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Journal

Angewandte Chemie International Edition, 58(8)

ISSN

1433-7851

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Publication Date

2019-02-18

DOI

10.1002/anie.201812419

Peer reviewed

A Three-dimensional Dynamic Supramolecular “Sticky Fingers” Organic Framework

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Abstract: *Engineering high recognition host-guest materials is a burgeoning area in basic and applied research. The challenge of exploring novel porous materials with advanced functionalities, prompted us to develop dynamic crystalline structures promoted by soft interactions. Herein, we demonstrate the first example of a pure molecular dynamic crystalline framework held together by means of weak “sticky fingers” van der Waals interactions. The presented organic fullerene-based material exhibits a non-porous dynamic crystalline structure capable of undergoing single-crystal to single-crystal reactions. Exposure to hydrazine vapors induce structural and chemical changes that evince the toposelective hydrogenation of alternating rings on the surface of the [60]fullerene. Control experiments confirm that the same reaction does not occur when performed in solution. This easily to detect change in the macroscopic properties paves the way for the real application of these materials.*

One of the important challenges in chemical science nowadays is the search for greener processes for a cleaner world.^[1] In chemistry, this usually translates into highly selective reactions with high rates and efficiencies. Even with the cutting-edge technological tools available today, which enable us to get a precise course of action of the reactions, there is still an immense work to be done in order to drive these reactions towards the desired product.^[2] Recently, novel synthetic strategies have been proposed that diverge from classical approaches. While the latter are usually based on the temperature, pressure and exact formulation control, reactivity control of the former is aimed through exploring novel environmental strategies, e.g. the successful surface chemistry approach,^[3] chemical topology^[4] or to perform chemical reactions in confined spaces,^[5] in which the reactivity differs in many aspects from those conducted in bulk solution. In that sense, the irruption of “porous materials” connected by intermolecular bonds such as Metal-Organic Frameworks^[6] (MOFs) and Covalent Organic Frameworks^[7] (COFs), or “porous molecular materials”^[8], that are built from discrete molecules^[9], such “porous organic cages”^[10], has provided meritorious results. The discovery and development of these materials has highlighted the interest of performing chemical reactions inside confined spaces to determine how this can influence the yield and the reactivity pathway in the reaction.^[11] Furthermore, MOFs show a key concept – compared to rigid zeolites and less processable COFs – which is flexibility.^[12] This flexibility could generate novel dynamic adsorption properties under realistic conditions, similar to the liquid protein reactions that occur for specific interactions

between enzymatic host and the substrate. Pure organic systems usually show excellent properties as high thermal stabilities, tunable structure-properties and biocompatibility, but have also drawbacks such as the mentioned rigidity and a limited processability. Therefore, the formation of dynamic structures (porous or non-porous acting as porous) by means of supramolecular interactions between molecules might be an interesting alternative. However, the crystallization of stable organic structures possessing porosity or showing the ability to incorporate molecules by internal structural reorganization (breathing effect) is still a real challenge, with few examples reported using hydrogen bonding^[8,13-29] or π - π -stacking^[19,20,24,30-35] as driving force.

In this manuscript, we report for the first time how a flexible non-porous organic molecule connected *via* supramolecular van der Waals interactions, usually called *sticky fingers*,^[36,37] behaves as an excellent dynamic molecular receptor. Furthermore, the inclusion of small molecules inside the materials will allow an unprecedented hydrogenation reaction that occurs only in a confined crystalline space and not in the traditional wet chemistry. The reaction is performed in a single-crystal to single-crystal (SCSC) fashion, letting us to study at the atomic detail how this material behaves upon the inclusion of these small molecules.^[38]

To study this process we have used one of the most versatile organic molecules, namely the [60]fullerene. These highly functionalized [60]fullerene cycloadducts are very appealing scaffolds for the construction of 3D crystalline materials due to the directionality of their malonate substituents.^[16,39-41] The hexakis-adduct has been synthesized by applying the well-known Bingel-Hirsch synthetic strategy^[42,43] (see Scheme 1a). The synthesis is carried out by the addition of the previously obtained bromomalonate (**2**) to a solution of C₆₀ in chlorobenzene, employing DBU as chemical base. This straightforward and reproducible protocol affords compound **3** in good yield (45%). Upon purification, the resulting hexaadduct is characterized by the usual analytical and spectroscopic techniques (see SI for further details). Crystallization of **3** from ethanol is achieved using the pressure tube technique as described in the SI. This method affords big regular orange crystals which are suitable for X-ray diffraction data collection (see SI for full synthetic details).

