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Authors: Rahul Banerjee, Bikash Garai, Arjit Mallick, Anuja Das, and Rabibrata Mukherjee

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# Self-exfoliated metal organic nanosheets *via* hydrolytic unfolding of metal organic polyhedra

Bikash Garai,<sup>[a,b]</sup> Arijit Mallick,<sup>[a,b]</sup> Anuja Das,<sup>[c]</sup> Rabibrata Mukherjee<sup>[c]</sup> and Rahul Banerjee<sup>\*[a,b]</sup>

**Abstract:** Few layer thick metal-organic nanosheets have been synthesized using water-assisted solid state transformation through a combined top-down and bottom-up approach. The metal-organic polyhedra (MOPs) convert into metal-organic frameworks (MOFs) which subsequently self-exfoliate into few layered metal-organic nanosheets. These MOP crystals experience a hydrophobicity gradient with the inner surface during contact with water because of the existence of hydrophobic spikes on their outer surface. When the amount of water available for interaction is higher, the resultant layers are not stacked to form bulk materials; instead few layered nanosheets with high uniformity were obtained in high yield. The phenomenon has resulted high yield production of uniformly distributed layered metal-organic nanosheets from three different MOPs, showing its general adaptability.

#### Introduction

Two-dimensional layered nanostructured materials have recently gained attention because of their potential for applications in various emerging fields such as optoelectronics. energy storage, ultrafiltration, semiconductors, supercapacitors and photovoltaic cells.<sup>[1]</sup> In general, two-dimensional layered bulk structures are grown by deposition of individual layers one by one through non-covalent interactions like hydrogen bonding.  $\pi$ - $\pi$  stacking, Van-der Waals and dipole-dipole interactions.<sup>[2]</sup> Although these interactions are 'weak' in comparison to the covalent bonding between atoms; the energy required to separate these layers in mono- or a few-layered stacks is significant.<sup>[2]</sup> Traditionally, the required energy for such delamination is supplied in the form of mechanical grinding, mechanical shearing, ultrasonication, and intercalation assisted peeling.<sup>[3]</sup> In all these cases, the bulk materials are separated into discrete layers and thus these methods have been categorised as a 'top-down approach'.[4] Such few layered nanostructures could also be synthesised via 'bottom-up approach' where the deposition of subsequent layers is restricted after the formation of the 1<sup>st</sup> layer.<sup>[5]</sup> These approaches include chemical vapour deposition, templated growth and

[a]	B. Garai, A. Mallick, Dr. R. Banerjee
	Physical and Materials Chemistry Division
	CSIR-National Chemical Laboratory
	Dr. Homi Bhabha Road, Pune-411008, India
	E-mail: r.banerjee@ncl.res.in
[b]	B. Garai, A. Mallick, Prof. Dr. R. Banerjee
	Academy of Scientific and Innovative Research (AcSIR)
	New Delhi, India

[c] A. Das, Prof. Dr. R. Mukherjee Instability and Soft Patterning Laboratory Department of Chemical Engineering Indian Institute of Technology, Kharagpur Kharagpur, India

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interfacial growth.<sup>[6]</sup> In recent years, research on delaminated layered metal-organic framework (MOF) structures<sup>[7]</sup> has gained attention because of their promising use in gas-separation, molecular sieving and isotope separation.<sup>[8]</sup> The performance of these materials in terms of separation–efficiency and catalysis





on active surfaces increases drastically when the separated layers are used over the bulk materials.<sup>[9]</sup> Routes utilized to obtain such MOF nanosheets include both 'top-down' and 'bottom-up' approaches but both these processes have their individual limitations.<sup>[10]</sup> In the top-down approach, the nanosheets are obtained with a good yield but it is difficult to control their thickness and therefore the generated nanostructures are non-uniform. On the other hand, nanosheets with uniform and controllable thickness are generated through bottom-up approaches, but the processes, in general, require difficult experimental set up. Thus, the synthesis of metalorganic nanosheets in high yield with uniform and controllable thickness in an efficient way requires a combination of both topdown and bottom-up approaches. However, because of their divergent nature, till date it has not been possible to combine both these approaches into a single unified approach. Herein, we have made an effort to combine both these approaches under one synthetic domain to convert metal-organic polyhedra (MOPs)<sup>[11]</sup> directly into two-dimensional metal-organic nanosheets with a few nm thickness in high yield and uniform morphological dispersion.  $\ensuremath{^{[12]}}$ 

