SUPPORTING INFORMATION

Playing with the Weakest Supramolecular Interactions in a 3D Crystalline Hexakis[60]Fullerene Induces Control over Hydrogenation Selectivity

Estefania Fernandez-Bartolome,[a] Arturo Gamonal,[a] José Santos,[a,b] Eider Rodríguez-Sánchez,[a] E. Carolina Sañudo,[c,d] Nazario Martín[a,b*] and José Sánchez Costa[a*]

1) Experimental Section

Materials. Chemicals and reagents were purchased from commercial suppliers and used as received.

Physical measurement

- NMR spectra were recorded on a Bruker Advance 300 (1H: 400 MHz) spectrometer at 298 K using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet.
- FT-IR spectra were recorded as neat samples in the range 400-4000 cm^{-1}on a Bruker Tensor 27 (ATR device) Spectrometer.
- TGA was performed using a TA Instrument TGAQ500 with a ramp of 2 ºC/min under air and nitrogen from 30 to 500 ºC.
- Elemental analysis (C, H and N) was performed on a LECO CHNS-932 Analyzer at the "Servicio Interdepartamental de Investigación (SIdI)" at Autónoma University of Madrid.
- Mass spectra Matrix assisted Laser desorption ionization (coupled to a Time-of-Flight analyzer) experiments (MALDI-TOF) were recorded on a MAT 95 thermo spectrometer and a Bruker REFLEX spectrometer respectively.
- Crystal Structure Determination: The data were collected with an orange block crystal of **2** and **2^{h}** with a MD2M–Maatel diffractometer at the XALOC beamline (BL13) at ALBA Synchrotron with the collaboration of ALBA staff, from a Silicon (111) monochromator (T = 100 K, λ = 0.82656 Å).[21] The crystal was taken directly from its solution, mounted with a drop of Paratone-N oil and immediately put into the cold stream of dry N2 on the goniometer. The structure was solved by direct methods and the refinement on F2 and all further calculations were carried out with the SHELX-TL[22] suite and OLEX2 program.[19]
- Powder X-ray diffractograms were obtained by using a Panalytical X'Pert PRO diffractometer (Cu-Kα1 X-radiation, λ1=1.5406 Å) with parallel-beam collimator, graphite secondary monochromator and Xenon detector. Theta / 2 theta sweep has been carried out from 5º to 90º range with an angular increase of 0.04º. Diffraction patterns were recorded at room temperature.

2) Synthesis of compounds 2 and 2hyd

Compound 2: 10 mg of hexakis adduct fullerene (synthesis described by in the article, Angew. Chemie Int. Ed., 2019,**58**, 2310-2315[16]) were dissolved in EtOH (12 mL) in a pressure tube (diameter 27 mm, height 55 mm). The tube was sealed and kept at 120 °C for 3 days in a furnace. A week after, orange orthoedric crystals suitable for X-ray diffraction analysis, were obtained (**2**) (5.5 mg, 50%).

^{1}H NMR (400 MHz, $(CD_3)_2CO$, δ): 4.33 (t, *J* =6.4 Hz, 24H, OCH_2), 1.68 (m, 24H, CH_2), 1.41 (m, 24H, CH_2), 0.92 (t, *J* = 7.4 Hz, 36H, CH_3) ppm (Figure S8); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 164.1, 145.8, 141.3, 69.3, 66.8, 45.7, 30.5, 19.2, 13.7 ppm (Figure S10). FTIR (neat, cm^{-1}): 2959 (m), 2933 (m), 2873 (m), 1738 (s), 1455 (m), 1433 (w), 1381 (m), 1354 (s), 1260 (s), 1202 (s), 1076 (s), 1014 (m), 966 (m), 963 (m), 925 (m), 844 (m), 814 (m), 759 (m), 730 (m), 713 (s), 699 (m), 657 (m), 621 (w), 540 (m), 527 (s), 432 (m) (Figure S13); elemental analysis calculated (%) for $C_{126}H_{132}O_{24}$: C 75.43, H 5.43; found C 75.22, H 5.49.

Compound 2hyd: Single crystals (about 5 mg) of **2** were put in a screw vial for chromatography (diameter 12 mm, height 32 mm). This tube was then placed in a clear glass vial (diameter 27 mm, height 55 mm) containing a saturated atmosphere of hydrazine monohydrate. The vial was sealed and kept at 67 °C for 7 days in a furnace to allow a gas phase/solid phase reaction between the organic reactant and the crystals. After this time, yellow crystals suitable for X-ray diffraction analysis, were obtained, **2$_{h}$**.