Compound **3** crystallized in the cubic space group Fd-3. The unit cell is composed of eight symmetry equivalent hexaadducts placed in four unequal layers. Importantly, in contrast to the major packing driving force of pristine [60]fullerene,^[44] in **3** there is no evidence of any supramolecular π - π contact between neighboring fullerene buckyballs (see Fig. 1g and Table S2). For **3**, the shortest separation between two adjacent fullerenes placed in different layers is of 5.168 Å, utterly out of the supramolecular π - π interaction range.^[45,46] Furthermore, the separation between a given fullerene and the next one located on the exact same position along the same axis is very long, 26.879 Å, being separated by five layers of fullerene, at different heights in the perpendicular axis and precluding any possible π - π interaction. Altogether, it is considered that the packing force must be driven by another kind of non-covalent interaction.

From the single crystal X-ray diffraction structure of **3** we can observe that six butyl-malonate groups are clearly distorted. Precisely, each -COOR group is placed over three positions giving rise to four different butyl branches (two of the branches coming from the same C₆₀-COOR group), for a total of 48 different positions over the whole packing. The illustration 1e-g gives an idea of how intricate the hexakis-fullerene network is, showing the interdigitated arrangement of the interacting butyl chains. Figure 1d-f, depicts one of these interactions, as well as a network view of the packing created by the hexaadducts through this interaction. The different occupancy factors and the contacts between carbons for this interaction and for the whole intricate network are detailed in the SI. Thus, the main information stemming from this crystallographic study is that these branches create a densely packed 3D structure maintained by van der Waals contacts established between the alkyl chains of neighboring hexakis[60]fullerenes.

