

**FABRICATION OF ULTRATHIN FILMS CONTAINING THE
METAL ORGANIC FRAMEWORK FE-MIL-88B-NH₂
BY THE LANGMUIR-BLODGETT TECHNIQUE**

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ABSTRACT

In this work, the fabrication of ultrathin films containing the metal organic framework (MOF) Fe-MIL-88B-NH₂ by the Langmuir-Blodgett (LB) technique has been explored. MOF crystals of two different sizes (1.5 ± 0.3 and 0.07 ± 0.01 μm) have been synthesized and assembled at the air-liquid interface by the LB method. The effect of the subphase pH and particle size on the film formation process has been studied. Moreover, for the first time, mixed MOF + polymer (a commercial soluble polyimide) LB films containing different MOF loadings have been fabricated. These experiments show that it is possible to obtain ultrathin MOF + polymer films with a controlled MOF density. Furthermore, MOF particles are homogeneously distributed in the polymer matrix, even with very large amounts of MOF (up to 95 wt%). LB films have been incorporated into materials of different nature, including glass and mica substrates and also polymeric membranes, and the modification of water contact angle after LB film deposition has been analyzed.

Keywords: Metal organic framework; Fe-MIL-88B-NH₂; Matrimid[®] polyimide (PI); Langmuir and Langmuir-Blodgett (LB) films; mixed matrix membranes (MMMs).

1. Introduction

The Langmuir-Blodgett (LB) technique was conceived to fabricate monomolecular films of amphiphilic molecules at the air-water interface with a controlled organization [1]. These films are subsequently transferred onto solid substrates to obtain LB films with the desired number of layers. Currently, this technique can be used to fabricate thin films of many other materials, including graphene [2], nanoparticles [3] and polymers [4]. However, in the literature only a few attempts have been reported for the fabrication of thin films of metal-organic frameworks (MOFs) at the air-liquid interface. Nanofilms of a family of MOFs called NAFS, which are formed by metalloporphyrin building units and metal ion connectors, have been obtained combining the LB and the layer-by-layer methodologies [5, 6]. Also, evidence of the formation of single-layer MOF nanosheets at the air-liquid interface has recently been reported for a compound of the same family [7]. Additionally, monolayers of polyvinylpyrrolidone-modified UiO-66 microcrystals have been obtained at the air-liquid interface using sodium dodecyl sulfate to consolidate the film [8]. Finally, LB films of three MOF crystals with different sizes and morphologies, $\text{Cu}_3(\text{btc})_2$, $\text{Cu}_2(\text{bdc})_2(\text{bpy})$ and $\text{Al}_{12}\text{O}(\text{OH})_{18}(\text{H}_2\text{O})_3(\text{Al}_2(\text{OH})_4)(\text{btc})_6$, have been deposited onto various substrates and characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) [9]. However, as far as we know, there are no previous studies in the literature dealing with the fabrication of mixed LB films containing MOF particles and polymers.

In this study, Fe-MIL-88B-NH₂ particles have been synthesized following two different routes, obtaining crystal sizes of 1.5 ± 0.3 and 0.07 ± 0.01 μm . These iron carboxylate-based MOF crystals have the distinctive feature of exhibiting a high flexible framework and adsorption capacity of interest for drug delivery, sensors or gas

separation. In addition, their non-toxic nature may have a significant impact in biomedical applications [10, 11]. Using these particles, LB films of the MOF crystals and mixtures of MOF + Matrimid[®] polyimide (PI) in different proportions have been prepared and characterized in order to evaluate the effect of the particle size on the film organization. Moreover, the fabrication of mixed LB films containing MOF and polymers would be very useful for the development of mixed matrix membranes (MMMs) [12, 13] with a controlled architecture.

MOF and polymer studied here could be considered as representative models of MMMs components. Additionally, they show potential characteristics for the formation of thin films at the air-water interface. Matrimid[®] is a commercial polymer that has been extensively used in MMMs because it provides high gas separation selectivity [12, 13]. Besides it is soluble in chloroform, which is a common solvent for the fabrication of Langmuir films. Fe-MIL-88B-NH₂ is a carboxylate based MOF that can be easily synthesized with a controlled size, moreover it presents good water stability as shown by 2-aminobenzene-1,4-dicarboxylic acid release experiments in deionized water [14]. Furthermore, MOFs containing amino groups are considered good candidates to form MMMs because they present good chemical compatibility with different kinds of polymers [15] and the hydrophilic group -NH₂ should favor MOF crystal spreading onto the water surface. Finally, it should be also mentioned that a recent study has shown the synthesis of MMMs Fe-MIL-88B/Matrimid[®] for H₂/CH₄ separation [16] which denotes the interest of the mixtures PI + iron carboxylate-based MOFs.

In the usual procedure for the fabrication of MMMs, the polymer-filler dispersion is cast on a flat surface. After solvent evaporation at room temperature, the membrane is heated in vacuum to remove the remaining solvent [12]. This method does not allow ultrathin membranes to be obtained. However, thinner membranes are of

considerable importance for the further study of the filler-polymer interaction and also for obtaining a more detailed characterization of the membrane structure and properties and of the subsequent influence on the MMMs performance. In this context, the preparation of systems by a direct bottom-up approach is necessary in order to achieve a fine control over the size and shape of nanomaterials, without the need for any further treatment such as delamination, suspension, or alignment on a substrate [7].

In this study, ultrathin MOF films have been transferred onto different materials, including glass and mica substrates and glassy polymer membranes based on polysulfone or PIM-1 (polymer of intrinsic microporosity). The modification of water contact angle after film deposition has been analyzed, showing that LB films could be of interest for the development of asymmetric membranes for liquid phase applications.

2. Materials and methods

2.1. MOF synthesis

Fe-MIL-88B-NH₂ particles were prepared following two different routes. In route A (Fe-MIL-88B-NH₂_A) particles of about 1.5 μm were synthesized by mixing two solutions at room temperature for 20 h. In the first solution 2.16 g of FeCl₃·6H₂O (Sigma Aldrich, ≥98%) was dissolved in a mixture of 7.6 mL of deionized H₂O and 12.4 mL of N,N-dimethylformamide (DMF, Sigma–Aldrich, > 99%). In the second solution 0.720 g of NH₂-BDC (2-aminobenzene-1,4-dicarboxylic acid, Sigma Aldrich, 99%) was added to 20 mL of DMF. Upon magnetic stirring the mixed solution (with a molar composition FeCl₃·6H₂O: NH₂-BDC: DMF: H₂O: 1:1:52:52) [17] was washed with acetone and then several times with ethanol by centrifugation. The final powder was dried at 100 °C overnight and collected. By using this simple method (mixing the

solutions during different times) it was difficult to tune the size and shape of the resulting crystals.

Therefore, to make the particle size more uniform and to decrease it to the nanometer range, route B (Fe-MIL-88B-NH₂_B) was followed, based on a previously reported work [18]. In this protocol, the particle size control and the high yield and crystallinity were achieved by using a triblock co-polymer in the synthesis. For the preparation of the Fe-MIL-88B-NH₂_B crystals, 0.32 g of Pluronic P-123 (PEG-PPG-PEG) was dissolved in 30 mL of deionized water. Then, 0.356 g of FeCl₃·6H₂O was added and the resulting solution was stirred for 1 h. After stirring, 0.12 g of NH₂-BDC was added. The reaction mixture was stirred for 2 h before being transferred into a stainless steel Teflon-lined autoclave for the crystallization at 110 °C for 42 h. The dark brown solid product was recovered by centrifugation and washed several times with ethanol to remove the surfactant and excess reactants.

