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**Non-aromatic carbonaceous species formed in the circumstellar  
environments of evolved stars**

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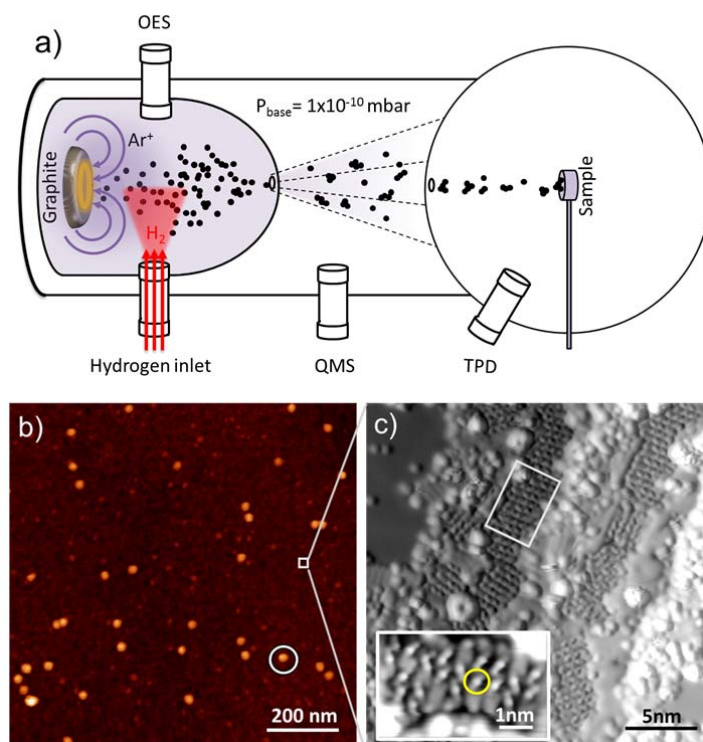
Stars, like our Sun, in their final stages of evolution reach the asymptotic giant branch (AGB) accompanied by a massive ejection of matter containing the vast chemical complexity that provides the building blocks of planets and life<sup>1,2</sup>. From observations of prototype carbon-rich AGBs a large number of organic species<sup>3-5</sup> have been discovered that are some of the basic ingredients of cosmic dust in the circumstellar envelope (CSE). However, the chemical nature of cosmic carbon and its role in the formation of small molecules is still controversial. Polycyclic aromatic hydrocarbons (PAHs) are widespread in regions of massive star formation, identified by the emission of aromatic infrared bands (AIBs)<sup>6</sup>, but a robust explanation of how they form is still lacking, especially in evolved AGB stars where AIBs are only detected at late stages when the star emits ultraviolet (UV) radiation<sup>7</sup>. Laboratory-based experiments are indispensable to elucidate the nature of cosmic dust<sup>8-12</sup>, but most rely on uncontrolled combustion or decomposition of molecular precursors under conditions very unlike those in evolved star photospheres. In this letter, using an unprecedented experimental setup<sup>13</sup> we investigate the basic chemistry operating in CSE to produce clusters and dust using exclusively gas-phase C atoms and molecular hydrogen. We show that gas-phase aggregation of C atoms in a molecular hydrogen atmosphere leads to the highly efficient formation of carbon nanoparticles, carbon clusters and aliphatic C, with no evidence for aromatics, which can be formed by additional processing of aliphatics on C-dust grains.

Our experimental set-up, *Stardust*<sup>13</sup> presents several advantages, in particular its versatility for the design of experiments that combine highly controlled UHV technology with *in-situ* characterization techniques, the latter being mandatory because of the high reactivity expected of the formed carbon nanostructures to atmospheric and residual gases<sup>14</sup>. A simplified block diagram of *Stardust* is shown in Fig. 1a and a technical description is given in Supplementary Information 1 and Supplementary Fig. 1. The working principle is the vaporization of C atoms from a graphite target with a sputter gas aggregation source, using Ar as the sputtering gas. This step is followed by injection of the most abundant gas species in AGB environments, H<sub>2</sub>. The vaporized C atoms react with H<sub>2</sub> and are subsequently dragged through a nozzle by differential pressure into the next chambers where they are collected on inert Au surfaces for further analysis. Once the carbonaceous cosmic-dust analogue passes the nozzle of the first chamber, no further growth takes place. The composition of the small, gas-phase species is analysed by mass spectrometry (MS) before sample collection at position QMS in fig. 1a. Finally, the deposit is characterized *in situ* in a third chamber by Thermal Programmed Desorption (TPD).