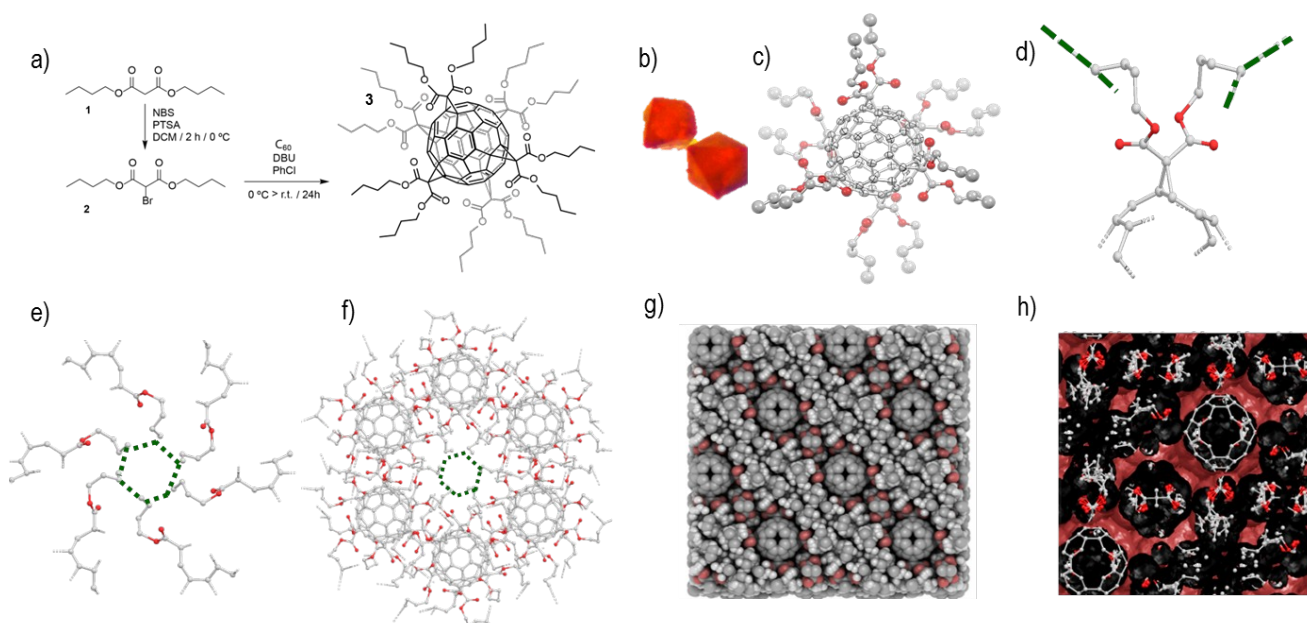


Figure 1. a) Scheme of the reaction sequence for the synthesis of **3**; b) orange-reddish single crystals of **3**; c) ORTEP illustration of a single hexakis-adduct of [60]fullerene including the malonates groups (only one branch of the distorted malonates is illustrated for clarity); d) Van der Waals connections of a single malonate group with its close neighbours (the bond direction is plotted as a deep green dashed line); e) expansion of the connection network illustrated in d with [60]fullerene units omitted for clarity ; f) the same six interacting malonate groups illustrated in e accompanied by their corresponding C₆₀ buckyballs; g) iRASP^[47] view of the packing and h) surface occupancy calculated with OLEX2 highlighting in red color the potential cavities surrounding the [60]fullerene.

Interestingly, a close look at the crystallographic data confirms that the densely packed 3D structure of fullerene-based **3** shows small cavities that are mainly surrounding the buckyball (Fig. 1h, in red color). Despite the presence of small cavities within the structure of the material, the closely packed aliphatic butyl chains prevent volatile molecules from diffusing through the crystal network, as evidenced from the BET close to zero value (see next section for further details).

To test the absorption of small molecules and the potential subsequent physical changes, single crystals of **3** were exposed to a number of organic and inorganic volatiles. Interestingly, exposure to hydrazine vapors led to an outstanding color change after 3 days at 67 °C. Observed changes involve the bright red crystals fading away into pale-yellow (Fig. 2a). The resulting material, obtained by a SCSC reaction, namely **4**, preserved a structure closely related to **3**, agreeing with the $C_{126}H_{132}O_{24}$ formulation that contains 24 hydrogen atoms more than **3** ($C_{126}H_{108}O_{24}$).

The new material is stable under atmospheric conditions and highly soluble in common organic solvents such as CH_2Cl_2 , CH_3Cl , and acetone. To our delight, the **4** could be determined both by single crystal and crystalline powder X-ray diffraction

Figure 2. **a)** Scheme of the SCSC reaction for the synthesis of **4**, including a picture of the crystal after and before exposure to hydrazine vapors; **b)** MERCURY illustration of the hydrogenated hexaadduct [60]fullerene, including the hydrogen atoms incorporated to the C_{60} and the malonates functional groups (only one branch of the distorted malonates is illustrated for clarity); **c)** view of the C_{60} hydrogenated fullerene with the added hydrogen atoms highlighted in black; **d)** Van der Waals connection of a single malonate group with its close neighbours; **e)** expansion of the connection network including the C_{60} buckyballs; **f)** iRASP view of **4**

studies. **4** retains the same space group as its precursor, although the value of the *a* axis diminishes from 26.878(1) to 26.156(3) Å (Table S1). From the X-ray crystal structure of **4**, it is concluded that half of the [60]fullerene's six-membered rings in **3** have been hydrogenated after the exposure of the crystals to the hydrazine vapors (see Fig. 2a and 2d, hydrogen atoms are denoted in black color).

Remarkably, under these reaction conditions, just half of the accessible six-membered rings result hydrogenated. More interestingly, the partial hydrogenation of **3** always takes place preserving the symmetry of the molecule, which is also evinced by the extremely simple ^{13}C NMR pattern (Fig. 3). This result has been reproduced several times, always obtaining the same hydrogenation pattern. As a result of the partial hydrogenation, the fullerene cage experiences a strong

distortion, arising from the sp^2 to sp^3 hybridization change of the hydrogenated six-membered rings. The XRD data show an increase of their C–C bonding distances, along with a decrease of the hybridization angle of the involved carbon atoms (see Fig. 2b-d and S18). Like its parent molecule (**3**), the hydrogenated hexakis-adduct (**4**) crystals show a non-porous nature (Fig. 2f).