#### **Results and Discussion**

Blue-colored crystals of the MOPs (MOP-MIA, MOP-EIA, MOP-PrIA) are readily synthesized from the solvothermal reaction between copper (II) nitrate and the corresponding organic linkers, 5-methoxy isophthalic acid (5-MIA), 5-ethoxy isophthalic acid (5-EIA) and 5-(*n*-propyloxy) isophthalic acid (5-PrIA), respectively in mixed DMF solvent at 90 °C (figure 1). MOP-MIA is obtained as orthorhombic crystals while MOP-EIA and MOP-PrIA are separated as polyhedral crystals (section S2 in ESI) after 48 h. The polyhedral architecture in all these MOPs is constructed from the co-ordination between metal ions and the organic linkers through the formation of a Cu-Cu paddle wheel SBU. These MOP units exist as discrete ones, describing their zero-dimensional architecture. The edges of each polyhedral architecture is defined by 6 square shaped faces and



Figure 2. Monitoring of the hydrolytic conversion through time dependent PXRD for (a) MOP-MIA, (b) MOP-EIA, and (c) MOP-PrIA. (d) The mechanism for the conversion of alkyloxy decorated MOPs into MOFs. Scanning electron microscopic images for monitoring the conversion of (e) MOP-MIA, (f) MOP-EIA, and (g) MOP-PrIA.

8 triangular faces. The alkyl groups from the ligands are located on the centre of the edges and are pointed outwards (figure 1). MOP-MIA was crystallized in the *P*-1 space group with 2 MOP units per unit cell, whereas MOP-EIA and MOP-PrIA were crystallized in *Pa*-3 space group having 4 MOP units in the unit cell.

When these polyhedral MOP crystals are treated with a measured amount of water (50 µL/mg), small sized [0.2 x 0.2 x 0.1 mm<sup>3</sup>] MOF crystals start forming after 10 min. The assynthesized crystals of the MOPs turn opaque after the initial contact with water. With time, the opacity of the MOP crystals increases and they finally split into crystals of the corresponding bulk MOF materials (figure 2). This conversion proceeds through an amorphous phase (figure 2a, 2b, 2c) observed during the opacity loss of the parent MOP crystals. Notably, this whole conversion occurs through an all-solid-state pathway, where no component of the starting materials dissolves in water, as evidenced from the UV-vis spectra of the collected filtrate (figure S13 in ESI). As the amount of water added to the system is increased, the thickness of the resulting MOF crystals starts decreasing and beyond a certain water concentration (1.5 mL/mg), no solid particles are visually observed. However, the Tyndall effect (figure 4b) from the obtained liquid indicates the presence of solid particles as dispersion in the aqueous medium. Although the nanometer scale size of these particles makes their structural characterization challenging, the respective successor MOF crystals were analyzed structurally through single crystal X-ray diffraction. MOF-MIA crystallizes in the P4/n space group generating square shaped pores [8 x 8 Å<sup>2</sup>], while MOF-EIA and MOF-PrIA crystallize in the P321 and P-3 space group, respectively. For the case of MOF-EIA and MOF-PrIA, two types of pores were found in their structure; the pore with bigger aperture [11.3 x 4.1 Å<sup>2</sup>] has hexagonal geometry and contains all the alkyloxy groups pointed towards the pore centre. The other set of pores are triangular [5.2 x 5.1 Å<sup>2</sup>] and contains only coordinated water molecules from the paddle wheel SBUs. All these MOFs have two dimensional layered structures and the stacking of the molecular layers generate channels in their extended form (figure S1-S3 in ESI).

The phase purity of all the as-synthesized MOPs and the resulted MOF crystals has been confirmed by matching the experimentally observed PXRD patterns with the corresponding simulated patterns (figure S4 and S5 in ESI). Some peaks in the observed MOP PXRD pattern remain unindexed because of higher thermal disorder of the alkyloxy groups and the non coordinated solvent molecules.[13] FT-IR spectra of the assynthesized MOP crystals reveal that the carboxylic O-H signal centred at 2900 cm<sup>-1</sup> disappears because of the co-ordination with metal ions. This co-ordination also causes a red-shift of the carboxylic acid C=O peak by 60 cm<sup>-1</sup>. No additional signal is observed in the FT-IR spectra after the conversion of the MOPs into the MOFs (figure S7-S10 in ESI). This phenomenon indicates the similarity in the chemical environment and bonding in the MOPs and the corresponding MOFs. Retention of the peaks for the alkyloxy O-C bond at 1054 and 1375 cm<sup>-1</sup> also suggests that the alkyloxy groups do not get fragmented during the conversion. All these MOPs are found to be thermally stable