Unlike previous experiments, our approach starts with atoms to produce nanoparticles, C-clusters and hydrocarbons, without the requirement for C-bearing molecular precursors, as is expected to occur in the atmospheres of AGB stars. The initial gas-phase vaporized C atoms may interact with residual or injected molecular hydrogen at different densities, and there are no other species involved except Ar. The vaporized C atoms have a density of about  $2.5 \times 10^{10}$  atoms·cm<sup>-3</sup>. Albeit some orders of magnitude higher than that estimated for the dust nucleation zone of stars<sup>15</sup>, it provides an effective method to accelerate the chemistry, which takes years in a real AGB envelope. Regarding the hydrogen, two cases are considered: low and high densities. In the first case, H<sub>2</sub> molecules are in the same proportion as C atoms, which can be achieved either using residual hydrogen or by introducing very low H<sub>2</sub> densities that are

estimated in the range of  $1.5 \times 10^{10} \text{ mol} \cdot \text{cm}^{-3}$ ; a value typically accepted for the dust nucleation zone at distances from the star of around  $10^{14} \text{ cm}^{15}$ . In the second case, a high  $\text{H}_2$  density is achieved by introducing extra hydrogen at a concentration estimated at  $1.5 \times 10^{12} \text{ mol} \cdot \text{cm}^{-3}$ , two orders of magnitude higher than that of vaporized C atoms. This situation provides a more appropriate simulation of the chemistry in CSE in terms of  $\text{H}_2/\text{C}$  abundance ( $\sim 3000^{16}$ ).

Fig. 1b shows a typical Atomic Force Microscope (AFM) image obtained of the C-dust collected on a  $\text{SiO}_x$  surface at position QMS, where two different morphological features can be identified. Firstly, C-nanograins (encircled in white in Fig. 1b) are efficiently produced as the most abundant constituents, with a surface density that increases with deposition time. These spherical grains exhibit an extremely narrow size distribution with an average size of 9 nm, corresponding to  $> 10^5$  C atoms. Although larger grains (typically 100 nm) are thought to be present in space, in *Stardust* the nanoparticle size is conditioned by geometry and experimental parameters and can be considered to represent the initial stages of carbonaceous dust formation and growth.



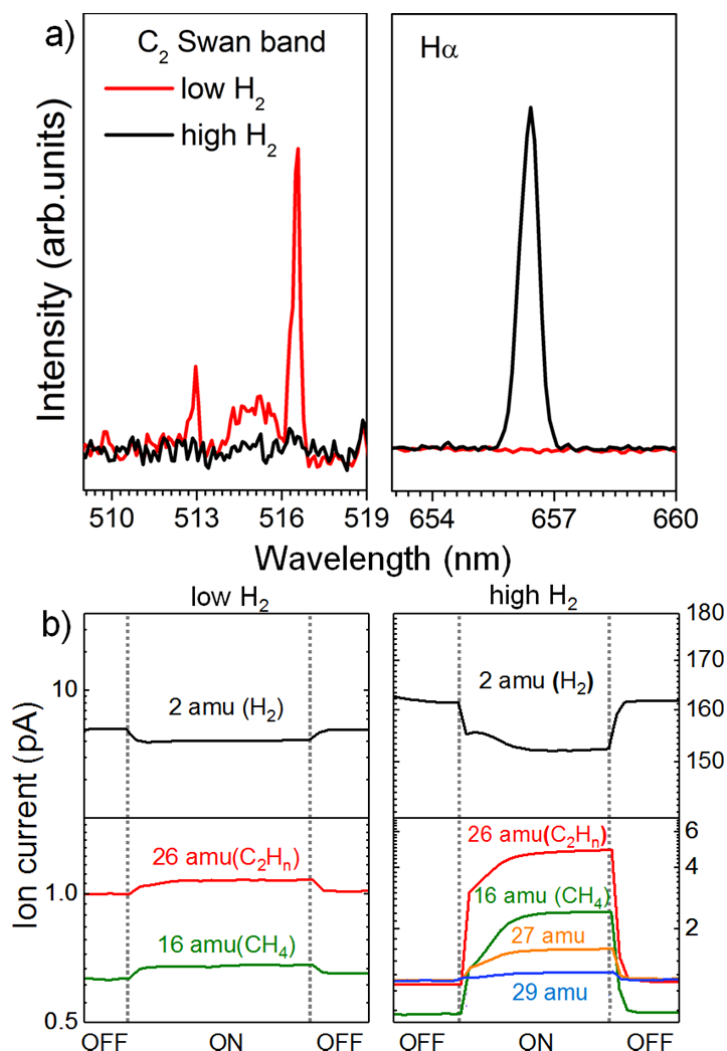
**Fig. 1 | Production and structure of cosmic dust analogues.** **a**, Schematic of the main components of the *Stardust* machine: aggregation zone (violet), expansion area where the quadrupole mass spectrometer (QMS) is installed, and analysis area, where thermal programmed desorption (TPD) is located. **b**, AFM image showing the presence of C-nanoparticles and small clusters forming a continuous layer. A single nanoparticle is encircled. **c**, STM image of a C-cluster film deposited on a metal surface. Scanned area:  $25 \times 25 \text{ nm}^2$ , recorded at 50 pA, 1400 mV. Inset: Zoom of the rectangular area  $5 \times 3 \text{ nm}^2$ ,  $I = 10 \text{ pA}$ ,  $V = 1400 \text{ mV}$ . A small molecule is encircled.