^{1}H NMR (400 MHz, $(CD_3)_2CO$, δ): 4.33 (t, *J* =6.4 Hz, 24H, OCH_2), 4.20 (t, *J* =6.4 Hz, 24H, OCH_2), 3.57 (s, 24H, CH), 1.68 (m, 24H, CH_2), 1.40 (m, 24H, CH_2), 0.92 (t, *J* = 7.4 Hz, 36H, CH_3) ppm (Figure S9). MS. (MALDI MS MS): m/z calc. for [M+1] 2014 and [M+1] 2022, found 2013.7 and 2021.8 m/z (Figure S11).

3) Crystal Data and Structural Refinement of 2 and 2hyd and selected distances of 2hyd

Table S1. Crystal data for compound **2** and **2hyd**

Compound	2	2hyd
CCDC	2049752	2049753
Chemical formula	$C_{126}H_{108}O_{24}$	$C_{126}H_{120}O_{24}$
Formula mass	2006.25	2018.25
Temperature (K)	100(2) K	100(2) K
Crystal system	Triclinic	Triclinic
Space group	P -1	P -1
***a*/Å**	15.460	15.480
***b*/Å**	17.120	17.080
***c*/Å**	20.310	20.480
α/◦	76.74	76.88
β/◦	69.11	69.85
γ/◦	72.20	71.46
***V*(Å^3)**	4737.81	4777.5
Z	2	2
Radiation type	Synchrotron	Synchrotron
c(calculated g/cm^3)	1.406	1.401
Absorption coefficient (mm^{-1})	0.101	0.101
***F*(000)**	2112	2136
Crystal size (mm^3)	0.111x0.109x0.1	0.117x0.12x0.1
Goodness of fit on F^2	1.036	1.613
***R*1, *wR*2 [*I*>2σ(*I*)]**	0.0795, 0.2243	0.1976, 0.4732
***R*1, *wR*2 (all data)**	0.0765, 0.2197	0.1385, 0.4191

Table S2. Selected bond lengths [Å] for compound **2**.

Selected bond lengths [Å]		Selected bond lengths [Å]	
C52A(H52B)-(H55C)C55A	3.793	**H55C-H55B**	2.341
C40B(H40D)-(H46C)C56B	4.070	**H40D-H46C**	2.359
C44B(H47B)-(H49D)C51B	3.465	**H47B-H49D**	1.946
C44B(H44D)-(H51C)C51B	3.971	**H44D-H51G**	2.374
C56B(H56D)-(H58A)C58A	3.919	**H56D-H58A**	2.296
C54B(H54C)-(H54C)C54B	3.859	**H54-H54C**	2.303

4) Asymmetric unit and arms conformations and principal interactions of 2

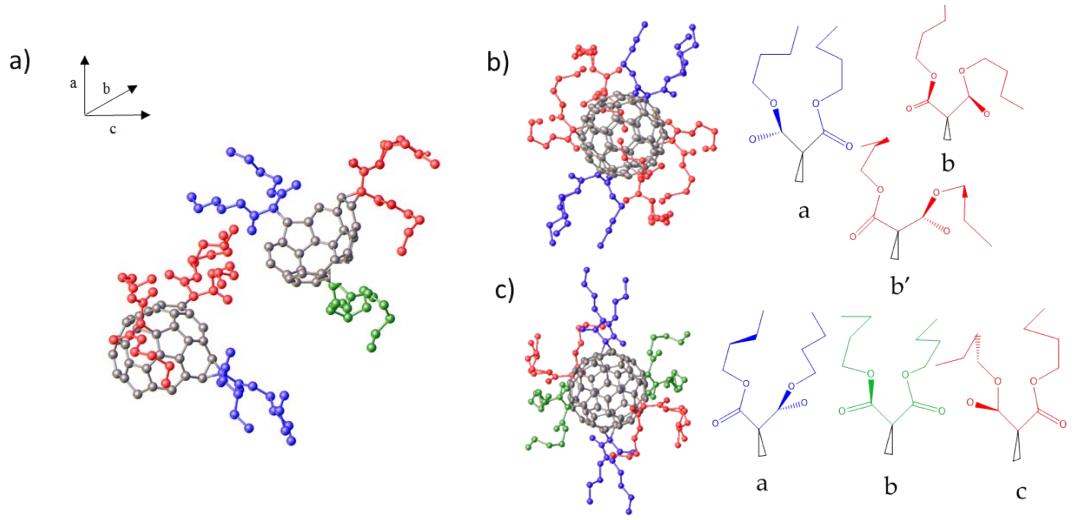

Figure S1. **a)** Asymmetric unit of **2**. **b)** Fullerene place on the vertex of the unit cell and a, b, arms conformation. **c)** Fullerene placed inside the unit cell and) a, b and c arms conformation.