2.2. Langmuir and Langmuir-Blodgett film fabrication

Langmuir film formation was studied in a commercial Langmuir Teflon trough, NIMA model 702, with dimensions of 720 mm × 100 mm and with symmetric double-barrier compression. Surface pressure (π -A) and surface potential (ΔV -A) vs. area isotherms and Brewster angle microscopy (BAM) images were obtained in this device. A second apparatus, a homemade Teflon trough with dimensions of 460 mm × 210 mm, was employed for the fabrication of Langmuir-Blodgett films. Both troughs were kept inside closed cabinets in a clean room at constant temperature (20 ± 1 °C). Ultra-pure Milli-Q water ($\rho = 18.2$ M Ω ·cm) was used in all the experiments. NaOH (99 % purity) and HCl (35 % purity) supplied by Panreac were used to adjust the pH of the subphase when required. Surface pressure (π) was continuously monitored in both devices using Wilhelmy balances with a filter paper plate. BAM images were obtained with a KSV

Nima Micro BAM. This equipment uses a red laser (50 mW, 659 nm) as incident beam. The lateral resolution of the optical system in the surface water plane is less than 12 μm . Surface potential measurements were performed with a KSV Nima Surface Potential Sensor.

Solutions of each component were prepared separately: (a) Matrimid[®] 5218 (kindly provided by Huntsman Advanced Materials) was dissolved in chloroform (Panreac, >99.9%) and stirred until a homogeneous solution was obtained. The solution concentration (4×10^{-5} M) was calculated using the molar mass of the repeat unit. (b) MIL-88B-NH₂ powder was dispersed in chloroform-methanol (1:4 in volume) and stirred during 48 hours to obtain a homogeneous dispersion of concentration of 0.1 $\text{mg} \cdot \text{mL}^{-1}$. The MOF + polymer mixtures were prepared mixing the pure component solutions in the appropriate proportion, then sonicating during 15 min and stirring until a homogeneous dispersion was obtained. The MOF percentage in the dispersion was calculated dividing the MOF mass by the (MOF + polymer) mass in the mixture. In each experiment, the desired volume of dispersion was spread drop by drop using a gas-tight Hamilton microsyringe held very close to the water surface. After spreading, the solvent was left to evaporate for 15 min before starting the compression of the film, which was performed at a constant compression speed of 5 $\text{cm}^2 \cdot \text{min}^{-1}$. Compression isotherms were registered at least three times in each trough to check the reproducibility of the results.

Langmuir-Blodgett films were fabricated onto solid substrates (quartz, glass and mica, depending on the target characterization: UV-vis spectroscopy, SEM and AFM, respectively) using the vertical dipping method. Quartz and glass substrates were cleaned with ethanol, while mica was first cleaved and then washed with ethanol. The films were transferred during the lift-up of the substrate, initially immersed in the

subphase, at a constant rate of 5 mm·min⁻¹. LB mixed films deposited onto glass and mica substrates were also characterized by measuring water contact angles.

Finally, LB films were deposited onto polymeric membranes made, respectively, of polysulfone and PIM-1 and water contact angles were measured. Deposition onto polymeric membranes took place during membrane immersion at a constant rate of 5 mm·min⁻¹. Polysulfone and PIM-1 membranes were previously prepared according to the literature [19, 20]. The polymer dispersions in chloroform were cast onto a flat glass plate and left overnight partially covered to slow down the natural evaporation of solvent. The dense polysulfone membrane was placed for 24 h under vacuum at 120°C for removing the remaining solvent while the PIM-1 membrane did not require such treatment. A soaking in methanol was enough to completely remove the solvent and activate its micropores.

2.3. Characterization of MOF and Langmuir-Blodgett films

The scanning electron microscopy (SEM) images were collected using a SEM Inspect F50 manufactured by FEI. This microscope offers a resolution of 1.2 nm at 30 kV working in high-vacuum. The LB films transferred onto glass and Fe-MIL-88B-NH₂ crystals were coated with a layer of platinum (10 nm). For particle size measurements, ImageJ software was used. The microscopy work was carried out in the Laboratorio de Microscopias Avanzadas at the Instituto de Nanociencia de Aragon.

MOF powder from both samples was analyzed by X-ray diffraction (XRD). The analysis was carried out at room temperature with a D-Max Rigaku diffractometer with a copper anode and a graphite monochromator to select Cu-K α 1 radiation ($\lambda = 1.5418$ Å).

Thermogravimetry analyses (TGA) of Fe-MIL-88-NH₂ powder were conducted using a Mettler Toledo TGA/SDTA 851e system. Samples (about 5 mg) were placed in 70 μ L pans and then heated in air flow up to 800 °C at a heating rate of 10 °C·min⁻¹.

Zeta-potential measurements were performed with a Brookhaven Instrument 90 Plus. MIL-88B-NH₂ powder was added in deionized water and sonicated for 20 minutes to obtain a homogeneous dispersion. To adjust the pH, diluted NH₃ (25%, Panreac) or H₂SO₄ (95-98%, Sigma-Aldrich) were used.

UV-Vis spectra of the polymer solution and Langmuir-Blodgett films were recorded in a Varian Cary 40 Bio spectrophotometer.

Atomic force microscopy (AFM) experiments to study the topography of the LB films transferred onto mica substrates were performed by means of a MultiMode 8 scanning probe microscope manufactured by Veeco, in tapping mode. A silicon cantilever provided by Bruker, with a force constant of 40 mN and operating at a resonant frequency of 300 kHz was used in these experiments. Images were recorded with a scan rate of 1 Hz, an amplitude set-point lower than 1 V, and in ambient conditions.

Water contact angle measurements were performed with a commercial optical tensiometer Theta Lite from Attension. Values given are the average of five measurements at different positions of each sample.

3. Results and discussion

3.1. MOF particles

The SEM images of Fe-MIL-88B-NH₂ MOF crystals following both routes A (Fe-MIL-88B-NH₂_A) and B (Fe-MIL-88B-NH₂_B) are shown in Fig. 1, where particle sizes of 1.5 ± 0.3 and 0.07 ± 0.01 μ m (average \pm standard deviation), respectively, are

obtained by measuring about 80 particles of each sample. Fig. S1 of the Supplementary Material shows the corresponding normalized cumulative number of particles as a function of particle size. The differential distribution was also calculated (see Fig. S1 inset), providing the predominant particle size (mode), which coincides with the average size of each sample. It should be noted that for the Fe-MIL-88B-NH₂_B sample, larger particles of around 0.3 μm, not included in the particle size measurements, can also be observed.

