SUPPLEMENTARY INFORMATION

2D magnetic MOFs with micron-lateral size by liquid exfoliation

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1. Materials and synthesis

1.1 Synthesis of bulk MUV-1-X

The materials were synthesized following the procedure previously reported by our group. We use ferrocene (0.16 mmol) and the appropriate derivative of the benzimidazole (0.34 mmol) is combined and sealed under vacuum in a layering tube (4 mm diameter). The mixture is heated at 250 °C for 3 days to obtain colorless crystals suitable for X-ray single-crystal diffraction. The product was cooled down naturally to room temperature, and the layering tube is then opened. The unreacted precursors are extracted with acetonitrile and benzene, and the main compound is isolated as colorless crystals (typical yield 80 %). Phase purity is established by X-ray powder diffraction.



Supplementary Figure 1. Schematic via of synthesis of the different members of **MUV-1-X** family, where X = Cl, Br, H and CH₃.

1.2 Standard protocol for 2D exfoliation of MUV-1 X

In all delaminations parameters were changed to analyse their effects and look for the optimum for the system. Unless otherwise specified, the conditions used in the exfoliation were: 2.5 mg of **MUV-1-X** material, 20 mL of acetone, 1 hour of sonication bath at low temperature using an ice bath and storing refrigerated exfoliation

2. Nanosheets characterization

2.1. Methods of liquid exfoliation and obtention of MUV-1-X family

2.1.1. Sonication bath

The sonic bath used for sonication is the Branson Model 5510 Ultrasonic Cleaner, with Mechanical Timer, 117V, and a fixed constant power of 40 KHz. This equipment facilitates solvent-material interaction causing delamination.

2.1.2. Sonication tip

750 Ultrasonic Processor Watt from the Thomas scientific company with b220 tip is used for sonic studies. This equipment works at a frequency of 20KHz, but in this case the amplitude can be modulated, reaching 50 times higher energies than in the sonic bath. This equipment facilitates solvent-material interaction causing delamination

2.1.3. Spin coating

The SCC-200 spin coater equipment connected to a vacuum system is used for all depositions, which are carried out on silicon oxide substrates at 25 rps using 10 μ l of the centrifugated solution with the exfoliated nanosheets. This technique allows to avoid depositing the material by removing the solvent quickly, thus avoiding accumulations of material and solvent, in addition to being much more distributed throughout the substrate.

2.1.4. Centrifuge

The centrifuge 5810 R of the Eppendorf company is used, which allows to control the temperature and reach 14000 rpm. This technique is used to carry out the sedimentation studies of the material once exfoliated.

2.2. Physical characterization of nanosheets

2.2.1. Raman spectroscopy

Raman spectra are acquired with a micro-Raman (model XploRA ONE from Horiba, Kyoto, Japan) with a grating of 2400 gr/mm, slit of 50 μ m, and hole of 500 μ m. The employed wavelength was 532 nm. The power density of the laser used for spectra measured at 532 nm was 170 μ W/ μ m². This technique allows to verify that the material has not been damaged after the exfoliation process.

2.2.2. Transmission Electronic Microscopy

The TEM images of **MUV-1-X** were taken with the JEM-1010 (JEOL) transmission electron microscope with AMT RX80 digital camera (8Mpx). at 80kV. The exfoliated material was deposited in a grid of Lacey Formvar / Carbon, 300 mesh, Copper approx. grid hole size: $63\mu m$.

The diffraction patterns were taken TECNAI G2 F20 (FEI) 200kV field emission transmission electron microscope (FEG) with a resolution (Point Resolution) of 0.24nm. It is equipped with a GATAN CCD camera and "Digital Micrograph" image acquisition and processing software. This technique allows to analyse the morphology and thickness of the nanosheets.

2.2.3. Optical Microscopy

Optical images are obtained with a NIKON Eclipse LV-100 Optical microscope, with which it can be observed, roughly, the height, by contrast, and lateral size of the flakes.

2.2.4. Atomic Force Microscopy

AFM measurements are collected in a Multimode atomic force microscope (Veeco instruments, Inc.). The images are obtained with a Si tip (frequency and K of ca. kHz and $42 \text{ N} \cdot \text{m}^{-1}$, respectively) using the tapping- mode in air at room temperature. Images are recorded with a 0.5-1 Hz scan rate. Processing and analysis of the images are carried out using the Nanotec WSXM-4.0 Beta. 6.5 software. With the AFM microscope the thickness of the nanosheets are studied.