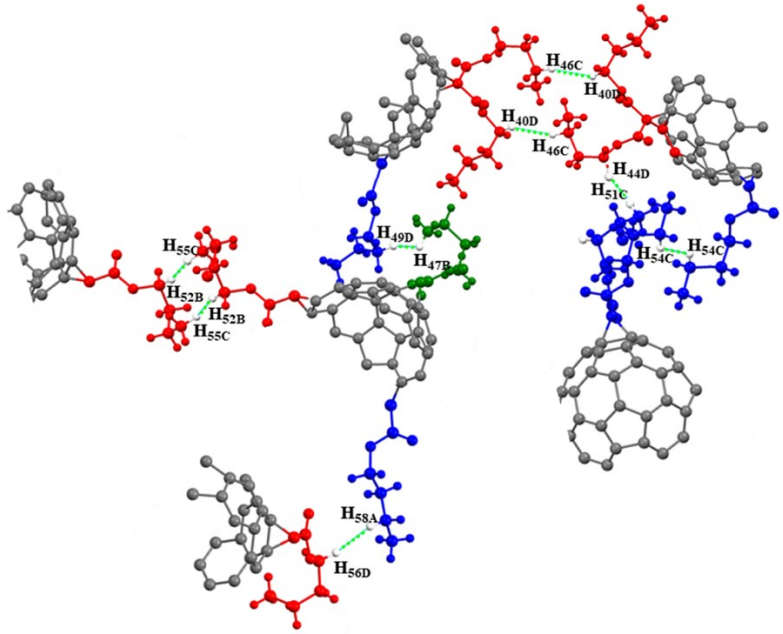

Figure S2. A depiction of the Van der Waals connections of the diverse malonate group with its close neighbors in **2**.

5) Thermogravimetric analysis of compound 2 and 2hyd

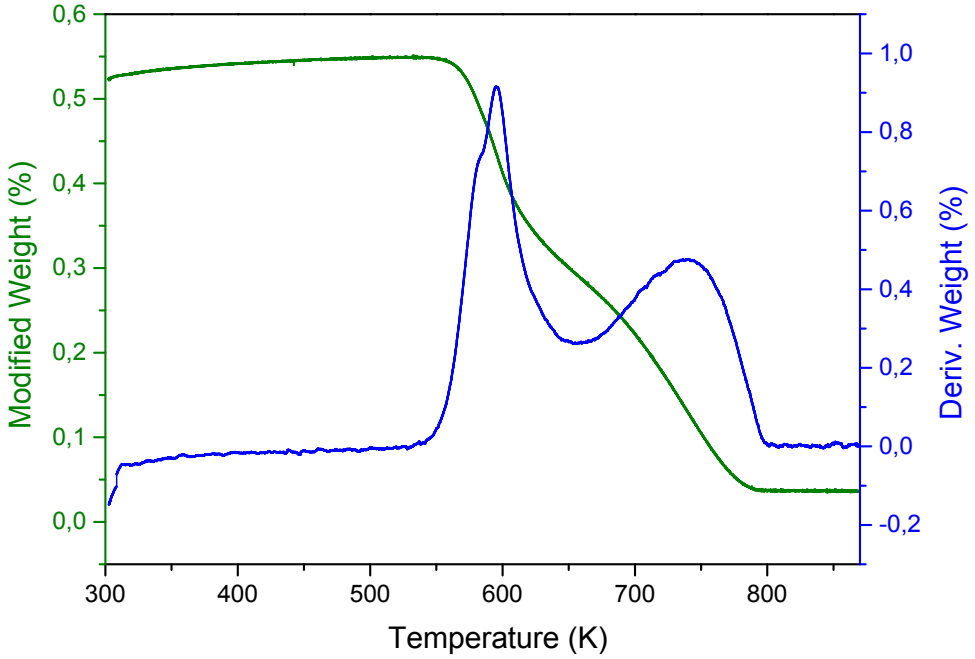

Figure S3. Thermogravimetric profile of **2** (0.5270 mg in air) showing the mass variation (green curve) and its first derivative (blue curve) upon heating at 2 °C/min rate.

