Introduction

Two-dimensional (2D) materials have attracted increasing attention in the last few years due to their potential expected applications.1 Graphene, a single layer of graphite, represents the first material of this kind.2 The fascinating physical properties3 and potential applications of graphene4,5 have stimulated the development of a number of 2D related materials including graphene oxide,6,7 BN,8 MoS2,9 and clays.10 However all of them show a rather limited or no chemical design and functionalities. Recently, it has been pointed out that covalent polymers,11 and layered covalent organic frameworks (COFs)12,13 or metal–organic frameworks (MOFs)14 could bring à la carte 2D materials with a variety of architectures, pre-designed cavities, and chemical functionalities.15 Even more importantly, suitable selection of the initial building blocks should enable prepara-

† Electronic supplementary information (ESI) available: Extended experimental details, additional Figures and theoretical calculations. See DOI: 10.1039/c4sc03115f

Materials and optical properties of ultralarge flakes of a metal–organic framework with molecular thickness†

Cristina Hermosa,ab Benjamin R. Horrocks,c José I. Martínez,d Fabiola Liscio,e Julio Gómez-Herrero*bf and Felix Zamora*af

The isolation of 2D-materials is already a success for graphene, graphene oxide, boron nitride and a few clays or metal chalcogenides, however despite the fact that some of them show very interesting physical properties, they lack useful functionalities. Metal–Organic Frameworks (MOFs) are multifunctional materials showing a wide range of physical and chemical properties that can be structurally designed by suitable selection of their building-blocks. This strategy may allow the production of layers with a variety of useful electronic and molecular recognition functionalities. Herein we isolate 2D-MOF flakes with areas of hundreds of square microns and an excellent control of the molecular thickness (from single up to ca. 50 layers). The samples exhibit such good photoluminescence and mechanical properties as to allow free-standing characterization of few layers flakes.

The isolation of 2D-materials is already a success for graphene, graphene oxide, boron nitride and a few clays or metal chalcogenides, however despite the fact that some of them show very interesting physical properties, they lack useful functionalities. Metal–Organic Frameworks (MOFs) are multifunctional materials showing a wide range of physical and chemical properties that can be structurally designed by suitable selection of their building-blocks. This strategy may allow the production of layers with a variety of useful electronic and molecular recognition functionalities. Herein we isolate 2D-MOF flakes with areas of hundreds of square microns and an excellent control of the molecular thickness (from single up to ca. 50 layers). The samples exhibit such good photoluminescence and mechanical properties as to allow free-standing characterization of few layers flakes.

Materials and optical properties of ultralarge flakes of a metal–organic framework with molecular thickness†

Cristina Hermosa,ab Benjamin R. Horrocks,c José I. Martínez,d Fabiola Liscio,e Julio Gómez-Herrero*bf and Felix Zamora*af

The isolation of 2D-materials is already a success for graphene, graphene oxide, boron nitride and a few clays or metal chalcogenides, however despite the fact that some of them show very interesting physical properties, they lack useful functionalities. Metal–Organic Frameworks (MOFs) are multifunctional materials showing a wide range of physical and chemical properties that can be structurally designed by suitable selection of their building-blocks. This strategy may allow the production of layers with a variety of useful electronic and molecular recognition functionalities. Herein we isolate 2D-MOF flakes with areas of hundreds of square microns and an excellent control of the molecular thickness (from single up to ca. 50 layers). The samples exhibit such good photoluminescence and mechanical properties as to allow free-standing characterization of few layers flakes.
Results and discussion

Flakes production and characterization

Prismatic crystals \([\text{Cu}([\mu-\text{pym}_2\text{S}_2])_{n}\cdot n\text{MeOH}]\) \((\text{pymS}_2 = \text{dipyrimidinedisulfide})\) were synthesized by slow evaporation of a dipyrimidinedisulfide MeOH : MeCN solution into a methanolic solution of CuCl$_2$·2H$_2$O (ESI† for details).