95 The other principal constituent of the C-dust analogues can be located on the flat regions of  
96 Fig. 1b, where a thin mantle of material is observed, for instance in the area marked by a white  
97 square (see Supplementary Figure 2). Structural resolution of these zones cannot be achieved  
98 using standard AFM, and more powerful *in situ* microscopies are required. Fig. 1c shows a  
99 scanning tunnelling microscope (STM) image obtained from the C analogues deposited on a Au  
100 surface. This image shows that the material is made up of a collection of individual structures  
101 no larger than 1 nm in width and with a maximum apparent height of 1 nm. The small size of  
102 these structures, such as that encircled in the inset of Fig. 1c, suggests that they correspond to  
103 individual molecules that typically comprise 3 – 5 C atoms. Some of these small molecules can  
104 self-assemble on the surface forming 2D islands, such as the region marked within a rectangle,  
105 magnified in the inset and in Supplementary Figure 3. This is a surface-mediated process  
106 suggesting electrostatic interactions between the molecules upon absorption on surfaces.

107 To further understand the nature of these carbon analogues we used gas-phase analysis  
108 techniques. Optical emission spectra (OES) were recorded at the OES position indicated in Fig.  
109 1a. The Swan C<sub>2</sub> lines are observed in Fig. 2a in the presence of low H<sub>2</sub> density, but are not  
110 found in the case of higher H<sub>2</sub> density. On the contrary, the H<sub>α</sub> emission line is only observed at  
111 high H<sub>2</sub> density. These observations suggest that excited H atoms are generated during the  
112 chemical evolution, involving  $C_2 + H_2 \rightarrow CCH + H$ . The absence of the C<sub>2</sub> lines at high H<sub>2</sub> density  
113 indicates that most of the excited C<sub>2</sub> formed is consumed in this reaction. Interestingly, C<sub>2</sub> and  
114 H species are only detected in the regions close to the magnetron, which compares very well  
115 to observations from the photosphere of evolved stars where some H has been found and C<sub>2</sub>  
116 bands are prominent<sup>17</sup>.

117 Fig. 2b presents the evolution of the masses of some relevant species during the experiment  
118 recorded at position QMS of Fig. 1a. For low H<sub>2</sub> concentration, a peak at 26 amu mainly  
119 corresponding to C<sub>2</sub>H<sub>2</sub> was detected along with fragments of C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and larger aliphatic  
120 molecules. A peak at 16 amu is also observed, corresponding to methane. In the case of high  
121 H<sub>2</sub> densities we also detect an increase in the main ionization fragments of ethane (C<sub>2</sub>H<sub>6</sub>),  
122 ethylene (C<sub>2</sub>H<sub>4</sub>), propane (C<sub>3</sub>H<sub>8</sub>) and larger alkanes. Importantly, here these species were  
123 formed directly from C atoms and molecular hydrogen, without introducing them as  
124 precursors, using ratios and aggregation processes similar to those reported to take place in  
125 CSE<sup>16,18</sup>. Fig. 2b shows a decrease in the partial pressure of H<sub>2</sub> when C evaporation is initiated,  
126 suggesting that H<sub>2</sub> is partially consumed by chemical reactions that occur in the aggregation  
127 zone. It is important to remark that neither benzene (C<sub>6</sub>H<sub>6</sub>) nor toluene (C<sub>7</sub>H<sub>8</sub>) are detected in  
128 in the MS measurements (Supplementary Figure 4).

