SUPLEMENTARY INFORMATION

Formation of a Surface Covalent Organic Framework based on Polyester Condensation

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1. Materials and Methods

THF was purchased from Aldrich and dried and purified by distillation under argon atmosphere. Triethylamine (minimum 99%), acetone, 4-(dimethylamino)pyridine, 1,3,5-tris(4-hydroxiphenyl)benzene and 1,3,5-benzenetricarbonyl trichloride were purchased from Aldrich and used without further purification.

Infrared spectra were recorded on a JASCO FT/IR-410 spectrometer in the range 3500-800 cm^{-1} and measured on a pellet of a mixture of the product and KBr. Spectra in the range 1500-2000 cm^{-1} are shown in Figure SI.1.

The morphology and microstructure of the prepared material were analyzed by Scanning Electron Microscopy (SEM). Powder sample was deposited on a glass substrate, coated with a thin gold conductive layer, and then measured in a JEOL JM6400 instrument equipped with microprobe of 40 kV and a microanalysis system XEDS (X-Ray Energy Diffraction Spectroscopy) model Oxford link Pentafet.

The thermogravimetric analyses were performed in a TGA TA INSTRUMENTS Q-500 analyzer. The temperature program was from 25 to 1000 ºC, with a temperature rate of 5ºC.min^{-1} under a nitrogen flow.

Elemental analyses were performed by the Microanalysis Service of the Universidad Autónoma de Madrid on a Perkin-Elemer 240 B microanalyzer.

2. Synthesis and characterization of bulk layered polyester 1.

To a mixture of 1,3,5-tris(4-hydroxyphenyl)benzene (0.050 g, 0.14 mmol), benzene-1,3,5-tricarbonyl trichloride (0.040 g, 0.14 mmol) and triethylamine (43 µL, 0.31 mmol) in 20 mL of dry THF was added 4-(dimethylamino)pyridine (DMAP) in catalytic quantity (0.034 g, 20 % mmol). The reaction was stirred during 24 h at 60 ºC under inert argon atmosphere. The resulting solution was filtered and washed with distilled water. Then, the solid was stirred in distilled water (5 mL) for 15 minutes, and thereafter in warm acetone (5 mL). Then the solid was filtered, washed three times with 10 mL of acetone and dried under vacuum for 15 h at 60 ºC. The product was isolated as a white solid (0.045 mg) without further purification.

Experimental elemental analysis for $[(C_{33}O_6H_{18})_{30}(HCl)_{65}(H_2O)_{30}]$ Found (Calcd.) %C: 65.0 (65.2) %; H: 3.73 (3.68) %.

According to the calculated formula, water molecules represent 3 % of the total mass, which can correspond to the loss of mass at T < 200 ºC observed in the ThermoGravimetric Analysis (TGA, see Figure SI.2). Following the same formulation, HCl molecules represent the 13% of the total weight, which can correspond to the loss of mass at T < 450ºC. This is usually explained as a consequence of absorption phenomena and has been reported in related COFs. In fact, elemental and thermogravimetric analysis together are consistent with a porous structure that can absorb small molecules such as H_2O and HCl, which are released at high temperatures.

The chemical identity of the product was confirmed by infrared spectroscopy (Figure SI.1), showing a C=O stretch frequency at 1742 cm^{-1}, which is, as expected for a polyester, in between the frequencies corresponding to the parent acid (1719 cm^{-1}) and the acyl chloride (1754 cm^{-1}).

Unfortunately, no diffraction pattern was observed by powder X-ray measurements indicating that a high density of defects decreases the crystallinity of the material obtained. Despite the lack of X-ray data, SEM measurements are fully consistent with a laminar structure (Figure SI.3).