Fig. 1 shows schematic views of the structure of the MOF \([\text{Cu}([\mu-\text{pym}_2\text{S}_2])_{n}\cdot n\text{MeOH}]\) in which the presence of a layered structure with cavities containing solvent molecules is remarkable. Large orange crystals of \([\text{Cu}([\mu-\text{pym}_2\text{S}_2])_{n}\cdot n\text{MeOH}]\) were suspended in water, then sonicated and centrifuged to obtain a homogeneous suspension of \([\text{Cu}([\mu-\text{pym}_2\text{S}_2])_{n}\cdot n\text{MeOH}]\) flakes production and characterization.

The productions of these large lateral dimensions are a consequence of the capillary forces introduced by the evaporation of the solvent during evaporation. The high ratio of holes with suspended layers implies that we are delaminating just by interaction with an excess of solvent.\(^9\)

Despite the fact that the bulk material showed intense red emission, the physical characterization of the layers of \([\text{Cu}([\mu-\text{pym}_2\text{S}_2])_{n}\cdot n\text{MeOH}]\) was not possible due to their reduced lateral size. In this work, we have been able to set up a method to produce ultra-large layers with control over the thickness that has allowed us to obtain free-standing few-layers flakes of this MOF and characterize their mechanical properties and its emission in 2D-materials ranging from single to a few layers. The results show the high potential of several chemically designed layered materials, such as MOFs, to produce novel 2D layered functional polymers.

The control over the thickness of the MOF layers is achieved by adjusting the sonication time in the exfoliation procedure (ESI† for experimental details). The statistical analysis of the thickness of the MOF layers shows the excellent control of the exfoliation within the sonication time and the production of homogeneous materials (Fig. S1†).

Free-standing flakes of \([\text{Cu}([\mu-\text{pym}_2\text{S}_2])_{n}\cdot n\text{MeOH}]\) are obtained by dip-coating with a water suspension of the polymer at 55 °C on a Si/SiO$_2$ (300 nm) substrate with predefined circular wells (diameters ranging from 0.5 to 3 μm and 400 nm depth; Fig. S2 in ESI†). The increase of temperature of the suspension helps to reduce the surface tension of water minimizing the formation of the meniscus in the wells and makes the solution slightly more volatile improving the ratio of free-standing vs. collapsed MOF layers.

The adjustment of withdrawal speed and solution concentration seems to be critical to obtain free-standing flakes during dip-coating. Inspection by optical microscopy revealed polymer flakes covering several holes of the substrate (Fig. 3b). Importantly, the existence of suspended layers implies that we are not facing the deposition of random material, or some kind of precipitation process, we are really delaminating the crystals.

Atomic force microscopy (AFM) images\(^9\) (Fig. 3a and c) confirm this observation and provide a narrow height distribution for the flakes that ranges between 4–8 nm corresponding, to 5 to 10 layers of \([\text{Cu}([\mu-\text{pym}_2\text{S}_2])_{n}\cdot n\text{MeOH}]\), with lateral dimensions ca. 300–3600 μm$^2$. Although in the ideal case such sheets consist of single monolayers, they are often manifested as incompletely exfoliated flakes comprising a small number (<10) of stacked monolayers.

Additionally the AFM images reveal holes where the flake is perfectly suspended and others where it has collapsed, probably as a consequence of the capillary forces introduced by the solvent during evaporation. The high ratio of holes with suspended layers indicates a strong tendency of this large polymer
The mechanical characterization of the suspended layers of MOF precursors was performed using a standard nanoindentation set up with AFM. Fig. 4a displays a scheme of the experimental set up. The mechanical load applied by the AFM tip can be considered to be a good approximation as a punctual force \( F \) that produces an indentation \( \delta \) given by:

\[
F(\delta) = \pi T\delta + \frac{Eh\delta^3}{a^2} \delta^3 \tag{1}
\]

Where \( F \) is the loading force, \( \delta \) is the indentation at the central point, \( T \) is the pretension accumulated in the sheet during the preparation procedure, \( q \equiv 1 \), \( h \) is the layer thickness and \( a \) is the drumhead radius. \( E \) is the Young’s modulus, a fundamental parameter that characterizes the stiffness of a material. Fitting eqn (1) to curves measured in up to 7 different drumheads in 8 layer flakes yielded values of \( E \) and \( T \) of 5 ± 0.5 GPa and 0.12 ± 0.09 N m⁻¹, respectively. Eqn (1) is a good approximation since the tip radius (≈ 25 nm) is much smaller than the hole radius (≈ 1000 nm) used to suspend the flakes in the experiments.