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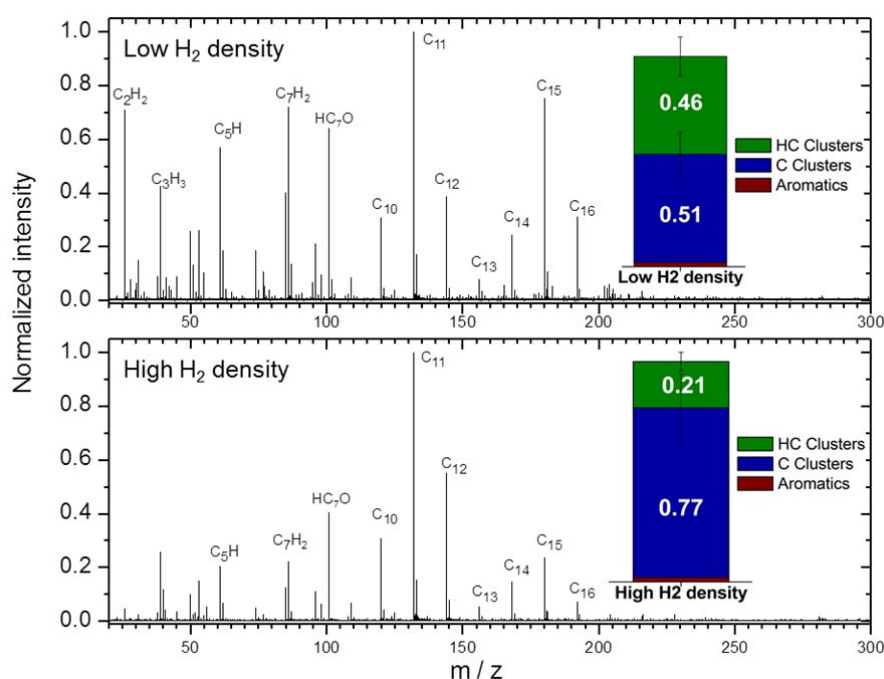


**Fig. 2 | Gas phase characterization.** **a**, Optical emission spectra recorded at position OES in Fig. 1a for low and high H<sub>2</sub> densities. **b**, *In situ* gas-phase detection at position QMS of masses 2, 16, 26, 27 and 29 (amu) for low and high H<sub>2</sub> densities. Dashed lines indicate the time period where the magnetron was switched on and off.

Additionally, we have used *ex situ* laser desorption ionization (LDI) mass-spectrometry in the so-called set-up *AROMA*<sup>19</sup>, a machine with high sensitivity for PAH detection. Fig. 3 provides the ion distribution obtained by desorption/ionization of representative samples grown with both H<sub>2</sub> densities, showing that the molecular species generated have < 20 carbon atoms. Above 300 amu the signal completely vanishes, showing that no traces of fullerenes could be detected (see Supplementary Figure 5). Pure carbon clusters are observed from C<sub>8</sub><sup>+</sup> to C<sub>19</sub><sup>+</sup>, and above C<sub>9</sub><sup>+</sup> these are poorly hydrogenated, which can be understood by the formation of close-cage structures with reduced dimensionality and, thus, lower reactivity<sup>20</sup>. We have found no evidence of formation of C<sub>60</sub>. C-clusters with a low degree of hydrogenation are observed for species containing 4 to 9 C atoms, which are discussed in Supplementary 5.