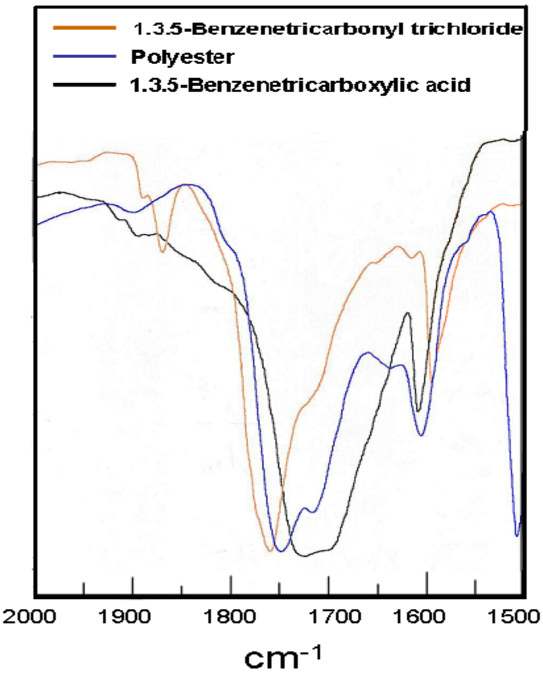

Figure SI.1 FT-Infrared spectrum in the region corresponding to C=O st. of a bulk sample of polyester **1** compared with the signal corresponding to parent acid and parent acyl chloride. The peaks at 1754 cm^{-1}, 1742 cm^{-1} and 1719 cm^{-1} correspond to benzene-1,3,5-tricarbonyl trichloride, Polyester and benzene-1,3,5-tricarboxylic acid, respectively.

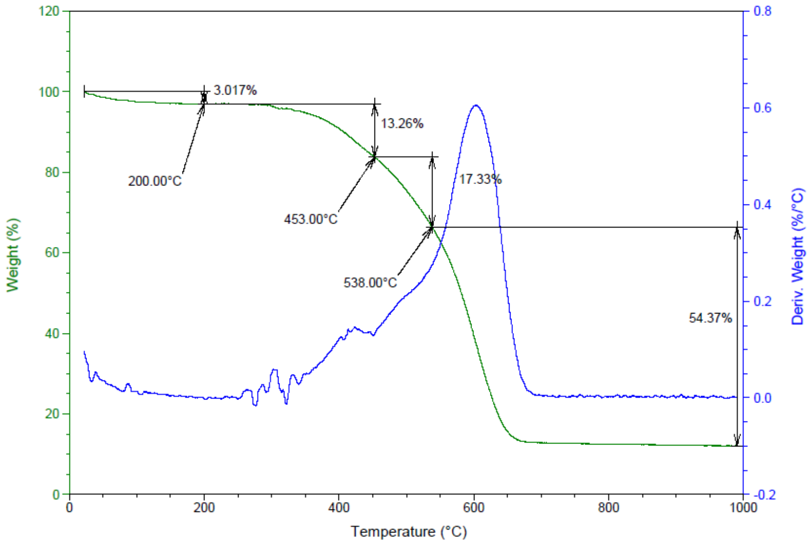

Figure SI.2 Thermogravimetric analysis of the layered polyester bulk material (**1**).