The same experimental set up can also be used to estimate the breaking force \( F_b \) and breaking strength given by \( \sigma^* = \frac{F_b E}{(\pi R_{\text{tip}})^{1/2}} \) where \( R_{\text{tip}} \) is the tip radius (we have used two different AFM tips with radii 25 and 15 nm). We measured breaking forces of about 40 nN yielding \( \sigma^* = 1 ± 0.4 \) GPa. Notice that the expression for the breaking force is for a linear material that tends to overestimate this figure.

Density functional calculations were carried out on \([\text{Cu(μ-pym}_2\text{S}_2)(\mu-\text{Cl})_n] \cdot n\text{MeOH}\) (ESI† for details) yielding \( E \) ranging from 3.4 GPa for the polymer single layer without solvent molecules, up to 4.1 GPa when methanol molecules are considered. Both figures are in good agreement with the experimental results.

Table 1 summarizes the results. The Young’s modulus measured for the MOF studied here is the lowest reported so far, being approximately 200 times lower than the one measured for pristine graphene. The breaking strength follows a similar trends.

### Table 1: Young modulus of different 2D materials

| Material                  | Value (GPa) | Ref. |
|---------------------------|-------------|------|
| Graphene                  | 800–1000    | 32, 33|
| MoS₂                      | 350–450     | 9    |
| Hexagonal boron nitride   | 250         | 8    |
| Graphene oxide            | 200         | 6, 7 |
| Carbon nanosheets         | 10–50       | 34   |
| 2D clays                  | 20          | 10   |
| \([\text{Cu(μ-pym}_2\text{S}_2)(\mu-\text{Cl})_n]\) | 5           | This work |
tendency being 150 times lower than the one for graphene, yet it was still possible to suspend very thin layers of this compound from solution, where the capillary forces tend to collapse the membranes. Therefore, contrary to what one might expect, the weak strength bonds are enough to retain the 2D-layer structure as mechanically coherent entities.

**Luminescence studies**

Studies of additional physical properties are of the greatest interest and never reported before for layers of MOFs of nanometer thickness. Therefore, since optical properties of single crystals of \([\text{Cu}([\mu-\text{pym}_2\text{S}_2])([\mu-\text{Cl}])_n]\cdot n\text{MeOH}\) were previously reported by us,\(^2^9\) we decided to study how these optical properties persist to isolated layers. To this end, samples of \([\text{Cu}([\mu-\text{pym}_2\text{S}_2])([\mu-\text{Cl}])_n]\cdot n\text{MeOH}\) were imaged in reflection to locate large ‘flakes’ and suitable candidates for spectroscopy were identified by their apparent colour in the optical microscope, which is observed due to interference effects in very thin few layers flakes on the Si/SiO\(_2\) substrate. These flakes were subsequently characterized by AFM in order to determine their thickness and thereby to calculate the number of layers in each flake – the individual flakes are easily recognizable by their individual shapes and orientations relative to each other. After locating a flake, confocal spectral images were obtained by rastering the laser focus across the selected area of the sample.