146 The results from LDI-MS (see Supplementary Fig. 5) are summarized in Fig.3 with double bond  
 147 equivalent (DBE) bar-graphs where the species generated are classified in families. The analysis  
 148 suggests a higher abundance of HC clusters when low H<sub>2</sub> density is used, suggesting the  
 149 presence of the more saturated aliphatic species at high H<sub>2</sub> density, not found by LDI-MS but  
 150 evidenced by QMS (Fig. 2). Masses corresponding to benzene or toluene, as key aromatic  
 151 species, are not (or only very marginally) detected, neither in the LDI-MS analysis (Fig. 3) or the  
 152 QMS measurements (see Supplementary Fig. 4). A few larger aromatic species, up to C<sub>16</sub>H<sub>10</sub>,  
 153 are detected to a maximum of 3% for both H<sub>2</sub> densities. Therefore, it appears that the  
 154 chemistry involved in the CSE does not favour the formation of PAHs, whose abundance can  
 155 reach up to 18% of the total carbon species in the ISM<sup>21</sup>.

156



157

158 **Fig. 3 | Ex situ laser desorption/ionization (LDI) mass-spectrometry** from samples grown with a low  
 159 (upper panel) and high (lower panel) H<sub>2</sub> densities. Insets: Stacked bar graphs summarizing the family  
 160 compositions by double bond equivalent (DBE) analysis. The error bars correspond to the relative  
 161 standard deviation obtained for the total ion signal over a mass range for each family of compounds.

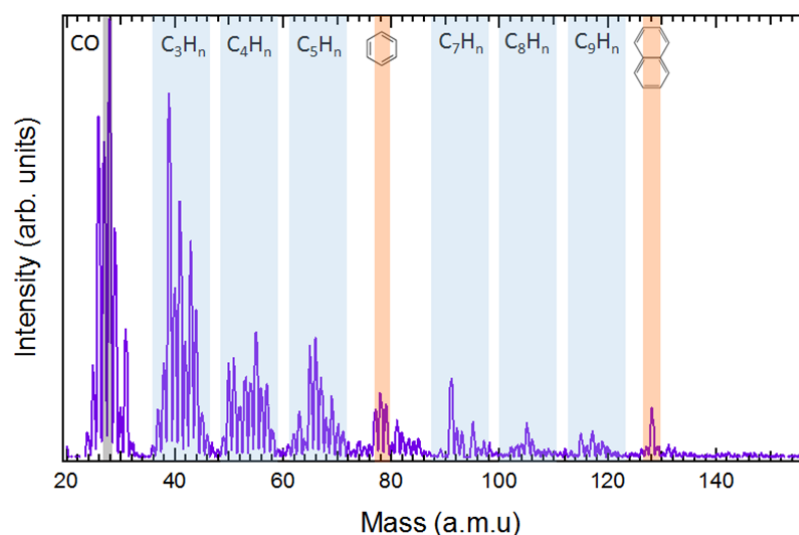
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163 Consequently, considering the MS results in Fig. 2b and Fig. 3, we can outline several aspects  
 164 of the chemistry involved. Time-dependent chemical kinetics models (see Supplementary 6) to  
 165 compute the evolution of the chemical composition of the gas mixture in *Stardust* show,  
 166 assuming that most of the carbon from the magnetron is atomic, that the following three-body  
 167 reactions initiate the chemistry: C+C+Ar and C+H<sub>2</sub>+Ar leading to C<sub>2</sub> and CH<sub>2</sub> species,  
 168 respectively. The kinetic simulations provide clear routes to the formation, via neutral  
 169 reactions, of the molecular species detected in Fig. 2b (CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>),

170 provided that the reacting species persist for sufficient time in the magnetron zone. This  
171 condition can be fulfilled in this type of magnetron where material has been reported to  
172 remain trapped<sup>22</sup> (see Supplementary for further discussion).

173 Fig. 4 shows a representative MS single scan at 430K from an *in situ* TPD experiment (see  
174 complete graph in Supplementary Figure 7). Albeit a precise assignment of masses is difficult  
175 to perform, families of  $C_nH_m$  hydrocarbons can be identified. The most abundant masses of 26  
176 amu, 39 amu and 41 amu, all belong to known fragments of larger aliphatic hydrocarbons<sup>23</sup>.  
177 Interestingly, in our experiment benzene and naphthalene were observed after annealing the  
178 deposited carbon above 355K. These aromatic species are most likely formed after a catalytic  
179 recombination of small hydrocarbons on the gold surface, a process reported in surface  
180 chemistry<sup>24,25</sup>, since they were not observed in the LDI-MS analysis which is highly sensitive to  
181 aromatics. The fact that aromatics could be formed after annealing of carbonaceous aliphatics  
182 deposited on a C-rich surface needs to be further explored as a possible mechanism for the  
183 formation of these species in warm CSE environments. Indeed, AIBs, the signature for PAHs,  
184 are not convincingly detected in AGBs but are observed at later stages when the star emits  
185 ultraviolet (UV) radiation and process the Carbon-dust<sup>7</sup>.