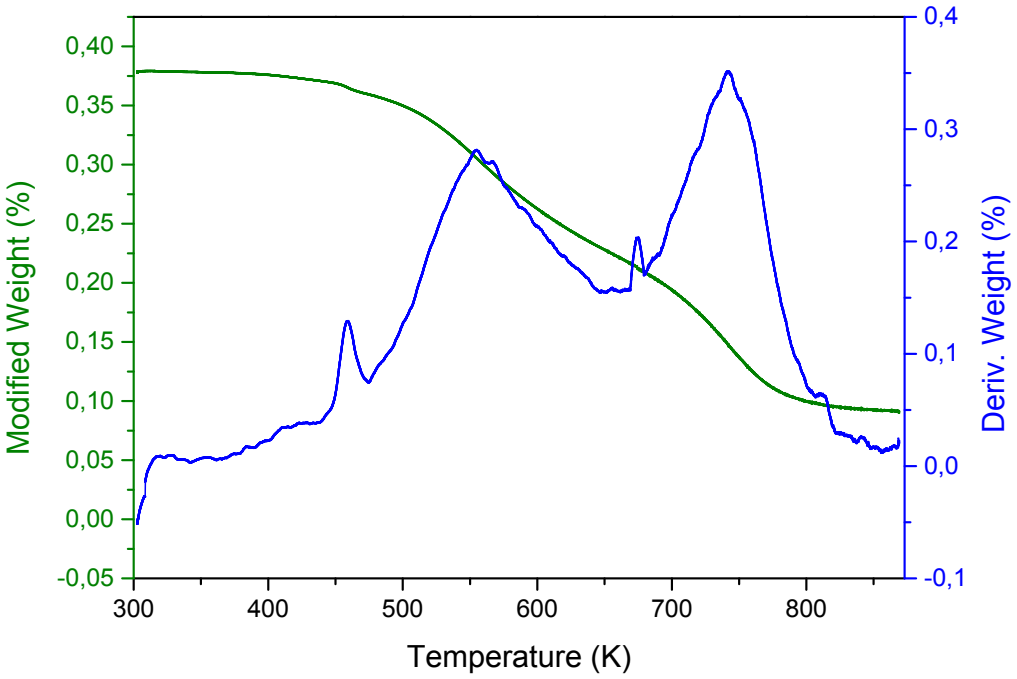

Figure S4. Thermogravimetric profile of **2hyd** (0.31359 mg in air) showing the mass variation (green curve) and its first derivative (blue curve) upon heating at 2 °C/min rate.

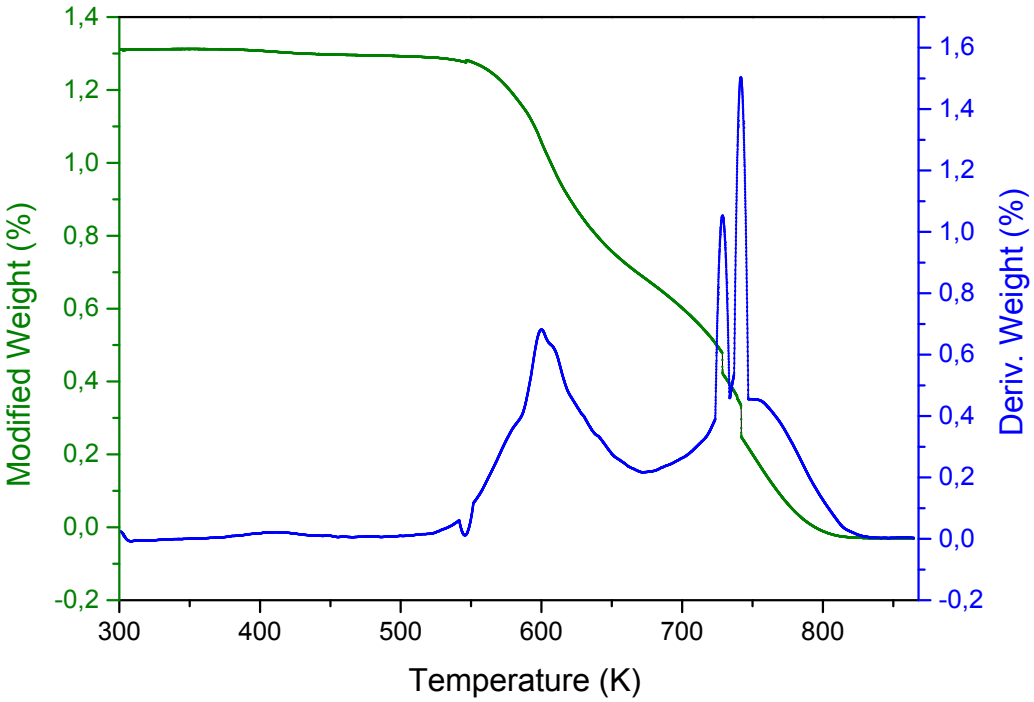

Figure S5. Thermogravimetric profile of **3** (1.3130 mg in air) showing the mass variation (green curve) and its first derivative (blue curve) upon heating at 2 °C/min rate.