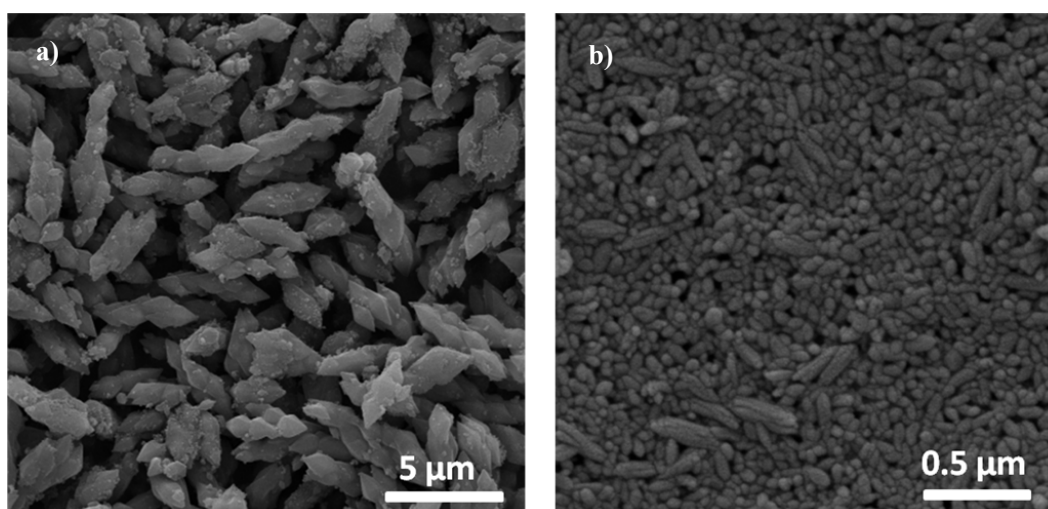


Fig. 1. SEM images of a) Fe-MIL-88B-NH₂_A ($1.5 \pm 0.3 \mu\text{m}$) and b) Fe-MIL-88B-NH₂_B ($0.07 \pm 0.01 \mu\text{m}$) MOF crystals.

X-ray diffraction patterns for samples Fe-MIL-88B-NH₂_A and Fe-MIL-88B-NH₂_B correspond with those reported for the DMF and water exchange forms [21], respectively, as can be observed in Fig. 2. The peak at 7.5 ° in sample Fe-MIL-88B-NH₂_A is related to the presence of DMF inside the pores, which would induce a swelling effect on the MOF framework. DMF molecules, bigger than water and MeOH, might prevent optimal formation of hydrogen-bonding interactions in the constriction of the MOF pores[22]. Sample Fe-MIL-88B-NH₂_B, synthesized in H₂O, corresponds to the activated or hydrated form where hydrogen bonds inside the pores and with the

water molecules lead to the framework shrinkage [22], and thus, a smaller effective pore size. This framework shrinkage can be observed by Fig. 2, where a peak at 10° related to narrow pores appears in the XRD pattern. This is in accordance with the TGA analyses (Fig. S2 of the Supplementary Material) where sample Fe-MIL-88B-NH₂_A shows a weight loss of ~20 wt% up to 250 °C corresponding to the removal of water and DMF molecules within the structure.

After washing with ethanol, the surfactant Pluronic P-123 was removed from the sample Fe-MIL-88B-NH₂_B, as can be observed by TGA (see Fig. S2). In fact, Pham et al. observed a weight loss difference of about 10% before and after washing which may be related to the surfactant [18]. The peaks of Fe-MIL-88B-NH₂_B are broader than those of Fe-MIL-88B-NH₂_A, consistent with a smaller particle size material.

The zeta-potential values of Fe-MIL-88B-NH₂_A crystals in aqueous solution at different pH values are included in the Supplementary Material (Fig. S3). These results will help to understand the influence of the pH (5-9) on the aggregation of the particles at the air-water interface.

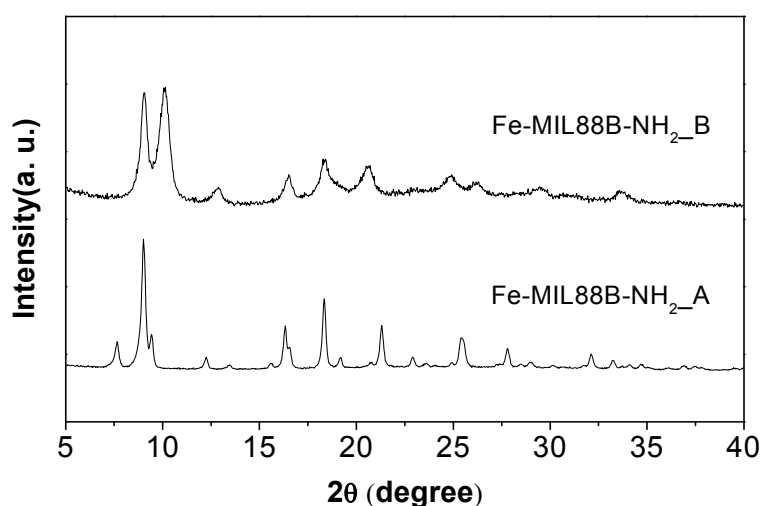


Fig. 2. XRD patterns of Fe-MIL-88B-NH₂_A and Fe-MIL-88B-NH₂_B crystals.

3.2. Langmuir and Langmuir-Blodgett films

Langmuir and Langmuir-Blodgett films of pure MOF particles, pure polymer, and mixed MOF + polymer were investigated. The fabrication and characterization of MOF and polymer films will be discussed first while experiments dealing with the fabrication of mixed films are analyzed at the end of this section.

3.2.1. Films of pure MOF

Films of Fe-MIL-88B-NH₂_A particles were fabricated spreading 3 mL of a diluted dispersion (0.1 mg·mL⁻¹) onto the aqueous surface. Fig. 3 shows the π - A isotherm and BAM images obtained during surface area reduction. The area in these isotherms is expressed in cm² of water surface available per mg of MOF.

At large areas per mg of MOF the surface pressure is zero and the water surface is almost uncovered. Upon further reduction of the surface area, π starts to rise and constantly increases until a value of ca. 14 mN·m⁻¹ is reached, when a change of slope can be observed which should be related with the film collapse. BAM images show that some areas of the water surface remained uncovered by the film even at high surface pressures; moreover, MOF particles seem to form three dimensional aggregates. Additional experiments (not shown here) were also conducted, using more concentrated spreading dispersions (0.2 and 0.3 mg·mL⁻¹) to increase the amount of MOF particles at the air-water interface, but the quality of the films was not improved since particle aggregation was increased.