Characterization of **3** and **4** was carried out by the standard spectroscopic techniques and was greatly facilitated by their high symmetry. The ^1H NMR spectra of **3** and **4** are shown in Figure 3 and described in detail in SI. Thus, ^1H NMR spectrum of **3** displays four signals at 4.33, 1.68, 1.41 and 0.92 ppm which are consistent with twelve butyl malonates. The hydrogenation of **3** is clearly evidenced in its ^1H NMR spectrum by the emergence of two nearly isochronous signals at 3.58 ppm, integrating for 24 protons. This is consistent with the total hydrogenation of four of the eight six-membered rings of **3**. Jointly with a $^{135}\text{DEPT}$ experiment, the C–H correlations found by a HSQC experiment allow identifying these new H signals as belonging to methyne carbon atoms from the fullerene's surface. Due to the environment changes induced upon hydrogenation, the $-\text{COOCH}_2-$ methylenes experience an up-field shift from 4.33 to 4.20 ppm. Furthermore, this signal also shows signs of splitting, probably arising from some methylenes lying over a hydrogenated ring, some over an unsaturated one.

Like precursor **3**, the ^{13}C NMR of **4** shows a fine and simple pattern derived from the high symmetry it possesses. Due to this symmetry, all the sp^2 carbons belonging to the fullerene cage show up as two signals at 144.0 and 134.3 ppm (significantly shielded compared to parent **3**, at 145.8 and 141.3 ppm, respectively). The signals of the hydrogenated sp^3 carbons show up as two peaks at 39.8 and 35.5 ppm (correlating with the protons at 3.58 ppm). Further MS experiments confirm the presence of the molecular peak of **4** (Fig. S16). The thermogravimetric analysis provides an insight into the thermal stability of hydrogenated compound **4**, which is stable up to 150 °C when it starts decomposing. In contrast, non-saturated **3** exhibits high stability, decomposing just over 275 °C (Fig. S13). This stability loss is attributed to the increased strain supported by the fullerene cage upon conversion of 24 sp^2 carbon atoms into sp^3 . This is dramatically observed in the XRD crystal structure, where the cage seems rather bulgy than spherical. The use of molecular hydrogen in the presence of a metal catalyst is the most recognized method for the hydrogenation of alkenes.^[48]

Despite its widespread use, catalytic hydrogenation requires exceptional security measures for handling molecular hydrogen and the use of rather expensive catalysts. An alternative option is represented by hydrazine. Nevertheless, hydrogenation of olefins employing hydrazine requires its decomposition over some metals to yield hydrogen or its oxidation to diimide^[49] in order to yield a reactive species capable of reducing the olefin.

The latter procedure involves the rather unstable diimide intermediate which is

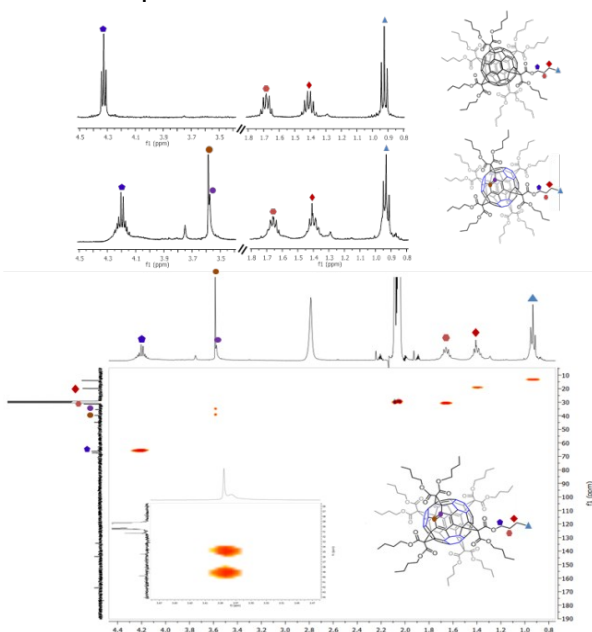


Figure 3. ^1H NMR spectra of compounds **3** (a) and **4** (b). HSQC NMR spectrum of compound **4** (c) and the amplified HSQC NMR spectrum (inset) of the novel hydrogen signals (3.58 ppm). The resonances of each spectrum have been assigned to key atoms under discussion with symbols and colors.