2.2.5. Electron Paramagnetic Resonance: EPR spectroscopy measurements were recorded with a Bruker ELEXYS E580 spectrometer operating in the Q band (34 GHz).

3. Important parameters of liquid exfoliation (MUV-1-Cl)

3.1. Sonication study



Supplementary Figure 2. Optical images of **MUV-1-Cl** delaminated with the sonication bath. Optical scale bars are 10 µm.



Supplementary Figure 3. Optical images of MUV-1-Cl delaminated with the sonication tip. Optical scale bars are $10 \ \mu m$.

3.2. Solvent study

3.2.1. Water

When using water as a solvent, the Raman spectrum indicates that the structure is deteriorated.



Supplementary Figure 4. Raman study of MUV-1-Cl flakes delaminated in H_2O . Optical scale bars are 5 μ m. The Raman spectrum of the solid is shown in blue, whereas the Raman spectrum of the substrate is shown in black. The arrows/shaded regions indicate the position of the bands characteristic of MUV-1-Cl, which are absent in this case. The green dot in the optical images indicate the regions where the Raman spectra have been measured.



Supplementary Figure 5. Optical images of MUV-1-Cl delaminated with H_2O . Optical scale bars are 5 μ m.



Supplementary Figure 6. TEM image of MUV-1-Cl delamintade with H₂O.

3.2.2. Diethyl ether

When using Et_2O as a solvent, the Raman spectrum indicates that the structure is deteriorated.



Supplementary Figure 7. Raman study of **MUV-1-Cl** flakes delaminated in Et_2O . Optical scale bars are 5 μ m. The Raman spectrum of the solid is shown in pink, whereas the Raman spectrum of the substrate is shown in black. The shaded regions indicate the position of the bands characteristic of **MUV-1-Cl**, which are absent in this case. The green dot in the optical images indicate the regions where the Raman spectra have been measured.



Supplementary Figure 8. Optical images of MUV-1-Cl delaminated with Et_2O . Optical scale bars are 10 μ m.



Supplementary Figure 9. TEM images of MUV-1-Cl with Et₂O. TEM scale bars are 2 μm .

3.2.3. Methanol

When using methanol as a solvent, the Raman spectrum indicates that the structure is maintained after the exfoliation.



Supplementary Figure 10. Raman study of **MUV-1-Cl** flakes delaminated in methanol. Optical scale bars are 5 μ m. The Raman spectrum of the solid is shown in green, whereas the Raman spectrum of the substrate is shown in black. The shaded regions indicate the position of the bands characteristic of **MUV-1-Cl**. The green dot in the optical images indicate the regions where the Raman spectra have been measured.



Supplementary Figure 11. Optical images of MUV-1-Cl nanosheets delaminated with methanol. Optical scale bars are $10 \ \mu m$



Supplementary Figure 12. TEM images of MUV-1-Cl. TEM scale bars are 4 µm

3.2.4. Propanol

When using propanol as a solvent, the Raman spectrum indicates that the structure is maintained after the exfoliation.



Supplementary Figure 13. Raman study of **MUV-1-Cl** flakes delaminated in propanol. Optical scale bars are 5 μ m. The Raman spectrum of the solid is shown in green, whereas the Raman spectrum of the substrate is shown in black. The shaded regions indicate the position of the bands characteristic of **MUV-1-Cl**. The green dot in the optical images indicate the regions where the Raman spectra have been measured.



Supplementary Figure 14. Optical images of **MUV-1-Cl** delaminated with propanol. Optical scale bars are 10 µm.



Supplementary Figure 15. TEM images of MUV-1-Cl with propanol. TEM scale bars are 2 μ m.

3.2.5. Acetonitrile

When using methanol as a solvent, the Raman spectrum indicates that the structure is maintained after the exfoliation.



Supplementary Figure 16. Raman study of **MUV-1-Cl** flakes delaminated in CH_3CN . Optical scale bars are 5 μ m. The Raman spectrum of the solid is shown in red, whereas the Raman spectrum of the substrate is shown in black. The shaded regions indicate the position of the bands characteristic of **MUV-1-Cl**. The green dot in the optical images indicate the regions where the Raman spectra have been measured.