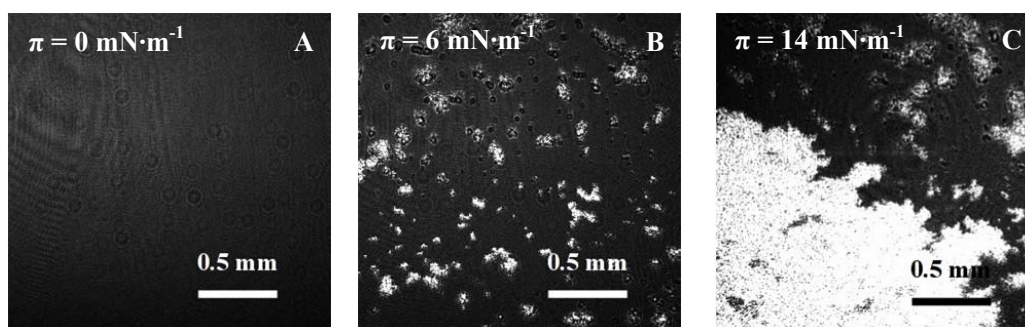
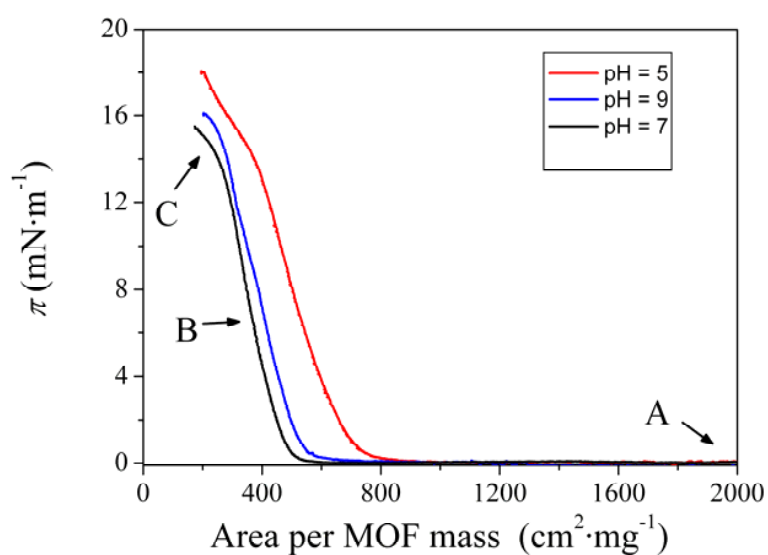


Fig. 3. Surface pressure-area isotherms obtained using a diluted dispersion of Fe-MIL-88B-NH₂_A particles (0.1 mg·mL⁻¹) onto pure water (pH = 7) and aqueous subphases (at pH = 5 and 9). BAM images were taken during film compression onto pure water (pH = 7) at the areas indicated by the arrows.

Using the diluted dispersion previously indicated (0.1 mg·mL⁻¹), LB films (one layer) were fabricated onto glass substrates during the upstroke of the substrate at a surface pressure of 12 mN·m⁻¹, to avoid film collapse, and characterized using SEM (see Fig. 4a). These images show that the LB films obtained did not completely cover the glass substrate. Moreover, although most of the particles were arranged in a two-

dimensional layer, some aggregates can be seen, which reflects the behavior observed at the air-water interface.

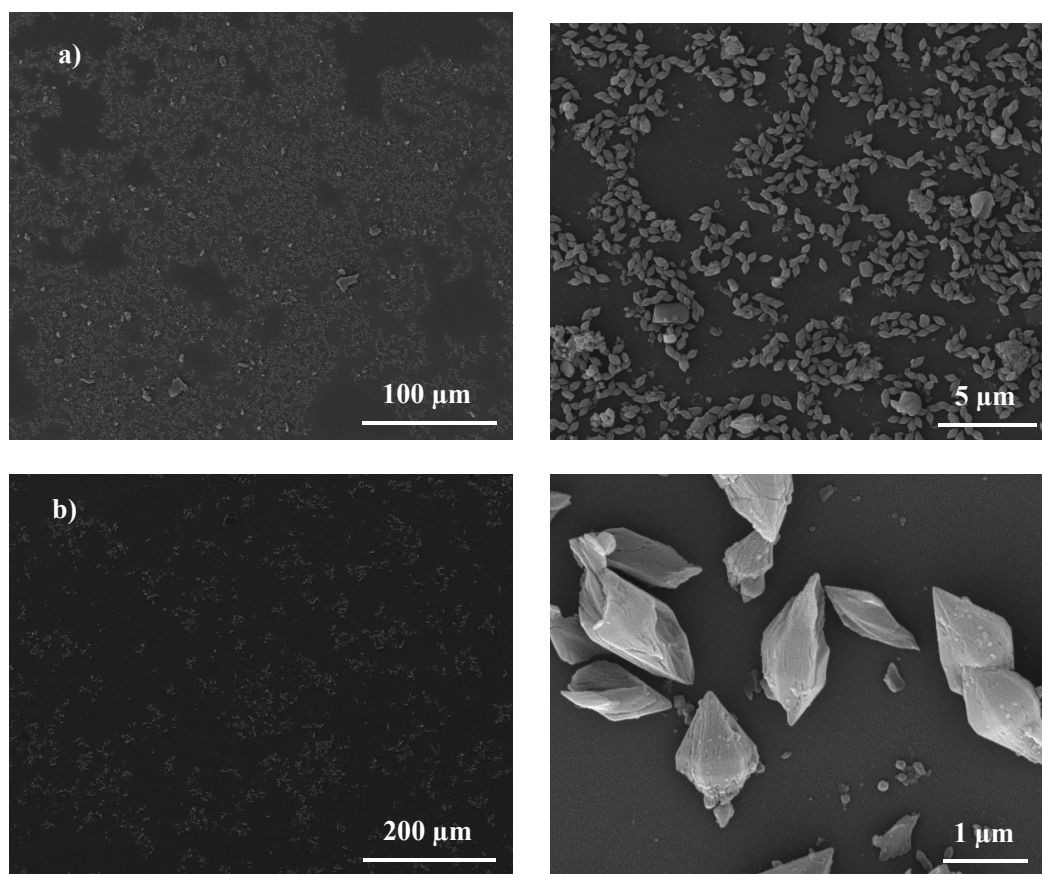


Fig. 4. SEM images of LB films (one layer) fabricated with Fe-MIL-88B-NH₂_A crystals ($\pi = 12 \text{ mN}\cdot\text{m}^{-1}$): a) at the air-water interface (pH = 7), b) at the air-aqueous solution interface (pH = 5).

In order to reduce particle aggregation, the influence of the pH on the organization of MOF particles at the air-liquid interface has been investigated using aqueous diluted solutions of HCl (pH = 5) or NaOH (pH = 9) as the subphase. π - A isotherms obtained at both pH values are represented in Fig. 3, together with the curve obtained with pure water (pH = 7). In the figure, it can be observed that at pH = 5 the surface pressure starts to rise at larger area than at pH = 7, as could be expected, due to electrostatic repulsion between positively charged particles, according to zeta-potential

values. However, the area does not change significantly at the surface pressure of transference ($12 \text{ mN}\cdot\text{m}^{-1}$). Moreover, at $\text{pH} = 9$, the expansion at the lift-off is less significant, which is in good agreement with a value of zeta-potential similar to $\text{pH} = 7$, and the area at $\pi = 12 \text{ mN}\cdot\text{m}^{-1}$ is almost the same as with pure water.

Langmuir films obtained at $\text{pH} = 5$ were transferred onto glass substrates during the upstroke of the substrate at a surface pressure of $12 \text{ mN}\cdot\text{m}^{-1}$ and characterized using SEM (see Fig. 4b). LB films obtained in these conditions did not improve significantly the substrate coating compared with LB films obtained at $\text{pH} = 7$, although the presence of aggregates was reduced. These experiments show that the aggregation of MOF particles at the air-liquid interface can be modulated by changing the pH of the subphase, although it was not possible to obtain a compact film using Fe-MIL-88B-NH₂_A particles.

Consequently, the next step was to investigate the effect of particle size on the behavior at the air-water interface. Langmuir films of Fe-MIL-88B-NH₂_B crystals were fabricated spreading 3 mL of a diluted dispersion ($0.1 \text{ mg}\cdot\text{mL}^{-1}$) onto pure water. Fig. 5 shows the π - A isotherms obtained with both kinds of crystal for comparison purposes.