186



187

188 **Fig. 4 | Representative scan from a TPD experiment** on C-analogues formed with high  $H_2$  density on a  
189 Au surface.

190

191 The combination of laboratory astrochemistry, surface science and astronomical observations  
192 can unveil the chemical routes that operate in the envelope of evolved stars, providing new  
193 insights into the chemistry of carbonaceous stardust formation. There are several models to  
194 account for the presence of aromatic species in CSE; one involves the polymerization of  
195 acetylene to benzene<sup>5</sup> and further growth by the hydrogen abstraction acetylene addition  
196 (HACA) mechanism<sup>26,27</sup>. Other scenarios involve the processing of SiC dust grains<sup>28</sup> or the  
197 catalytic activity of  $C_2H_2$  on silicate surfaces<sup>29</sup>. Our results suggest that PAHs are not efficiently

198 formed during gas-phase growth in CSE, which we show to generate aliphatic material and C-  
199 clusters together with amorphous carbon grains. However, the species that are deposited on  
200 dust grains are susceptible to further processing and can auto-catalyse to form aromatic  
201 species upon thermal activation, which could be provided as a result of the significant rise in  
202 dust temperature that occurs in highly UV-irradiated environments.

203

## 204 **Methods**

205 **Fabrication of the dust analogues.** The carbon dust analogues were fabricated using a scaled-  
206 up MICS working under UHV conditions (base pressure  $1 \times 10^{-9}$  mbar). The magnetrons were  
207 loaded with a graphite target of 99.95% purity. The Ar flux used for the experiments was 150  
208 sccm. The typical power applied to the magnetron was 100 W and the working aggregation  
209 length (distance between the magnetron and the exit nozzle) was 374 mm.

210 Extra-pure  $H_2$  (99.99% purity) was injected during fabrication through one of the lateral  
211 entrances of the aggregation zone of the MICS (see Supplementary Figure 1). The doses used  
212 for these experiments were: 0,  $4 \times 10^{-4}$  and 1 sccm, with an Ar flux maintained at 150 sccm. The  
213 substrates employed for collecting the NPs are boron-doped Si(100) with its native oxide for  
214 AFM; polycrystalline Au for AROMA experiments; Au(111) for TPD analysis.

215 **Atomic Force Microscopy (AFM)** measurements were performed in the dynamic mode using a  
216 Cervantes AFM System equipped with the *Dulcinea* electronics from Nanotec Electronica S.L.  
217 All images were analyzed using WSxM software<sup>30</sup>.

218 **Scanning tunneling microscopy (STM).** Samples for scanning tunnelling microscopy (STM)  
219 were prepared in *Stardust* and transferred without exposing the samples to the atmosphere to  
220 the STM chamber, located in a different laboratory, using a UHV suitcase with an ion-getter  
221 pump (base pressure  $< 1 \times 10^{-9}$  mbar) to avoid chemical reaction with environmental gases<sup>14</sup>.  
222 Samples are deposited on an atomically flat single crystal Au(111) surface pre-cleaned by  
223 repeated sputtering/annealing cycles, which consisted of sputtering for 10 min using  $Ar^+$  ions  
224 at an energy of 1.25 kV and subsequent annealing at 800 K for 5 min. Clean Au(111) is later  
225 exposed to the carbon analogues for 5 minutes keeping the sample at room temperature, then  
226 immediately transferred to the UHV suitcase and to the STM chamber. The total time between  
227 sample growth and insertion in the STM cryostat was limited only by the pumping of the load  
228 lock volume. STM measurements were performed at 4K in a LT-STM (Scienta Omicron) with a  
229 base pressure  $< 10^{-11}$  mbar.