Figure 3. N<sub>2</sub> adsorption isotherm for MOP-EIA. The available surface area as per BET equation is 450  $m^2g^{-1}.$ 

upto 300 °C with removal of trapped and coordinated solvent molecules (figure S11 in ESI). However, the thermal stability gets enhanced to 450 °C for the case of bulk MOFs (figure S12 in ESI). Thermal removal of the solvent molecules from the MOP core results in the gain of readily accessible surface and pores for incoming guest and other molecules. Adsorption of N<sub>2</sub> by MOP-EIA measures an availability of 450 m<sup>2</sup>g<sup>-1</sup> surface as per the BET equation, one of the highest values reported till date for discrete MOPs (figure 3).<sup>[14]</sup> The available surface areas for the other two MOPs are less and this variation of the surface area results from the stability of the MOP units that originated from their crystal packing. MOP-EIA has a closely packed structure where the distance between adjacent MOP units is minimal [8.5 x 8.5 x 8.5  $Å^3$ ]. A similar spacing box bears a dimension of 8.4 x 12.9 x 21.0 and 11.0 x 9.0 x 8.6 Å<sup>3</sup> for MOP-MIA and MOP-PrIA, respectively (figure 1e, 1f and 1g). This close packing reduces the interstitial voids and minimizes the possibility of structural collapse during removal of solvent.

As evidenced from the structure of MOPs, the hydrophobic alkyl functionalities located on the outer surface of the MOPs are in a disfavoured situation as they directly face the incoming water molecules. On the other hand, for the less hydrophobic inner surface, water contact should be a favourable situation. Thus, a strain gets developed between the two surfaces and in order to minimize this strain, the system tries to equally distribute the hydrophobic groups among the two surfaces. This equalization is achieved through the mechanism explained in figure 2d.<sup>[11]</sup> Thus, from each MOP crystal, several layers of MOFs are formed and are parallely arranged as per their packing along the corresponding crystal planes.

It is evident from figure 4a that MOP units from the bulk crystals first unfold to minimize the surface strain upon interaction with water through the combination of hydrophobic repulsion and hydration pressure to generate an amorphous phase. The neighboring MOP units join along the

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Figure 4. (a) Schematic representation for the generation of MOF and MOF nanosheets from the MOP crystal under influence of different quantity of water. (b) Tyndall effect showing existence of nanoscopic particles in the aqueous suspension of MOF nanosheets. (c, d, e) TEM images of the nanosheets derived from MOP-MIA, -EIA and -PrIA, respectively. Rendered 3D topographic AFM image, obtained in intermittent contact mode showing the cross-sectional profile for (f) MIA-NS, (g) EIA-NS and (h) PrIA-NS.

crystallographic axes through unfolding of the closed structures and causes the generation of extended nanosheets. When the amount of water present in the system is limited, the conversion occurs at controlled rate because of the slower diffusion of water. This result in the generation of properly grown MOF layers, well stacked to produce micrometer sized single crystals. However, when the water content is higher, the excess amount of water does not allow the layers to stack upto the full extent which is required for the growth of the single crystals of the MOFs. As a result, the metal-organic nanosheets remain dispersed in water forming an aqueous suspension. The absence of stacking in their extended form causes the diminishing of the PXRD peak at  $2\theta$  = 5°, corresponding to the 100 plane (figure S6 in ESI). However, their chemical bonding and the chemical environment

around each functional moiety remains intact, as evidenced from the similar FT-IR spectra as that of the corresponding bulk MOFs. SEM images of the nanostructures clearly indicate their hexagonal morphology and that with time these structures are getting peeled-off from the bulk MOP materials and finally form the 2-dimensional sheets with nm scale thickness (figure 2e, 2f and 2g). TEM imaging provides an input about their lateral dimension and the nanosheets are found to have aspect of 1.7 x 1.7  $\mu$ m<sup>2</sup> for MIA-NS, 2.0 x 2.0  $\mu$ m<sup>2</sup> form EIA-NS and 1.8 x 1.8  $\mu$ m<sup>2</sup> for PrIA-NS (figure 4c, 4d and 4e). The statistical variation in the dimension of the nanosheets has been determined using an AFM, by scanning several samples derived from each of the sources. The average height of the features are found to be 15.3  $\pm$  1.2 nm, 17.2  $\pm$  1.1 nm and 11.8  $\pm$  0.6 nm for sheets obtained