When Fe-MIL-88B-NH₂_B particles are used, the surface pressure starts to rise at a larger area per mass of MOF and the maximum value of surface pressure is also increased significantly. This seems to indicate a stronger interaction between the aqueous subphase and MOF particles, which is logical because the crystal size reduction increases the area/volume ratio. Furthermore, BAM images reveal that the water surface coverage is increased using nanometric particles.

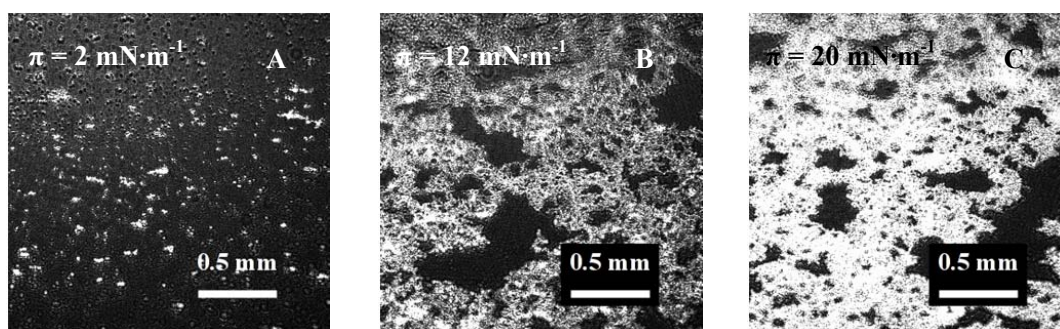
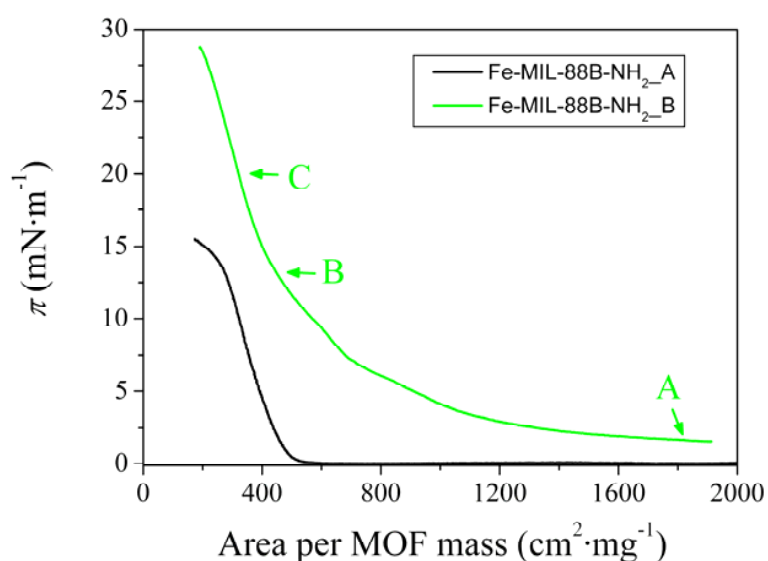


Fig. 5. Surface pressure-area isotherm obtained with Fe-MIL-88B-NH₂_B particles onto pure water (green line) compared to the isotherm of Fe-MIL-88B-NH₂_A particles (black line). BAM images were taken during film compression at the areas indicated by the arrows.

LB films (one layer) of Fe-MIL-88B-NH₂_B particles have been transferred during the upstroke of the glass substrate, at a surface pressure of 22 mN·m⁻¹, where the area per mg of MOF is almost the same as that at which Fe-MIL-88B-NH₂_A particles were transferred (about 295 cm² per mg of MOF), and characterized by SEM (see Fig. 6). LB films obtained in these conditions reflect the difference in behavior observed at the air-water interface, since the glass substrate coating was increased using Fe-MIL-

88B-NH₂_B particles. However, the film obtained was not compact enough to completely coat the substrate.

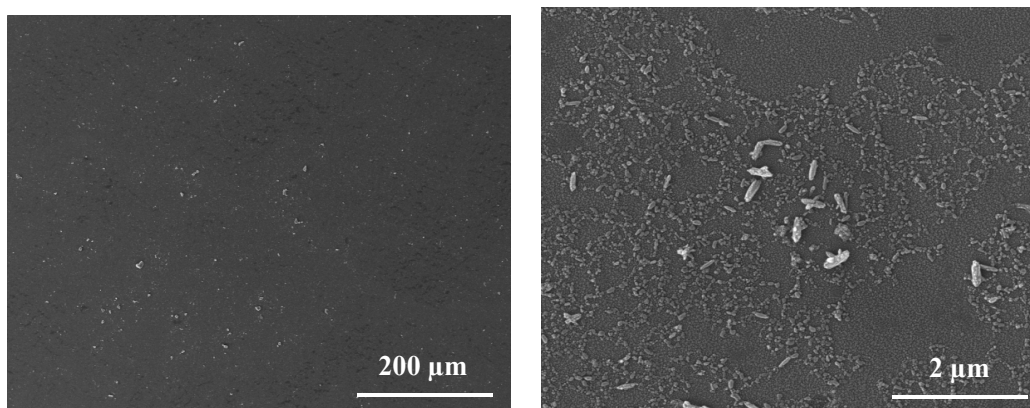


Fig. 6. SEM images of LB films (one layer) fabricated with Fe-MIL-88B-NH₂_B crystals at $\pi = 22 \text{ mN}\cdot\text{m}^{-1}$.

3.2.2. Films of pure polymer

Most aromatic polyimides do not form stable monolayers and cannot be deposited by the LB technique [23]. Therefore, the amphiphilic precursor method has traditionally been used to fabricate polyimide LB films [4]. In this method, long alkyl chain polyamic acid salts or esters are deposited onto solid substrates and imidized by thermal treatment [24]. Only a few examples of LB film formation by direct spreading of soluble polyimides onto the air-water interface can be found in the literature [23, 25-27].

Films of the polymer PI were obtained spreading 1 mL of the polymer solution (repeat unit concentration $4 \times 10^{-5} \text{ M}$) onto the water surface. Fig. 7 shows the π - A and ΔV - A isotherms of the PI film and BAM images obtained during film compression. The surface pressure starts to rise at ca. 1.20 nm^2 per repeat unit and continuously increases during compression, reaching π values around $30 \text{ mN}\cdot\text{m}^{-1}$ without any sign of film collapse. The area extrapolated to zero pressure from the condensed film is close to 0.90

nm^2 per repeat unit, which is similar to the values obtained for other previously studied aromatic polyimides [23].