6) DSC measurement of 3 and Optical reflectivity measurement of 2 and 3

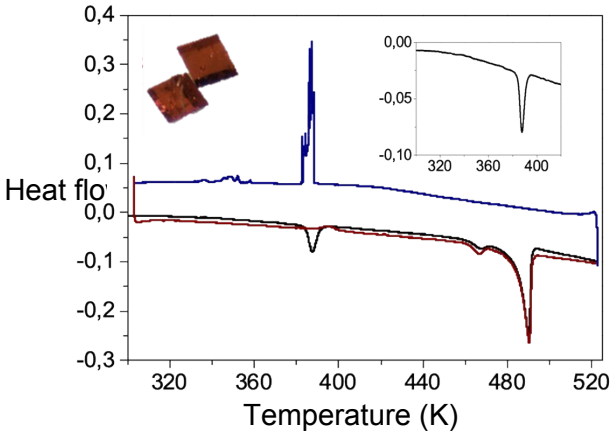

Figure S6. DSC curves as a function of temperature of **3** for three consecutive heating and cooling ramps.

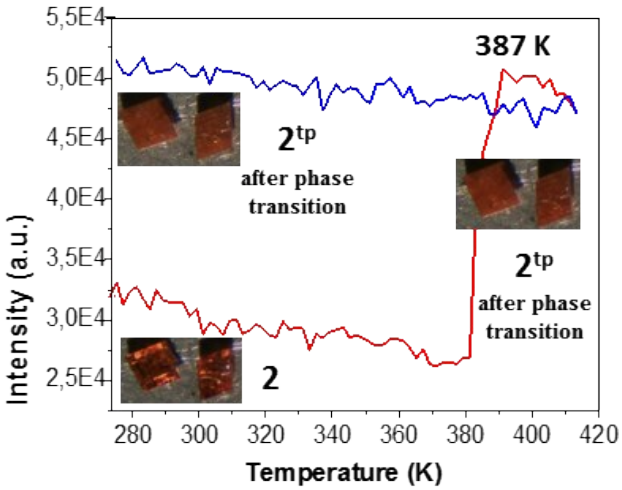

Figure S7. Optical reflectivity as a function of temperature showing the amplification of an endothermic peak at 387 K and images in the first heating ramp of **2.**

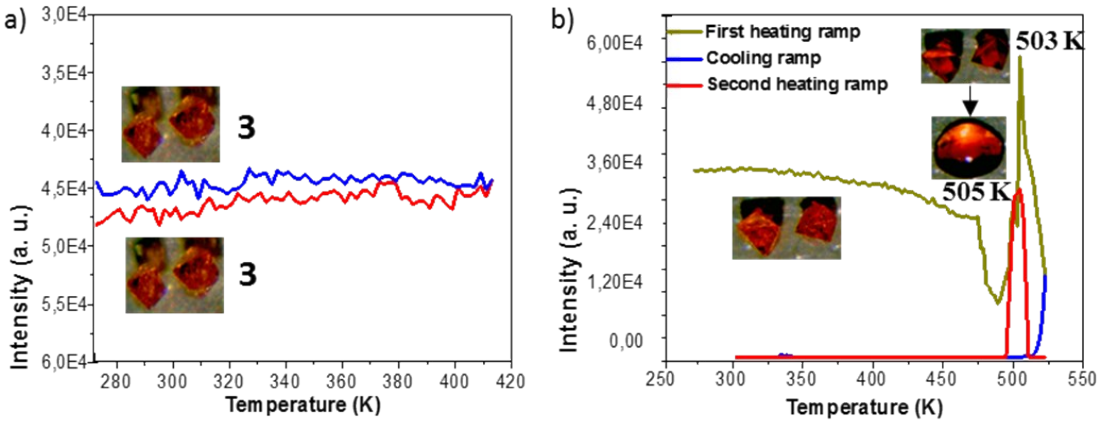

Figure **S8**. **a)** Optical reflectivity of **3** showing a non-detectable phase transition in the first heating ramp. **b)** Optical reflectivity as a function of temperature measures of **3** of three consecutive heating and cooling ramps.