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from MOP-MIA, -EIA and -PrIA respectively. The error bar corresponds to the standard deviation of the data over all the samples. The aspect of the features were also verified from the AFM, by taking the average over many samples, and their values were found to be rather close to that obtained from TEM analysis (Aspect: 1.63  $\pm$  0.21  $\mu$ m for MIA-NS, 1.96  $\pm$  0.16  $\mu$ m for EIA-NS and 1.82  $\pm$  0.13  $\mu$ m for PrIA-NS) shown in figures 4c-4e. The molecular thickness of each layer has been calculated as 2.0 nm from the crystal structure. Hence we could clearly say that each of these nanosheets contain around 6-8 stacks of the molecular layers. While figure 4f-4h shows the detailed AFM image of a single sheet, image of larger scan area indeed verifies that the sheets are of uniform thickness. One such image showing uniform size and thickness dispersion of PrIA nanosheets has been shown in figure S19d of ESI. The size of the nanosheets has again measured from particle size analysis with Dynamic Light Scattering experiment where the effective diameter of the nanosheets is found to be 2.1, 1.7 and 3.3 µm for MIA-NS, EIA-NS, and PrIA-NS, respectively (section S11 in ESI).

PXRD patterns collected during the hydrolytic conversion of the MOPs indicate that an amorphous phase is first attained because of the interaction with water. This amorphous phase is responsible for conversion into metal-organic nanosheets as per the postulated mechanism. And thus, transformation of the crystalline MOP units into the amorphous phase is an instance of the 'top-down' approach for nanosheet synthesis. This amorphous form is then transformed into the nanosheets following the 'bottom-up' approach. Additionally, for the 'topdown' segment of the conversion pathway, no energy was needed to be supplied in terms of ultrasonication or mechanical shearing. Rather, the nanosheets were separated from the bulk amorphous phase by themselves utilizing the interaction with a pool of water molecules. Hence, the generation of the nanosheets is best-described as 'self-exfoliation'. The benefit of this method has been tested by comparing with the nanomaterials obtained from two paths of top-down approach, mechanical grinding and ultrasound treatment to the bulk MOF crystals (figure S17 in ESI). But in both these cases, the obtained materials do not posses regular morphology to be termed as nanosheet.

The chemical stability of the obtained nanosheets was tested through checking their chemical integrity as well as suspension stability. It has been seen from the UV-vis spectra (figure S14 in ESI) for the aqueous suspension of the nanosheets that they do not disintegrate into Cu(II) in presence of water for more than 30 days. The DLS particle size analysis for the aqueous suspension of the nanosheets also concludes that the effective diameter of the nanosheets does not change for the period of 30 days (section S11 in ESI).

#### Conclusions

In conclusion, for the first time, we have been able to combine 'top-down' and 'bottom-up' approaches for synthesizing metal-organic nanosheets. By controlling the amount of water present in contact media of MOP during their hydrolytic conversion into MOFs, control on their growth has been achieved. Thus, metal-organic nanosheets with uniform size and thickness were obtained at high yield in a single conversion step. Additionally, no external energy was supplied for the separation of the nanosheets from the bulk materials, revealing true 'self-exfoliation'.

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**Keywords:** metal-organic polyhedra • hydrophobicity • metalorganic nanosheets • cage compounds • layered materials