Each image corresponds to \(10^4\) individual spectra and the colour-scale is determined by integration of the spectra over a certain range of Raman shift. Fig. 5c shows an image of elastically-scattered light \((<100 \text{ cm}^{-1}\) Raman shift from the laser line 488 nm). Several large flakes are clearly visible and the identical flakes can also be identified in the optical and AFM images of Fig. 5a and b, respectively. Height analysis of the AFM images revealed that these flakes correspond to a single layer (height ca. 2 nm).\(^2^9\)

Fig. 5d shows the Raman/luminescence spectra of the sample from Fig. 5a–c. It is clear that there are similarities as well as differences between the flake spectra and the bulk spectrum. Three bands (indicated by grey vertical lines) are present in the bulk and flake spectra near 580 nm, 615 nm and 650 nm. We assign these features to PL because the same emission wavelength was observed with a different excitation wavelength of 531 nm \((\text{ESI Fig. S9 feature (iii)}); they are blue-shifted in the flake spectra compared to the bulk spectrum by about 5–10 nm. In Fig. 5d we also observe bands centred at 526 nm \((1470 \text{ cm}^{-1} \text{ Raman shift})\) and 569 nm \((2920 \text{ cm}^{-1} \text{ Raman shift})\). Similar features appear in Fig. 5b \((\text{ESI})\), although more details are visible because the longer wavelength excites PL to a lesser extent. Because these bands appear at fixed energy with respect to the laser, we assign them to Raman processes described by C–H bending and C–H stretching modes of the 2D-MOF and associated solvent (MeOH) molecules.

Density functional calculations (B3LYP/6-31G(d)) \((\text{ESI for details})\) of the vibration modes of the ligand confirm that there are groups of vibrations near 1470 cm\(^{-1}\) \((\text{Fig. S9 in ESI})\) which are associated with normal modes that are combinations of sp\(^2\) C–H bending and either C–C or C–N modes of the ring. These features are sharp in the bulk spectrum, but are broad and weak for flakes, which can be understood in terms of the partial loss of translational symmetry in the thin layers. In addition, it should be noted that solvent exchange effects MeOH/H\(_2\)O are known for this compound\(^2^9\) and these may have a strong influence on the Raman features in this region because solvent molecules present in the bulk crystal are less easily exchanged than those present near the surface, which will exchange even in air. These solvent effects could explain the differences in behaviour of \([\text{Cu}([\mu-\text{pym}_2\text{S}_2])([\mu-\text{Cl}])_n]\cdot n\text{MeOH}\) compared to graphite\(^2^7\) and MoS\(_2\) (ref. 38) with respect to the evolution of Raman spectra with sample thickness.

Other properties appear less sensitive to solvent effects. The luminescence properties of flakes on silicon oxide with thickness ranging from single, few to many layers, shift to the red, but otherwise do not significantly change as the number of layers increases \((\text{see also Fig. S8 and S9})\).

Finally, we also measured Raman spectra of flakes suspended over circular holes \((\text{Fig. 6 and S11})\). It is observed that the spectrum of free-standing flakes are qualitatively the same, though with a slightly larger intensity, to those lying on the...
Atomic Force Microscope (AFM) techniques were used in dynamic mode using a Nanotec Electronica system operating at room temperature in ambient conditions. The images were processed using WSxM.28 For AFM measurements, commercial Olympus Si/N and Ti/Pt cantilevers were used with a nominal force constant of 0.75 N m\(^{-1}\) and 2 N m\(^{-1}\), respectively (ESI† for details). Mechanical characterization of the free-standing flakes was performed by indenting an AFM tip at the centre of the suspended area. Only membranes showing a flat and homogeneous surface were selected for the measurements. Curves acquired on the Si/SiO\(_2\) (300 nm) non-deforming substrate were used as a reference for calculating the applied force and the resulting deflection of the layers (indentation \(\delta\)).

**Conclusions**

In summary, we report the use of liquid phase exfoliation and dip-coating as a simple and efficient top-down method for the production of flakes of a metal–organic framework with lateral dimensions of hundreds of square microns and with an excellent control of the thickness. The isolated layers on SiO\(_2\) have been characterized by AFM and Raman, they show red emission, and this observation remains for isolated free-standing flakes. The mechanical characterization confirms the stability of these layers. To the best of our knowledge, this is the first time that the physical properties of layers of a free-standing MOF are reported. Mechanical stability of layers based on MOFs\(^{15}\) will be a requirement for device fabrication. Herein we have shown a proof-of-concept on the feasibility of materials based on MOF-layers. Obviously, polymers such as covalent organic fragment-works (COFs) will be a source of 2D-materials in the near future.