7) ^{1}H NMR spectra of 2 and 2hyd

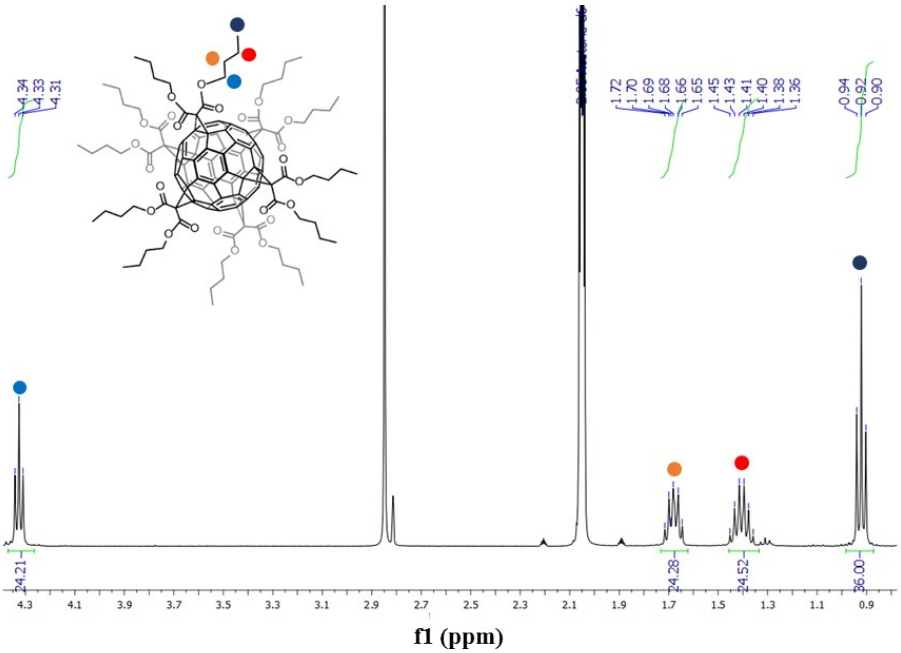

Figure S9. ^{1}H NMR spectrum (400 MHz, $(CD_3)_2CO$) of **2**

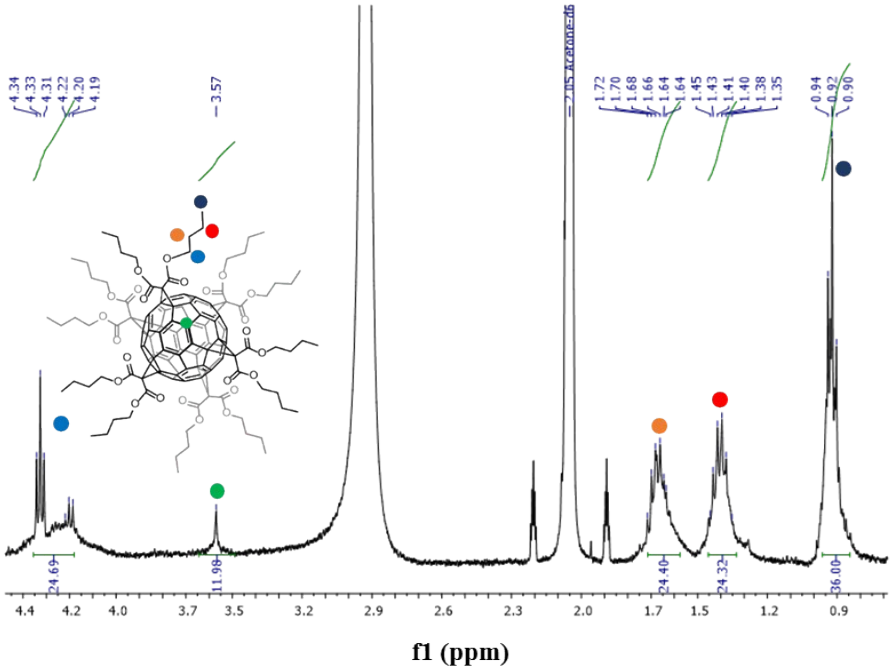

Figure S10. ^{1}H NMR spectrum (400 MHz, $(CD_3)_2CO$) of **2hyd**.