Supplementary Figure 17. Optical images of **MUV-1-Cl** delaminated with CH₃CN. Optical scale bars are 10 μm.



Supplementary Figure 18. TEM images of MUV-1-Cl with CH₃CN. TEM scale bars are 2 μ m.

3.3. Chemical stability of the flakes after the exfoliation



Supplementary Figure 19. Raman study of **MUV-1-Cl** nanosheets exfoliated in propanol for three days, the chemical structure is lost almost entirely on the third day. Optical scale bars are 10 μ m. The Raman spectrum of the solid is shown in orange, whereas the Raman spectrum of the substrate is shown in black. The shaded regions indicate the position of the bands characteristic of **MUV-1-Cl**. The green dot in the optical images indicate the regions where the Raman spectra have been measured.

Transmission electronic microscopy images with CH₃CN as solvent.



Supplementary Figure 20. TEM images of MUV-1-Cl nanosheets exfoliated in propanol, on the 8^{th} day there is already a clear degradation of the nanosheets. TEM scale bars are 2 μ m.



Supplementary Figure 21. Image showing the change in colour of the solution that indicates the degradation of the material.



Supplementary Figure 22. Raman study of **MUV-1-Cl** nanosheets exfoliated in acetone, which maintain their composition for 10 days. Optical scale bars are 10 μ m. The Raman spectrum of the solid is shown in orange, whereas the Raman spectrum of the substrate is shown in black. The shaded regions indicate the position of the bands characteristic of **MUV-1-Cl**. The green dot in the optical images indicate the regions where the Raman spectra have been measured.



Supplementary Figure 23. TEM images of **MUV-1-Cl** nanosheets exfoliated in acetone, without degradation for 10 days. TEM scale bars are 2 µm.

Solvent	Exfoliation	Stability just after the exfoliation	Stable for several days in solution
Hexane	X	X	X
Dicholoromethane	X	X	X
Tetrahydrofurane	X	X	X
Dimethylformamide	X	X	X
Water		X	X
Diethyl ether		X	X
Methanol			X
Propanol			X
Acetonitrile			
Acetone			

Supplementary Table 1. Summary of the behaviour of the **MUV-1-Cl** during and after the delamination process using different solvents.

3.4. Sonication study

Exfoliation study using different exfoliation times: 15, 30, 60, 120 and 240 minutes.

3.4.1. 15 minutes

Transmission electronic microscopy images of different flakes subjected to a 15-minute exfoliation process.



Supplementary Figure 24. TEM images of **MUV-1-Cl** with acetone for 15 minutes. TEM scale bars are 2 µm.

Optical images of different flakes subjected to a 15-minute exfoliation process.



Supplementary Figure 25. Optical images of **MUV-1-Cl** delaminated with acetone for 15 minutes. Optical scale bars are 10 µm.

3.4.2. 30 minutes

Transmission electronic microscopy images of different flakes subjected to a 30-minute exfoliation process.



Supplementary Figure 26. TEM images of **MUV-1-Cl** with acetone for 30 minutes. TEM scale bars are 2 µm.

Optical images of different flakes subjected to a 30-minute exfoliation process.



Supplementary Figure 27. Optical images of **MUV-1-Cl** delaminated with acetone for 30 minutes. Optical scale bars are 10 µm.

3.4.3. 60 minutes

Transmission electronic microscopy images of different flakes subjected to a 60-minute exfoliation process.



Supplementary Figure 28. TEM images of **MUV-1-Cl** with acetone for 60 minutes. TEM scale bars are 2 µm.

Optical images of different flakes subjected to a 60-minute exfoliation process.



Supplementary Figure 29. Optical images of **MUV-1-Cl** delaminated with acetone for 60 minutes. Optical scale bars are 10 µm.

3.4.4. 120 minutes

Transmission electronic microscopy images of different flakes subjected to a 120-minute exfoliation process.



Supplementary Figure 30. TEM images of **MUV-1-Cl** with acetone for 120 minutes. TEM scale bars are 2 µm.

Optical images of different flakes subjected to a 120-minute exfoliation process.



Supplementary Figure 31. Optical images of **MUV-1-Cl** delaminated with acetone for 120 minutes. Optical scale bars are 10 µm.

3.4.5. 240 minutes

Transmission electronic microscopy images of different flakes subjected to a 240-minute exfoliation process.