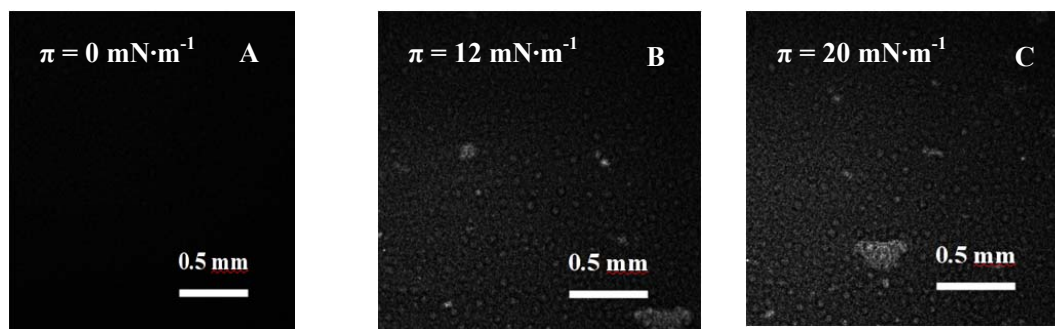
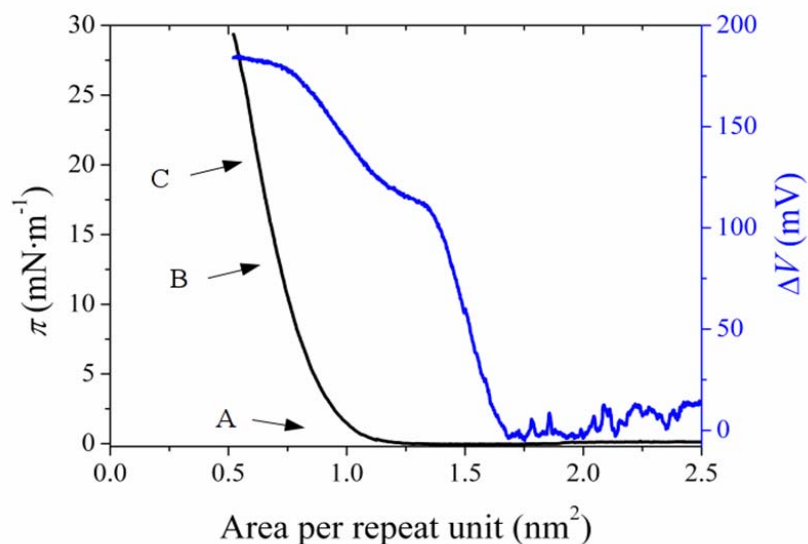


Fig. 7. Surface pressure-area (black line) and surface potential-area (blue line) isotherms of PI film fabricated at the air-water interface. BAM images were taken during film compression.

The surface potential oscillates over areas greater than 1.70 nm^2 per repeat unit, which is indicative of the coexistence of polymer domains and uncovered water surface areas. From this point, ΔV continuously increases when the molecular density increases. Moreover, there is a slope change around the onset of the surface pressure. Finally, ΔV reaches a maximum value of ca. 180 mV at 0.72 nm^2 per repeat unit and remains almost

constant under further compression. As expected, BAM images show polymer domains and uncovered water areas before the surface pressure onset. These domains merge to form a compact and almost homogeneous film that totally covers the water surface at a surface pressure around $12 \text{ mN}\cdot\text{m}^{-1}$. Further compression produces the appearance of brighter domains that could be due to partial 3D collapse of the film.

All these experiments indicate that an almost homogeneous Langmuir film is formed at surface pressures around $12 \text{ mN}\cdot\text{m}^{-1}$. In addition, the film stability was checked keeping the surface pressure constant at this value. An area loss below 15% was observed in 12 h which confirmed that stable Langmuir films were obtained.

Langmuir-Blodgett films (1 layer) were transferred during the upstroke of the substrate at a surface pressure of $12 \text{ mN}\cdot\text{m}^{-1}$ onto quartz, glass and cleaved mica and characterized by UV-vis spectroscopy, SEM and AFM, respectively.

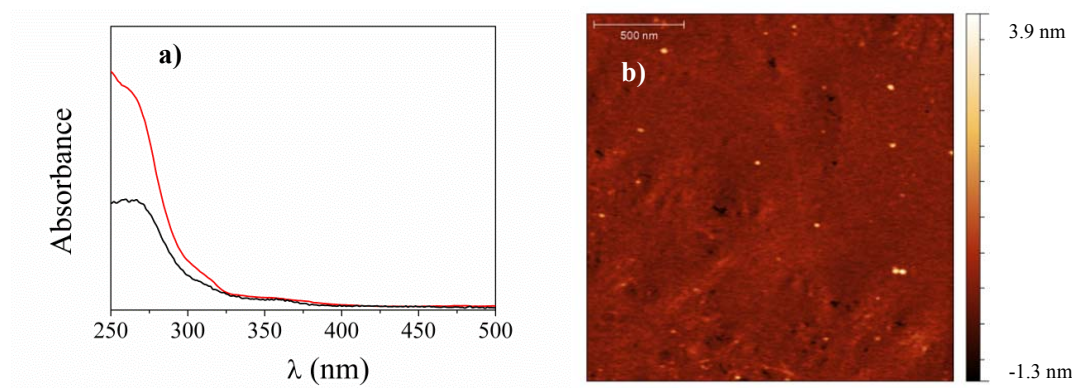


Fig. 8. Characterization of PI LB films transferred at $\pi = 12 \text{ mN}\cdot\text{m}^{-1}$: a) UV-vis spectra of the LB film (black line) and PI solution in chloroform (red line), (b) AFM image of the LB film.

The UV-vis spectrum of the LB film and the solution spectrum (Fig. 8a) are very similar, with peaks at ca. 360 and 260 nm and a shoulder at about 310 nm, revealing that peaks are not shifted during film compression (monomer aggregation is not

relevant). AFM images (Fig. 8b) show that a flat film with very low roughness was obtained; only some small aggregates of heights around 3 nm can be observed. The film thickness was also evaluated by scratching the film with the AFM tip, yielding a value of ca. 1.1 nm. Taking into account the film thickness and the area at $\pi = 12\text{mN}\cdot\text{m}^{-1}$ (0.72 nm^2 per repeat unit), the film density is similar to the polymer density in the solid state provided by the supplier ($1.2\text{ g}\cdot\text{cm}^{-3}$). This confirms that a compact monolayer is formed.

3.2.3. Mixed MOF + polymer films

Langmuir and Langmuir-Blodgett MOF + PI mixed films containing different MOF percentages have been fabricated and characterized.

Initially, six different mixtures of Fe-MIL-88B-NH₂_A + PI containing 7, 13, 21, 28, 34 and 40 wt% of MOF, respectively, were analyzed. To compare the behavior of the pure PI and mixed films, π -*A* isotherms for all the mixtures investigated were represented using the area per polymer repeat unit. This comparison showed that all the mixtures behave very similarly to the PI film, within the experimental error. Also, the BAM images were almost indistinguishable from those of the PI film. This behavior reveals that the polymer film structure in the mixed films is almost the same as that in the PI film and suggests that MOF particles are situated on top of the polymer, without significantly altering the structure of the monolayer, as confirmed by SEM images. It is probable that the large size of the MOF particles ($1.5 \pm 0.3\ \mu\text{m}$), in comparison to the thickness of the polymer layer (1.1 nm), did not allow a stronger interaction between the Fe-MIL-88B-NH₂ and the PI at the air-water interface. To verify this hypothesis two additional mixtures containing, respectively, 90 and 95 wt% of MOF were also characterized and similar π -*A* isotherms were obtained.

To further explore the structure of the films obtained at the air-water interface, LB films (1 layer) were fabricated onto glass slides using the same procedure as that described for the pure PI film and characterized by SEM. Representative images of four mixtures containing 13, 28, 40 and 95 wt% of MOF are shown in Fig. 9.