8) ^{13}C NMR spectrum of 2

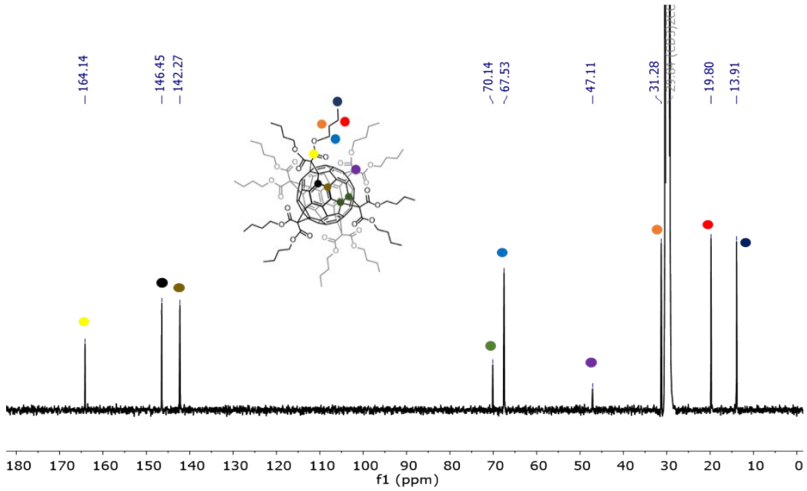

Figure S11. ^{13}C NMR spectrum (100 MHz, $(CD_3)_2CO$) of **2**.

9) Mass Spectrometry of compound 2hyd

In the interesting region of the spectrum, we may observe 5 signals corresponding to: starting material (M=2005.63) and products corresponding to successive hydrogenations, i.e. 2009.65 (M+4H), 2013.66 (M+8H), 2017.68 (M+12H), and 2021.71 (M+16H). These values agree with those found via crystallography 2013.66 (M+8H) and 2021.71 (M+16H) and with (-4) smalless fraction corresponding 2009.65 (M+4H) 2017.68 (M+12H). The latest are -4 in mass indicate that an intermediate is formed, which can be expected in a SCSC reaction. Importantly, the resolution of the spectrometer employed is ±0.1 Da, although exploring the second decimal helps shedding light on the origin of the peaks. In the case of the above-mentioned peaks, an increase in the second decimal is observed, which is characteristic to the addition of hydrogen (+1.008 Da). On the other hand, all peaks above 2021.71 do not follow this trend and are consistent with the oxidation of the hydrogenated compounds, e.g. 2037.71 (2021.71+O), 2053.71(2021.71+2O). These oxygenated compounds are usually observed in fullerene and its derivatives after their exposure to air.

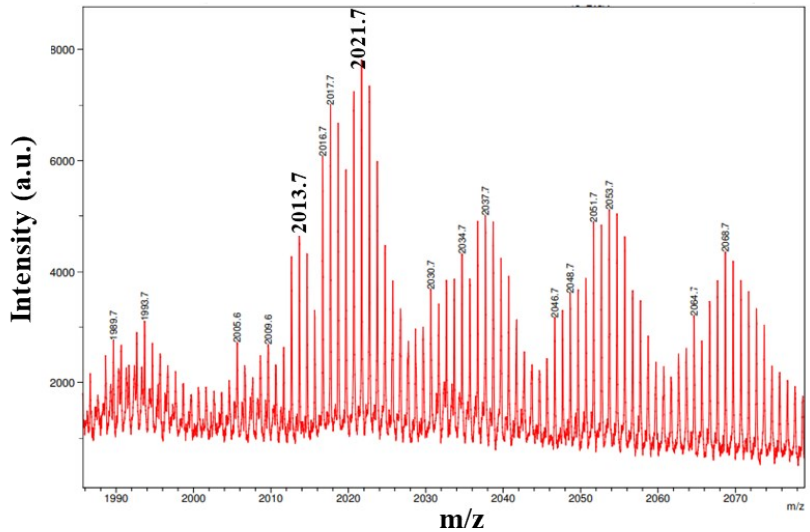

Figure S12. Mass Spectrometry of compound **2h**yd. Two detected peaks at **2013.7** and **2021.8 m/z** that correspond to [**3b** + 8 protons] and [**3b** + 16 protons], respectively.