**Acknowledgements**

The authors acknowledge financial support from MICINN (MAT2013-46753-C2-1-P and MAT2013-46753-C2-2-P and Consolider CSD2010-00024).

**Notes and references**

1 J. Sakamoto, J. van Heijst, O. Lukin and A. D. Schluter, Angew. Chem., Int. Ed., 2009, 48, 1030–1069.

2 A. K. Geim and K. S. Novoselov, Nat. Mater., 2007, 6, 183–191.

3 K. S. Novoselov, V. I. Fal’ko, L. Colombo, P. R. Gellert, M. G. Schwab and K. Kim, Nature, 2012, 490, 192–200.

4 Y. M. Lin, A. Valdes-Garcia, S. J. Han, D. B. Farmer, I. Meric, Y. N. Sun, Y. Q. Wu, C. Dimitrakopoulos, A. Grill, P. Avouris and K. A. Jenkins, Science, 2011, 332, 1294–1297.

5 L. B. Gao, G. X. Ni, Y. P. Liu, B. Liu, A. H. C. Neto and K. P. Loh, Nature, 2014, 505, 190–194.

6 C. Gomez-Navarro, M. Burghard and K. Kern, Nano Lett., 2008, 8, 2045–2049.

7 J. W. Suk, R. D. Piner, J. H. An and R. S. Ruoff, ACS Nano, 2010, 4, 6537–6564.

8 L. Song, L. J. Ci, H. Lu, P. B. Sorokin, C. H. Jin, J. Ni, A. G. Kvashnin, D. G. Kvashnin, J. Lou, B. I. Yakobson and P. M. Ajayan, Nano Lett., 2010, 10, 3209–3215.

9 A. Castellanos-Gomez, M. Poot, G. A. Steele, H. S. J. van der Zant, N. Agrait and R. Blanco-Bollinger, Adv. Mater., 2012, 24, 772–774.

10 D. A. Kunz, E. Max, R. Weinberger, T. Lunkenhein, J. Breu and A. Fery, Small, 2009, 5, 1816–1820.

11 P. Kissel, R. Erni, W. B. Schweizer, M. D. Rossell, B. T. King, T. Bauer, S. Gotzinger, A. D. Schluter and J. Sakamoto, Nat. Chem., 2012, 4, 287–291.