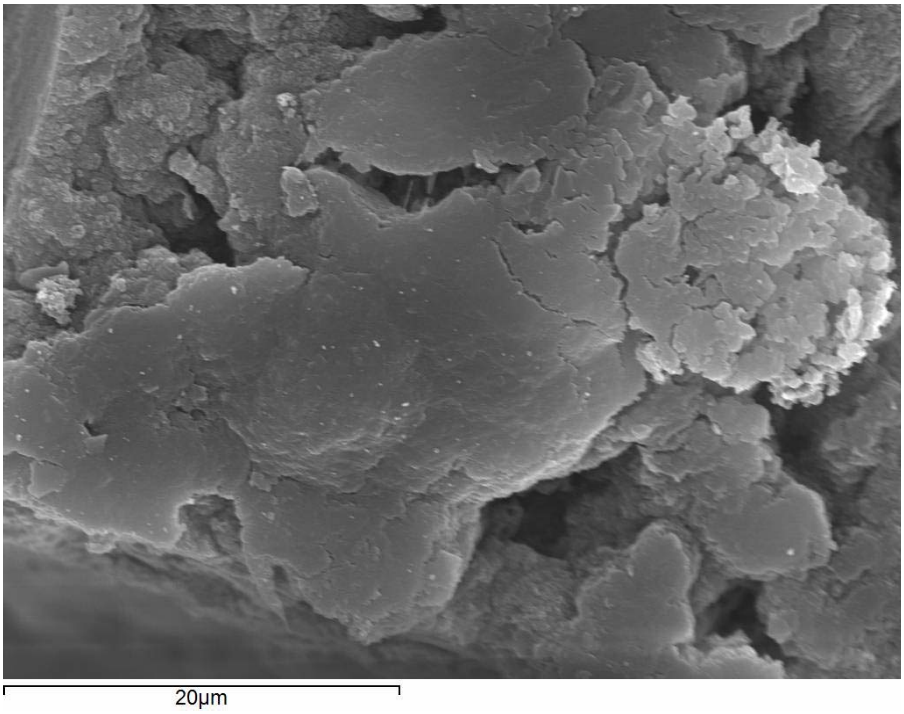

Figure SI.3 SEM image taken from a bulk sample of layered polyester **1** showing its layered nature.

3. Experimental UHV-STM setup

The experiments were carried out in an ultrahigh-vacuum (UHV) system whose base pressure is below $5x10^{-11}$ Torr. The system is equipped with a variable temperature scanning tunneling microscope (VT-STM)[S1], low energy electron diffraction (LEED), Auger electron spectroscopy (AES), sample and STM tip transfer and heating capabilities, an STM tip cleaning system by field emission, several interchangeable evaporation cells, a quartz crystal microbalance, an ion gun for sample cleaning purposes, and a quadrupole mass spectrometer for deposition control.

Au(111) surfaces were prepared by successive cycles of sputtering with Ar+ ions (600 eV beam energy; ion current of 1.5-2 μA) and annealing at 900 K until the herringbone (22x√3) reconstruction, characteristic of clean Au(111), was observed in STM images.

1,3,5-tris(4-hydroxiphenyl)benzene (TPB) was first outgassed in UHV and then sublimated from a home-made evaporator (containing a tantalum crucible) on Au(111) at room temperature. The evaporator crucible was heated at about 420 K to obtain a deposition rate of approximately 0.02 monolayers per minute.

Benzene-1,3,5-tricarbonyl trichloride (TMC) was kept in a glass container that was connected to the preparation chamber by a variable-leak valve. The storage vessel can be pumped separately by the turbo pump to outgas the impurities. During the evaporation process, the deposition rate was controlled by the quadrupole mass spectrometer (observed fragments: m/z = 75, m/z = 166, HCl: m/z = 36). TMC was dosed into the preparation chamber until a given partial pressure was achieved.

Ordered SCOFs were typically obtained by depositing close to 0.5 monolayer TPB at room temperature, followed by reaction with TMC, while keeping the sample surface at 575K for 10 min under a partial TMC pressure of $2x10^{-9}$ Torr.

During the adjustment of the deposition rates of both molecules the Au (111) sample was held in the STM chamber separated from the main chamber by a gate valve.

4. STM measurements

The STM experiments were performed with a home-built variable temperature instrument [S1]. This VT-STM, connected to a continuous flow liquid helium UHV cryostat, allows imaging at sample temperatures in the range of 40K to 400K. STM data were acquired with a fully automated workstation that incorporates digital feedback control based on DSP (digital signal processor) technology [S2]. All the surface manipulation experiments, data acquisition, and image processing were performed using the WSxM software [S3]. STM images were acquired in constant-current mode at low temperature (105-120 K) using W tips.