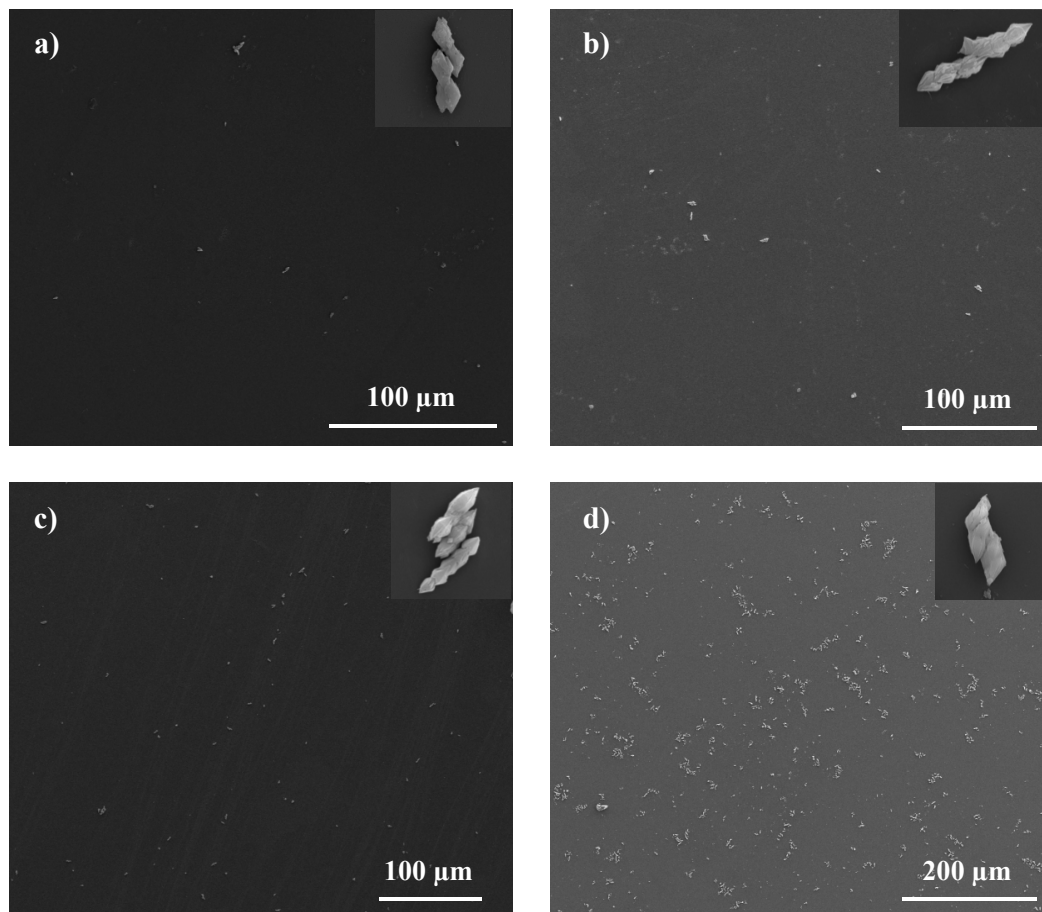


Fig. 9. LB films (1 layer) Fe-MIL-88B-NH₂_A + PI, with different MOF content, transferred at $\pi = 12 \text{ mN}\cdot\text{m}^{-1}$: a) 13 wt% MOF, b) 28 wt% MOF, c) 40 wt% MOF and d) 95 wt% MOF. Inset figures show a magnification of MOF particles in the samples.

As expected, the presence of MOF particles in the films is increased at higher loadings of MOF. Moreover, the particles are homogeneously distributed in the polymer matrix and do not form large aggregates. Instead, they form two-dimensional clusters of crystals, even working with high amounts of MOF. These results confirm for the first

time that, using the LB technique, it is possible to fabricate ultrathin polymer + MOF films, where the MOF density in the film can be tuned. These films will be of great interest for the study of ultrathin mixed matrix membranes with a controlled architecture.

Finally, mixed Fe-MIL-88B-NH₂_B + PI LB films containing 90 wt% MOF have been fabricated to demonstrate that mixed films containing high amounts of nanometric particles can also be produced using the LB technique. Fig. 10 shows SEM images of a mixed LB film (1 layer) transferred at $\pi = 12 \text{ mN}\cdot\text{m}^{-1}$ onto a glass substrate. It can be observed that the quantity of MOF particles in the film is significantly larger than in the film containing the same percentage of Fe-MIL-88B-NH₂_A particles. This confirms that nanometric particles can be more densely packed than micrometer-size crystals, as was also shown for pure MOF films.

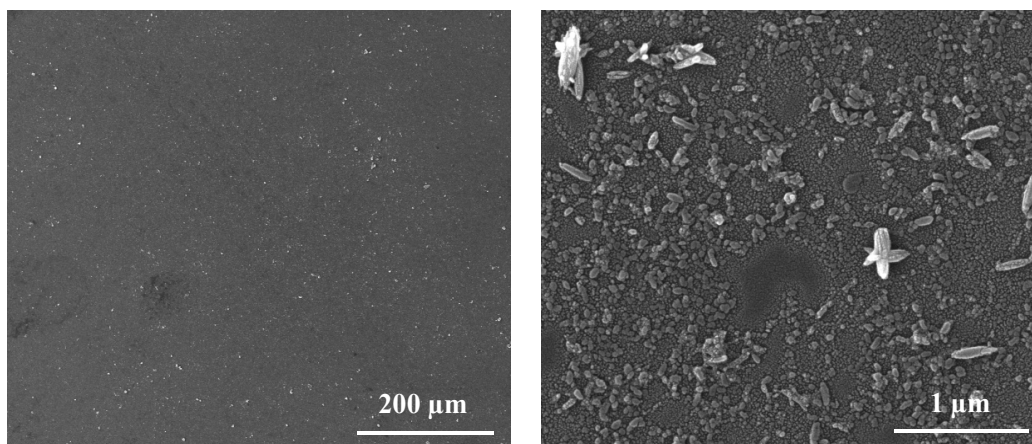


Fig. 10. Fe-MIL-88B-NH₂_B + PI LB film, with 90 wt% MOF, transferred at $\pi = 12 \text{ mN}\cdot\text{m}^{-1}$.

3.3. Water contact angle modification after LB deposition

As a first approach to explore the potential applications of ultrathin films obtained in this study, LB films Fe-MIL-88B-NH₂_A + PI, containing 13 wt% of MOF, have been transferred onto different materials and the water contact angle has been measured before and after the deposition of one LB film (see Table 1). The materials used were glass, mica and two kinds of polymeric membranes made of polysulfone and PIM-1, respectively. The aim of these experiments was to show that LB films can be deposited not only onto hydrophilic materials but also on polymeric materials of interest for the fabrication of membranes. In all the studied materials a modification of the water contact angle is observed after the transference of just one LB film, which is remarkable since these films are ultrathin (as discussed above the height of the polymer monolayer is just 1.1 nm).

On hydrophilic materials (glass and mica) a reduction of the hydrophilic character is observed after the deposition of one LB film. Water contact angle increment is more marked in glass than in mica, as could be expected since the roughness of the glass surface is bigger and it is well known that increasing the surface roughness improves the substrate coverage. Moreover, mica is highly hydrophilic and the existence of small defects in the film would indicate that water contact angle measurement reflect not only the surface of the LB film but also the nature of the substrate. Concerning polymeric films, they become more hydrophilic after the incorporation of LB films. This indicates that mixed LB films MOF + polymer would be of interest for the development of asymmetric membranes. The increment of the hydrophilic character of polymeric membranes could be of especial relevance for the treatment of liquid mixtures comprising compounds of different polarities.