12 A. P. Cote, A. I. Benin, N. W. Ockwig, M. O’Keeffe, A. J. Matzger and O. M. Yaghi, Science, 2005, 310, 1166–1170.
13 R. Mas-Ballestre, C. Gomez-Navarro, J. Gomez-Herrero and F. Zamora, *Nanoscale*, 2011, 3, 20–30.
14 D. J. Tranchemontagne, J. L. Mendoza-Cortes, M. O’Keeffe and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, 38, 1257–1283.
15 J. W. Colson and W. R. Dichtel, *Nat. Chem.*, 2013, 5, 453–465.
16 S. R. Batten, S. M. Neville and D. Turner, *Coordination Polymers: Design, Analysis and Applications*, RSC Publishing, 2009.
17 A. U. Czaja, N. Trukhan and U. Muller, *Chem. Soc. Rev.*, 2009, 38, 1284–1293.
18 A. Carne, C. Carbonell, I. Imaz and D. Maspoch, *Chem. Soc. Rev.*, 2011, 40, 291–305.
19 R. Mas-Ballestre, J. Gomez-Herrero and F. Zamora, *Chem. Soc. Rev.*, 2010, 39, 4220–4233.
20 M. Lackinger and W. M. Heckl, *J. Phys. D: Appl. Phys.*, 2011, 44, 464011.
21 S. Stepanow, M. Lingenfelder, A. Dmitriev, H. Spillmann, E. Delvigne, N. Lin, X. B. Deng, C. Z. Cai, J. V. Barth and K. Kern, *Nat. Mater.*, 2004, 3, 229–233.
22 T. Bauer, Z. K. Zheng, A. Renn, R. Enning, A. Stemmer, J. Sakamoto and A. D. Schluter, *Angew. Chem., Int. Ed.*, 2011, 50, 7879–7884.
23 Z. Zheng, C. S. Ruiz-Vargas, T. Bauer, A. Rossi, P. Payamyar, A. Schütz, A. Stemmer, J. Sakamoto and A. D. Schluter, *Macromol. Rapid Commun.*, 2013, 34, 1670–1680.
24 Z. K. Zheng, L. Opilik, F. Schiffmann, W. Liu, G. Bergamini, P. Ceroni, L. T. Lee, A. Schütz, J. Sakamoto, R. Zenobi, J. VandeVondele and A. D. Schluter, *J. Am. Chem. Soc.*, 2014, 136, 6103–6110.
25 P. Amo-Ochoa, L. Welte, R. González-Prieto, P. J. Sanz Miguel, C. J. Gómez-Garcia, E. Mateo-Martí, S. Delgado, J. Gómez-Herrero and F. Zamora, *Chem. Commun.*, 2010, 46, 3262–3264.
26 P. Z. Li, Y. Maeda and Q. Xu, *Chem. Commun.*, 2011, 47, 8436–8438.
27 J. C. Tan, P. J. Saines, E. G. Bithell and A. K. Cheetham, *ACS Nano*, 2012, 6, 615–621.
28 P. J. Beldon, S. Tominaka, P. Singh, T. S. Dasgupta, E. G. Bithell and A. K. Cheetham, *Chem. Commun.*, 2014, 50, 3955–3957.
29 A. Gallego, C. Hermosa, O. Castillo, I. Berlanga, C. J. Gómez-García, E. Mateo-Martí, J. I. Martinez, F. Flores, C. Gómez-Navarro, J. Gómez-Herrero, S. Delgado and F. Zamora, *Adv. Mater.*, 2013, 25, 2141–2146.
30 I. Horcas, R. Fernandez, J. M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero and A. M. Baro, *Rev. Sci. Instrum.*, 2007, 78, 013705.
31 J. W. Suk, R. D. Piner, J. An and R. S. Ruoff, *ACS Nano*, 2010, 4, 6557–6564.
32 C. Lee, X. D. Wei, J. W. Kysar and J. Hone, *Science*, 2008, 321, 385–388.
33 P. Li, Z. You, G. Haugstad and T. H. Cui, *Appl. Phys. Lett.*, 2011, 98, 253105.
34 A. Turchanin, A. Beyer, C. T. Nottbohm, X. H. Zhang, R. Stosch, A. Sologubenko, J. Mayer, P. Hinze, T. Weimann and A. Golzhauser, *Adv. Mater.*, 2009, 21, 1233–1237.
35 P. Payamyar, K. Kaja, C. Ruiz-Vargas, A. Stemmer, D. J. Murray, C. J. Johnson, B. T. King, F. Schiffmann, J. VandeVondele, A. Renn, S. Gotzinger, P. Ceroni, A. Schütz, L. T. Lee, Z. K. Zheng, J. Sakamoto and A. D. Schluter, *Adv. Mater.*, 2014, 26, 2052–2058.
36 E. Cadelano and L. Colombo, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, 85, 245434.
37 D. Graf, F. Molitor, K. Ensslin, C. Stampfer, A. Jungen, C. Hierold and L. Wirtz, *Nano Lett.*, 2007, 7, 238–242.
38 C. Lee, H. Yan, L. E. Brus, T. F. Heinz, J. Hone and S. Ryu, *ACS Nano*, 2010, 4, 2695–2700.
39 R. Leino and J. E. Lonnqvist, *Tetrahedron Lett.*, 2004, 45, 8489–8491.