5. Thermal stability of SCOF on Au(111)

The thermal stability of the polymer SCOF formed on the Au(111) surface was tested by annealing for 5 min periods at high temperature and subsequent imaging by STM at room temperature. No degradation was observed for temperatures as high as 775 K.

6. DFT computational details

Our first-principles methodology is based on the pseudopotential density functional theory (DFT) [S4] as implemented in the Siesta code [S5,S6]. We make use of the generalized gradient approximation (GGA) for the exchange-correlation functional [S7] and norm-conserving Troullier–Martins pseudopotentials [S8] in Kleinman–Bylander factorized form [S9]. As for the basis set, we use double ζ basis function composed of numerical atomic orbitals of finite range augmented by polarization functions (DZP basis set). The range of each orbital is determined by an orbital energy confinement of 0.01 Ry. In all calculations, we use periodic boundary conditions and a supercell large enough to avoid interactions between the COF sheet (calculated without considering the gold substrate) and its periodic images. The Brillouin zone of the two-dimensional structures was sampled with 64 k-points, which ensures convergence of the calculated total energies. The atomic coordinates and unit-cell vectors were considered optimized when the remanent force on each atom was less than 0.04 eV/Å.

7. X-ray photoemission spectroscopy (XPS) measurements

Figure SI.4 shows the C1s spectra taken after depositing TPB + TMC on Au(111) at room temperature (top) and after annealing to 575 K (bottom). Contrary to the Cl 2p signal, and similar to the O 1s signal, there is only a small decrease of the total intensity (~15%). In general, the analysis of the C spectra is complicated due to the larger number of different types of C atom and the possible contamination of the sample during measurements. Before the reaction takes place, the C signal can be clearly decomposed in (at least) three components at 284.0, 285.0 and 288.7 eV. The first one is due to the C atoms in the benzene rings of TPB, as has been confirmed by measuring a single layer of TPB on Au(111). Then, the higher binding signals must be due to TMC, the one at 285.0 coming from the C atoms in the benzene ring, and the 288.7 peak coming from the C atom in the Cl-C=0 configuration [S10].

A tentative deconvolution of the spectra after annealing is shown in the bottom panel. The signal at 288.7 still remains, coming from the C atoms in the carbonyl group of the polyester compound. In addition, there are peaks at 284.3, from the C atoms in the TPB-related rings, 285.0, from the C atoms in the TMC-related rings, and a new contribution at 286.6 eV, probably due to the C atoms in the TPB-related rings bonded to the ester-O.

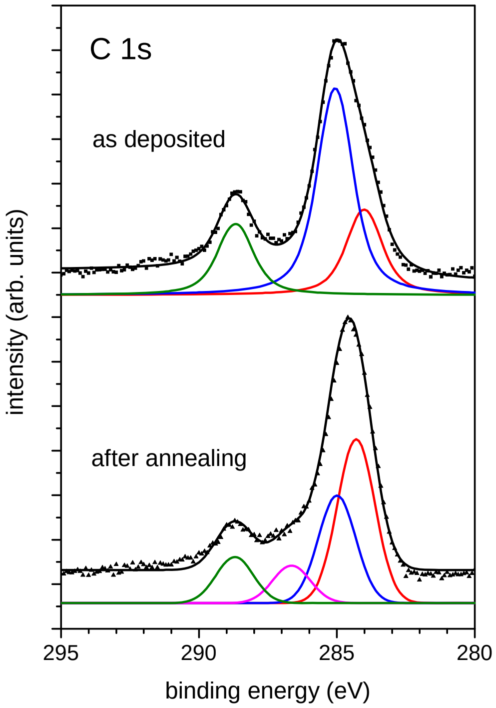

Figure SI.4. C 1s photoemission spectra taken after depositing TPB + TMC on Au(111) at room temperature: as deposited (top); after annealing to 540 K (bottom).

8. References

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