Supplementary Figure 32. TEM images of **MUV-1-Cl** with acetone for 240 minutes. TEM scale bars are 2 µm.

Optical images of different flakes subjected to a 240-minute exfoliation process.



Supplementary Figure 33. Optical images of **MUV-1-Cl** delaminated with acetone for 240 minutes. Optical scale bars are 10 µm.

3.5. Exfoliation study based on the initial amount of material

Study with different amount of **MUV-1-C**l material in acetone, sounding for 1 hour. The study is done with 1.25, 2.5, 5, 10 and 15 mg. All samples were centrifuged at 8000 rpm for 1 hour.



Supplementary Figure 34. Optical images of MUV-1-Cl delaminated with acetone using different amounts of material 0,0625 mg/mL (a), 0,125 mg/mL (b), 0,25 mg/mL (c), 0,5 mg/mL mg (d) and 0,75 mg/mL (e). Optical scale bars are 10 μ m.

3.6. Centrifugation study

The centrifugation study was carried out under different conditions, seeking to optimize the separation of the exfoliated material from the non-exfoliated material.

First, the deposition was studied without centrifuging the material.



Supplementary Figure 35. Optical images of MUV-1-Cl delaminated with acetone for 60 min without centrifugation. Optical scale bars are $10 \mu m$.





Supplementary Figure 36. Optical images of MUV-1-Cl delaminated with acetone for 60 min centrifuging at 1500 rpm for 15 min (a), 30 min (b) and 60 min (c). Optical scale bars are 10 μ m.

3.6.2. 5000 rpm

Supplementary Figure 37. Optical images of **MUV-1-Cl** delaminated with acetone for 60 min centrifuging at 5000 rpm for 15 min (a), 30 min (b) and 60 min (c). Optical scale bars are 10 μ m.

3.6.3. 8000 rpm

Supplementary Figure 38. Optical images of **MUV-1-Cl** delaminated with acetone for 60 min centrifuging at 8000 rpm for 15 min (a), 30 min (b) and 60 min (c). Optical scale bars are 10 μ m.

3.6.4. 10000 rpm

Supplementary Figure 39. Optical images of **MUV-1-Cl** delaminated with acetone for 60 min centrifuging at 10000 rpm for 15 min (a), 30 min (b) and 60 min (c). Optical scale bars are 10 μ m.

3.6.5. TEM study of the centrifuged material at 5000, 8000 and 10000 rpm for 1 hour.

Supplementary Figure 40. TEM of **MUV-1-Cl** delaminated with acetone for 60 min centrifuging at 5000 rpm for 60 min. TEM scale bars are 2 µm.

Supplementary Figure 41. TEM of **MUV-1-Cl** delaminated with acetone for 60 min centrifuging at 8000 rpm for 60 min. TEM scale bars are 2 µm.

Supplementary Figure 42. TEM of MUV-1-Cl delaminated with acetone for 60 min centrifuging at 10000 rpm for 60 min. TEM scale bars are 2 μ m.

3.7. TEM and optical images of large amounts of nanosheets

Supplementary Figure 43. TEM images of **MUV-1-Cl** exfoliated in acetone for 1 hour, many few-layers nanosheets are observed. TEM scale bars are $2 \mu m$.

Supplementary Figure 44. TEM images of **MUV-1-Cl** exfoliated in acetone for 1 hour, many few-layers nanosheets are observed. TEM scale bars are 4 µm.

Supplementary Figure 45. Optical image of **MUV-1-Cl** exfoliated in acetone for 1 hour, many few- layers nanosheets are observed. Optical scale bars are 20 μ m.

3.8. Large number and lateral size of exfoliated nanosheets

3.8.1. Optical and Atomic Force Microscopy of MUV-1-Cl with flakes of different thicknesses.

Supplementary Figure 46. Few layers Atomic Force Microscopy images of **MUV-1-Cl** flakes with its corresponding height profiles. Optical scale bars are 10µm. AFM scale bars are 2µm.

Supplementary Figure 47. Few layers Atomic Force Microscopy image of MUV-1-Cl flake with its corresponding height profiles. Optical scale bar is 10 μ m. AFM scale bar are 2μ m.

Supplementary Figure 48. Few layers Atomic Force Microscopy image of **MUV-1-Cl** flakes with its corresponding height profiles. AFM scale bars are 2µm.