10) Different views before and after hydrogenation of compounds 2 and 2hyd

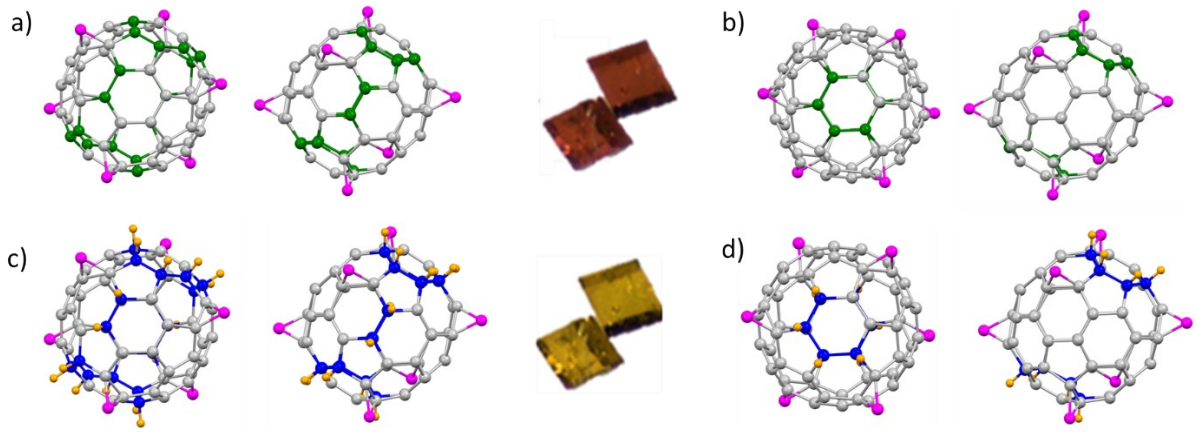

Figure S13. Different views before (**2**) **a)** and **b)** and after hydrogenation (**2hyd**) c) and d)

11) Infrared Spectra 2, 2hyd and 3

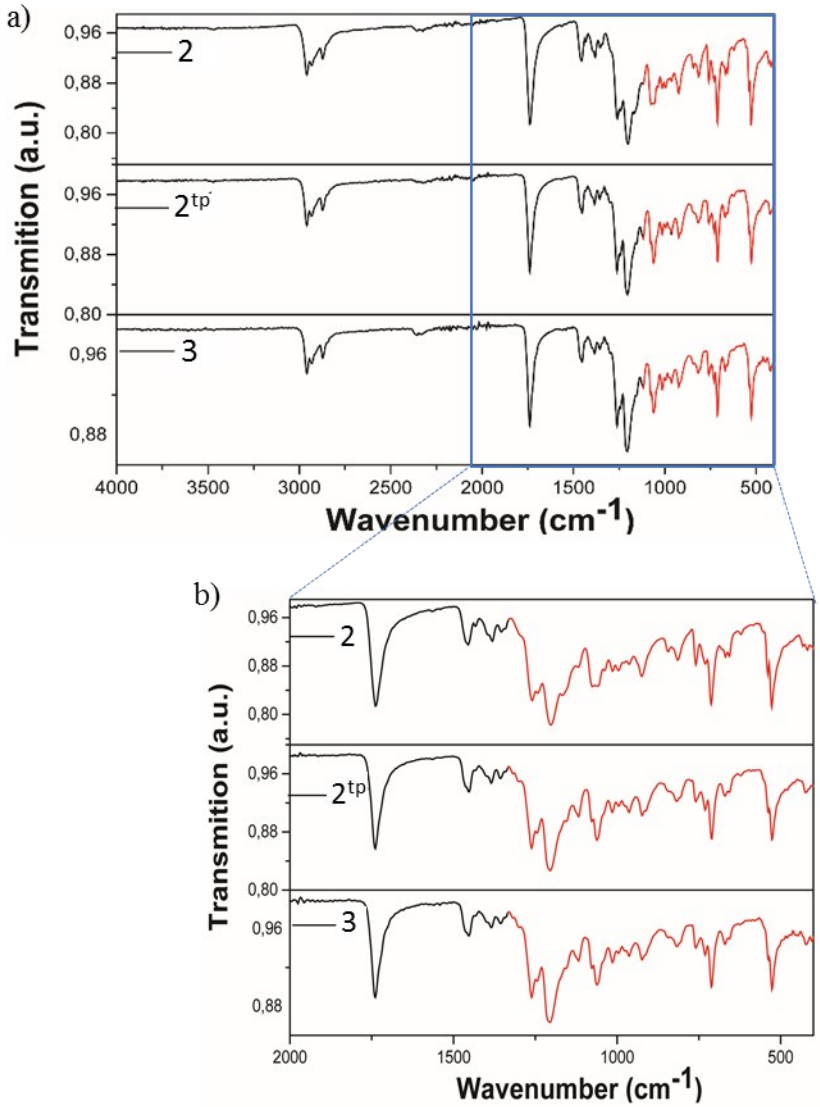

Figure S14. **a)** Infrared spectra of compound **2** before and after the heating of crystals at 114 °C (387 K) and compound **3**. **b)** Amplification of the IR spectrum between 2000 and 400 cm^{-1} to show the main shifts of the bands.

12) References

20. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **42**, 339–341 (2009).

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