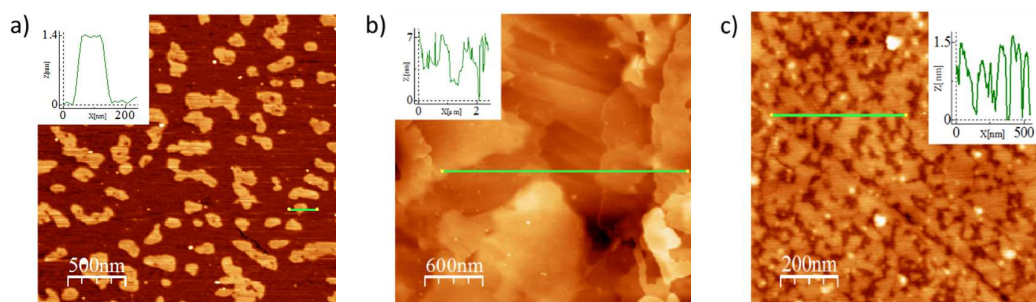

Figure S18: AFM topography images and height profile of a bis-pyrazolinofullerene 6 pM dichloromethane solution deposited on a) mica and b) HOPG. c) The deposition of 20 µL of a 0.06 pM dichloromethane solution on HOPG let the formation of single islands of the compound on surface.

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.
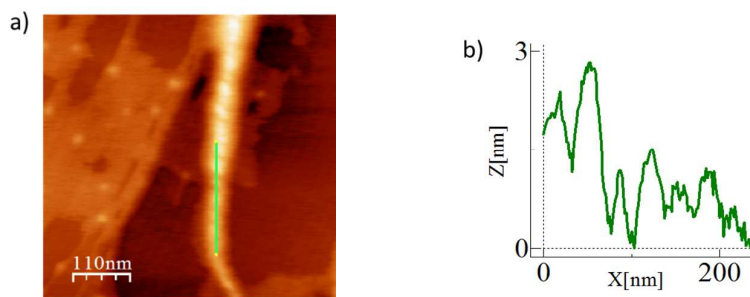

Figure S19. a) Detail of a fiber where an interrupted chain structure can be observed b)

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.
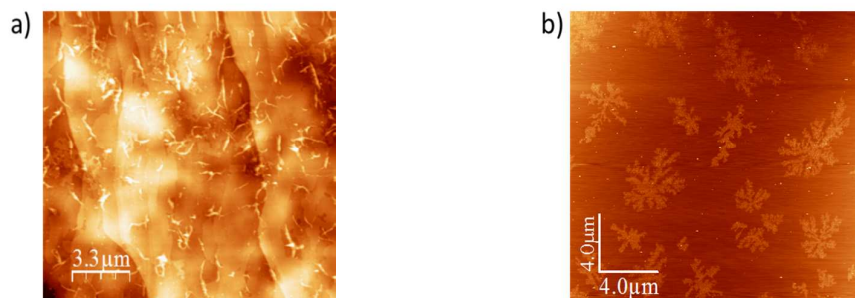

Figure S20. a) Topography image of a 6 pM bis-pyrazolinofullerene toluene solution drop casted on HOPG surface b) Topography image of a 6 pM bis-pyrazolinofullerene toluene solution drop casted on mica surface

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.
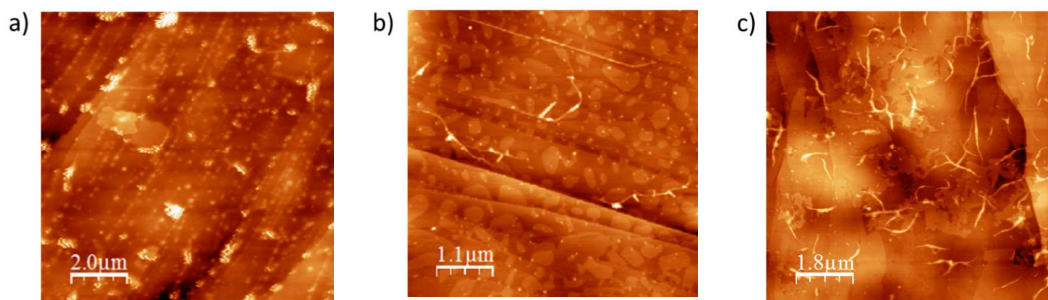

Figure S21. The control of the solvent evaporation is an important parameter involved in the

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.

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[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.