4. Characterization of metal organic nanosheets of MUV-1-X

4.1. Selected Area Diffraction Pattern (SAED) and Energy Dispersive X-ray Analysis (EDX) of MUV-1-X

All family members were characterized using selected areal electron diffraction. In addition, Dispersive X-ray Analysis was performed on MUV-1-Br and MUV-1-Cl to analyze what proportion they are in.

Supplementary Figure 49.TEM and SAED of a flake of MUV-1-CH₃. TEM scale bar is 1 μ m. SAED scale bar is 1 nm⁻¹.

Supplementary Figure 50. SAED, theoretical diffraction patterns along the [001] direction, TEM, and EDX, of a flake of **MUV-1-Cl**. TEM scale bar is 1 μ m. SAED scale bar is 1 nm⁻¹. Indexing of the diffraction pattern has been performed with SingleCrystal 3.0.

Supplementary Figure 51. EDX, TEM and SAED of a flake of MUV-1-H. TEM scale bar is 1 μ m. SAED scale bar is 1 nm⁻¹.

Supplementary Figure 52. EDX, TEM and SAED of a flake of **MUV-1-Br**. TEM scale bar is 1 μ m. SAED scale bar is 1 nm⁻¹.

4.2. Optical of MUV-1-Br, MUV-1-CH₃ and MUV-1-H.

Supplementary Figure 53. Optical images of $MUV-1-CH_3$ delaminated with acetone. Optical scale bars are 10 μ m.

Supplementary Figure 54. Optical images of MUV-1-H delaminated with acetone. Optical scale bars are $10 \ \mu m$.

Supplementary Figure 55. Optical images of MUV-1-Br delaminated with acetone. Optical scale bars are $10 \ \mu m$.

4.3. Raman and Atomic Force Microscopy of MUV-1-X

Supplementary Figure 56. AFM and Raman study of thickness of $MUV-1-CH_3$ flakes. AFM scale bars are $2\mu m$. The shaded regions indicate the position of the bands characteristic of $MUV-1-CH_3$.

Supplementary Figure 57. AFM and Raman study of thickness of **MUV-1-Cl** flakes. AFM scale bars are $2\mu m$. The shaded regions indicate the position of the bands characteristic of **MUV-1-Cl**.

Supplementary Figure 58. AFM and Raman study of thickness of **MUV-1-H** flakes. AFM scale bars are $2\mu m$. The shaded regions indicate the position of the bands characteristic of **MUV-1-H**.

Supplementary Figure 59. AFM and Raman study of thickness of **MUV-1-Br** flakes. AFM scale bars are $2\mu m$. The shaded regions indicate the position of the bands characteristic of **MUV-1-Br**.

4.4. Transmission electron Microscopy of MUV-1-X

Supplementary Figure 60. TEM of different flakes of MUV-1-CH₃. Scale bars are 2 μ m.

Supplementary Figure 61. TEM of different flakes of MUV-1-Cl. Scale bars are 2µm.

Supplementary Figure 62. TEM of different flakes of MUV-1-H. Scale bars are 2 μ m.

Supplementary Figure 63. TEM of different flakes of MUV-1-Br. Scale bars are 2 μ m.

Supplementary Figure 64. From left to right are the characterization of the different members of the family MUV-1-CH₃, MUV-1-H, MUV-1-Cl and MUV-Br. From top to down. Raman spectra for MUV-1-X flakes with different thicknesses, AFM images and height profiles of different flakes of MUV-1-X. Low-magnification TEM image for MUV-1-X flakes with its correspondents selected area electron diffraction (SAED).

5. Electron Paramagnetic Resonance

The EPR were performed with all the optimized exfoliation conditions previously described, using 2,5 mg of **MUV-1-Cl** which were sonicated for 1 hour in 20 mL of anhydrous acetone. After exfoliating, about 2 mL of the suspension were taken from the top of the solution and introduced in an EPR tube.

Supplementary Figure 65. EPR spectra of a dispersion of few layers **MUV-1-Cl** at different temperatures, showing the characteristic sextet of Mn^{2+} (which is an impurity present in acetone, see Figure S50). Upon magnetic ordering of the flakes, a clear shift to lower magnetic fields is observed. The image on the right is an enlargement of the one of the left.

Supplementary Figure 66. EPR spectra at 4K of a solution of pure acetone (the same that is used as solvent for exfoliating the flakes). The signal corresponds to a Mn^{2+} impurity.