230 **Optical emission spectroscopy (OES).** The light emitted by the plasma generated in front of  
231 the magnetron was collected through a fused silica window and an optical fibre of fused silica,  
232 and analysed by OES (see position in Fig. 1a) using a 193 mm focal length, motorized Czerny-  
233 Turner spectrograph (Andor, model Shamrock SR-193-i-A) equipped with a CCD camera (iDus  
234 DU420A-BVF). Two diffraction gratings with 1200 grooves/mm and 1800 grooves/mm,  
235 installed in a movable turret, provide spectral ranges of 300-1200 nm and 200-950 nm,  
236 respectively, and nominal spectral resolutions of 0.22 nm and 0.15 nm, respectively (for an  
237 input slit width of 20  $\mu m$ ). The relative spectral efficiencies of the all the spectroscopic  
238 equipment was quantified for both diffraction gratings with a calibrated tungsten lamp.

239 **In situ mass spectrometry (MS).** The gaseous species produced during the fabrication of the C-  
240 dust analogues were detected *in situ* with a quadrupole mass spectrometer (QMS) (0-100  
241 amu).

242 **Laser desorption/ionization (LDI) mass-spectrometry: the AROMA machine.** AROMA  
243 (Aromatic Research of Organics with Molecular Analyzer) is dedicated to the analysis, with

micron-scale resolution, of the carbonaceous molecular content of cosmic dust analogues. The experimental setup consists of a microprobe laser desorption ionization chamber and a segmented linear quadrupole ion trap connected to an orthogonal time of flight mass spectrometer (LQIT-oTOF). For each detected  $m/z$  peak with a signal-to-noise ratio (S/N) greater than 10, a chemical formula was assigned using the mMass software<sup>31</sup>, an open source mass spectrometry tool. The double bond equivalent (DBE) for each molecular formula was then calculated using the following equation for a given chemical formula of hydrocarbon species  $C_cH_h$ :  $DBE = c - (h/2) + 1$ . This method allows sorting of the detected ions into families of compounds<sup>32</sup>. This is done using empirical factors that delineate DBE boundaries in complex natural organic matter<sup>33</sup>. Hydrocarbons with  $0.5 < DBE/C < 0.9$  are considered to be aromatics. The line  $DBE/C \sim 1$  corresponds to C clusters and the species falling in the zone  $0.9 \leq DBE/C < 1$  are referred to as HC clusters, which includes  $C_nH_2$  polyynes. Once all the detected species were sorted, the ion signal percentage was calculated for each family by dividing the sum of peak intensities detected in each family by the total ion intensity.

**Thermal Programmed Desorption (TPD).** Experiments were performed *in-situ* to determine the mass spectra of the carbon analogues deposited on low reactivity surfaces annealed at increasing temperatures. TPD was performed using a Pfeiffer HiQuad QMG 700 with QMA 400 mass spectrometer with a CP 400 ion counter preamplifier. The instrumentation permits measurement of masses between 0 and 512 amu with a detection limit of  $10^{-15}$  mbar. After carbon analogue deposition the samples were placed in front of the quadrupole at a short distance ( $>1$  cm) ensuring that the majority of the collected gas species derive from the surface of the sample surface. Atomically flat Au(111) and HOPG substrates were used in the experiments, yielding comparable TPD spectra, which precludes significant on-surface chemistry during the annealing process. Au(111) surfaces were cleaned *in-situ* by the standard methodology of sputtering/annealing. HOPG was mechanically cleaved *ex-situ* and consecutively introduced into the vacuum system, which ensures an atomically fresh graphite surface prior to deposition. The carbon analogues were deposited during 100 minutes. This amount of carbon material ensures there is enough to obtain well-defined signals in the TPD experiments. A temperature ramp of  $12.5^\circ\text{C}\cdot\text{min}^{-1}$  was applied from room temperature to the maximum temperature examined ( $400^\circ\text{C}$ ).

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283 **Author contributions.** *In-situ* experiments in *Stardust* were performed by L.M, G.S, P.M, and  
284 M.A.; C.J. and H.S. performed LDI experiments. P.M.; K.L, R.O and A.M performed STM images.  
285 L.M. performed AFM images. R.J.P, V.J.H. and I.T. performed the OES experiments. M.A. made  
286 the kinetic calculations. G.J.E. and J.A.M-G wrote the first version of the manuscript. J.A.M-G  
287 supervised *in-situ* experiments, and C.J. and J.C the astrochemical interpretation. All authors  
288 discussed and contributed to the final version of the manuscript.

289 **Competing interests.** The authors declare no competing interests.

290 **Additional information.** Additional text, figures and references are provided.

291

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