extremely short-lived in solution. To rationalize the stabilization of the diimide species, generated *in situ* from the oxidation of hydrazine, within the network of **3**, we understand that it must be achieved by its confinement inside the pockets surrounding the fullerene moieties, where concerted hydrogen transfer from *cis*-diimide to half of the fullerene's remaining cyclohexatriene rings takes place. Attempts to duplicate this result in solution resulted either in no evolution of the reaction or led to a complex mixture of by-products, none of them consistent with the chromatographic R_f of **4** (Figure S4).

The work herein presented describes the first reported van der Waals crystalline structure of a [60]fullerene hexakis-adduct. These non-covalent (dispersion stabilization) interactions, also known as *sticky fingers*, are established between the non-polar

butyl chains linked to the malonate functionalities. The large number of butyl branches shown in the XRD experiments is explicit of a dynamic interaction between interdigitating aliphatic chains. The resulting material shows small cavities by the surface of the fullerene, although, the overall structure is non-porous. Despite this apparent non-porosity, the dynamic nature of the *sticky fingers* interaction allows for the diffusion of volatiles to the cavities. Interestingly, hydrazine molecules allocated inside these pockets trigger the toposelective hydrogenation of half of the remaining cyclohexatriene rings of the hexaadduct in a SCSC reaction accompanied by a color change in the visible. We believe that further design of new suitably functionalized hexaadducts will allow obtaining materials with customizable pockets ready for capturing different volatiles and gases. Therefore, the new and groundbreaking strategy described in this manuscript on topochemical solid-state reactions involving fullerenes will contribute to the creation of novel carbon-based advanced absorbent materials with a variety of direct technological applications.

Experimental Section

Experimental Details. Preparation of dibutyl 2-bromomalonate (**2**), [60]fullerene hexakis-adduct (**3**) and hydrogenated fullerene (**4**) are described in the Supplemental Information. Furthermore, the SI includes details of the X-ray

diffraction and the NMR employed in this work. **Crystal Structure Determination:** The data of **3** were collected with an orange block crystal with a Bruker APEX II CCD diffractometer at the Advanced Light Source beamline 11.3.1 at Lawrence Berkeley National Laboratory from a silicon (111) monochromator ($T = 100$, K, $\lambda = 0.7749$ Å). The data of **4** were collected with a yellow block crystal with a MD2M-Maatel diffractometer at the XALOC beamline (BL13) at ALBA Synchrotron with the collaboration of XALOC-ALBA staff, from a Silicon (111) monochromator. X-ray crystallographic data for **3** and **4** have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under deposition number CCDC 1870483-1870484.

Acknowledgments

JSC is grateful to the Spanish MINECO for financial support through National Research Project (CTQ2016-80635-P) and the Ramon y Cajal Research program (RYC-2014-16866) for funding support. IMDEA Nanociencia acknowledges support from the 'Severo Ochoa' Programme for Centres of Excellence in R&D (MINECO, Grant SEV-2016-0686). This research used resources of the Advanced Light Source, which is a DOE Office of Science User Facility under contract no. DE-AC02-05CH11231. NML acknowledges support from the European Research Council (ERC-320441-Chirallcarbon), JS and NM thank the MINECO of Spain (project CTQ2014-52045-R) and the CAM (FOTOCARBON project S2013/MIT-2841). We would like to thank to XALOC-ALBA synchrotron source under the project no. (2018012561).

Keywords: Supramolecular Chemistry • Fullerene • Single-crystal-to-single-crystal reaction • topological chemistry

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