Material	Water contact angle	
	Uncoated	Coated
Glass	$27 \pm 0.2^\circ$	$66 \pm 0.5^\circ$
Mica	$\sim 0^\circ$	$19.6 \pm 0.4^\circ$
Polysulfone membrane	$81 \pm 1^\circ$	$69 \pm 1^\circ$
PIM-1 membrane	$94 \pm 1^\circ$	$74.5 \pm 0.5^\circ$

Table 1. Water contact angle values (average \pm standard deviation) on different materials before and after being coated with one mixed LB film Fe-MIL-88B-NH₂_A + PI containing 13 wt% of MOF.

4. Conclusions

Particles of the metal organic framework Fe-MIL-88B-NH₂ with two different sizes ($1.5 \pm 0.3 \mu\text{m}$ and $0.07 \pm 0.01 \mu\text{m}$) have been synthesized and assembled into ultrathin films using the Langmuir-Blodgett technique. Pure MOF films and mixed MOF + PI films have been fabricated and the effect of the particle size on the film organization has been analyzed. In pure MOF films, particle aggregation of larger crystals can be modulated by changing the pH of the subphase. Moreover, LB films obtained with nanometric particles are denser than the films fabricated with larger particles. Additionally, mixed LB films with different MOF loadings have been fabricated, showing for the first time that it is possible to obtain ultrathin polymer + MOF films, where the MOF density in the film can be tuned and the particles are homogeneously distributed in the polymer matrix. Finally, LB films have been transferred onto different materials and the water contact angle has been measured before and after the deposition of one LB film, showing that they can be used to modify the hydrophilicity of different surfaces.

Acknowledgements

Financial support from the Spanish MINECO (Projects MAT2013-40556-R and CTQ2012-33198), the Aragón Government (DGA) and the ESF are gratefully acknowledged. S. S. thanks the DGA for a fellowship. We also acknowledge the use of the Servicio General de Apoyo a la Investigación-SAI (Universidad de Zaragoza). The authors thank Dr. Carlos Cuestas for technical support in the SEM image acquisition and Dr. Santiago Martín for his assistance with AFM and water contact angle measurements.

Supplementary material

Normalized cumulative number of particles (N/N_T) as a function of particle size, derivation of the cumulative particle size distributions and TGA analysis for the MOF samples Fe-MIL-88B-NH₂_A and Fe-MIL-88B-NH₂_B are given in the Supplementary material together with zeta-potential values of Fe-MIL-88B-NH₂_A crystals in aqueous solution at different pH values.

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APPENDIX: SUPPLEMENTARY MATERIAL

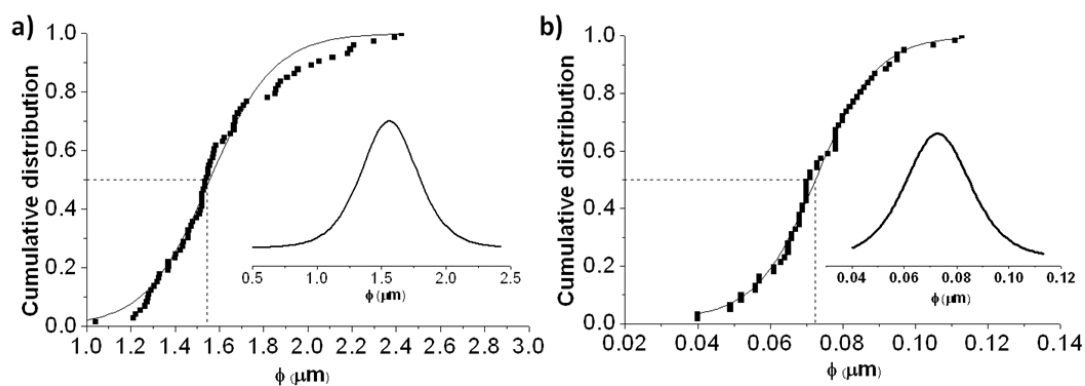


Fig. S1. Normalized cumulative number of particles (N/N_T) for about 80 particles as a function of particle size for: a) Fe-MIL-88B-NH₂_A, b) Fe-MIL-88B-NH₂_B. The inset shows the derivation of the cumulative particle size distributions.

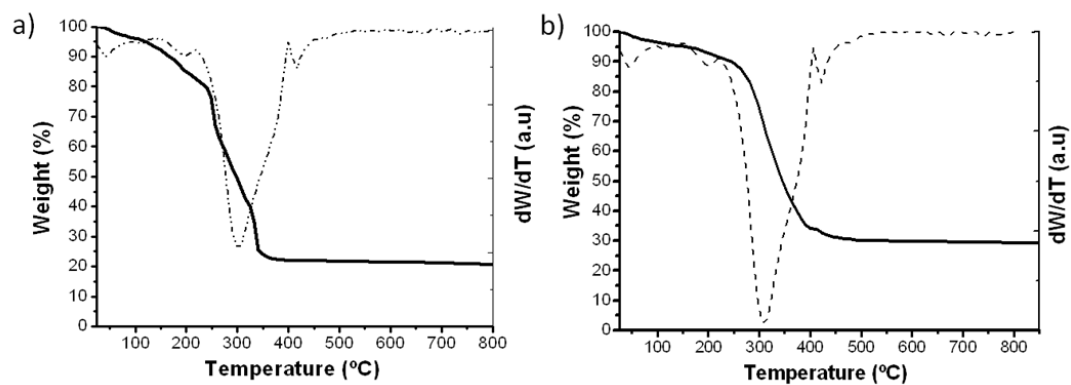


Fig. S2. TGA analysis of Fe-MIL-88B-NH₂ crystals: a) Fe-MIL-88B-NH₂_A sample, b) Fe-MIL-88B-NH₂_B sample.

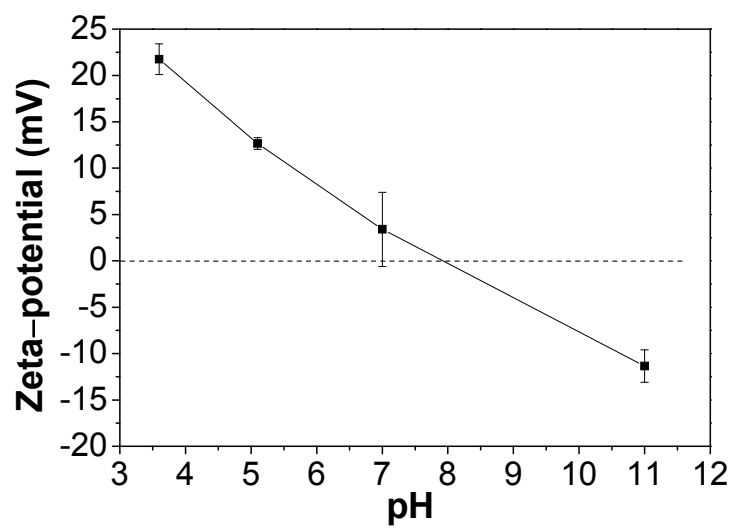


Fig. S3. Zeta-potential values of Fe-MIL-88B-NH₂_A crystals at different pH values.