- a) A. H. Castro Neto, *Physical Review Letters* 2001, *86*, 4382-4385; b)
   M. Osada, T. Sasaki, *Adv. Mater.* 2012, *24*, 210-228; c) B.
   Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, *Nat. Nanotech.* 2011, *6*, 147-150; d) X. Song, J. Hu, H. Zeng, *J. Mater. Chem. C*, 2013, *1*, 2952-2969; e) Z. Yin, H. Li, H. Li, L. Jiang, Y. Shi, Y Sun, G. Lu, Q. Zhang, X. Chen, H. Zhang, *ACS Nano* 2012, *6*, 74-80.
- [2] a) M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh, H. Zhang, *Nat. Chem.* 2013, *5*, 263-275; b) H. Zhang, *ACS Nano*, 2015, *9*, 9451-9469;
  c) J. Zhang, Y. Chen, X. Wang, *Energy Environ. Sci.* 2015, *8*, 3092-3108; d) M. Zhao, Y. Wang, Q. Ma, Y. Huang, X. Zhang, J. Ping, Z. Zhang, Q. Lu, Y. Yu, H. Xu, Y. Zhao, H. Zhang, *Adv. Mater.* 2015, *27*, 7372-7378.
- [3] a) C. Backes, N. C. Berner, X. Chen, P. Lafargue, P. Laplace, M. Freeley, G. S. Duesberg, J. N. Coleman, A. R. McDonald, *Angew. Chem. Int. Ed.* 2015, *54*, 2638-2642; b) S. C. Junggeburth, L. Diehl, S. Werner, V. Duppel, W. Sigle, B. V. Lotsch, *J. Am. Chem. Soc.* 2013, *135*, 6157-6164; c) W. Liu, C. Zhao, R. Zhou, D. Zhou, Z. Liu, X. Lu, *Nanoscale*, 2015, *7*, 9919-9926; d) L. Mustafa, R. Aliaksandra, F. D. John, N. C. Jonathan, *Nanotechnology*, 2013, *24*, 265703; e) V. Nicolosi, M. Chhowalla, M. G. Kanatzidis, M. S. Strano, J. N. Coleman, *Science*, 2013, *340*, 1226419; f) A. O'Neill, U. Khan, J. N. Coleman, *Chem. Mater.* 2012, *24*, 2414-2421.
- [4] a) P.-Z. Li, Y. Maeda, Q. Xu, *Chem. Commun.* 2011, 47, 8436-8438; b)
  R. J. Smith, P. J. King, M. Lotya, C. Wirtz, U. Khan, S. De, A. O'Neill, G.
  S. Duesberg, J. C. Grunlan, G. Moriarty, J. Chen, J. Wang, A. I. Minett,
  V. Nicolosi, J. N. Coleman, *Adv. Mater.* 2011, 23, 3944-3948; c) K.-G.
  Zhou, N.-N. Mao, H.-X. Wang, Y. Peng, H.-L. Zhang, *Angew. Chem. Int Ed.* 2011, *50*, 10839-10842.
- [5] a) U. Kim, I. Kim, Y. Park, K.-Y. Lee, S.-Y. Yim, J.-G. Park, H.-G. Ahn, S.-H. Park, H.-J. Choi, ACS Nano, 2011, 5, 2176-2181; b) W. Lu, C. M. Lieber, Nat. Mater. 2007, 6, 841-850; c) R. Makiura, R. Usui, Y. Sakai, A. Nomoto, A. Ogawa, O. Sakata, A. Fujiwara, ChemPlusChem, 2014, 79, 1352-1360.
- [6] a) Y.-H. Lee, X.-Q. Zhang, W. Zhang, M.-T. Chang, C.-T. Lin, K.-D. Chang, Y.-C. Yu, J. T.-W. Wang, C.-S. Chang, L.-J. Li, T.-W. Lin, Adv. Mater. 2012, 24, 2320-2325; b) L. Omiciuolo, E. R. Hernández, E. Miniussi, F. Orlando, P. Lacovig, S. Lizzit, T. O. Menteş, A. Locatelli, R. Larciprete, M. Bianchi, S. Ulstrup, P. Hofmann, D. Alfè, A. Baraldi, Nat. Commun. 2014, 5,5062; c) V. Rubio-Giménez, S. Tatay, F. Volatron, F. J. Martínez-Casado, C. Martí-Gastaldo, E. Coronado, J. Am. Chem. Soc. 2016, 138, 2576-2584; d) R. Sakamoto, K. Hoshiko, Q. Liu, T.

Yagi, T. Nagayama, S. Kusaka, M. Tsuchiya, Y. Kitagawa, W.-Y. Wong, H. Nishihara, *Nat. Commun.* **2015**, *6*, 6713.

- a) O. K. Farha, I. Eryazici, N. C. Jeong, B. G. Hauser, C. E. Wilmer, A. A. Sarjeant, R. Q. Snurr, S. T. Nguyen, A. Ö. Yazaydın, J. T. Hupp, J. Am. Chem. Soc. 2012, 134, 15016-15021; b) T. A. Makal, X. Wang, H.-C. Zhou, Cryst. Growth & Des. 2013, 13, 4760-4768; c) A. Gallego, C. Hermosa, O. Castillo, I. Berlanga, C. J. Gómez-García, E. Mateo-Martí, J. I. Martínez, F. Flores, C. Gómez-Navarro, J. Gómez-Herrero, S. Delgado and F. Zamora, Adv. Mater., 2013, 25, 2141-2146.
- [8] a) L. Cao, Z. Lin, F. Peng, W. Wang, R. Huang, C. Wang, J. Yan, J. Liang, Z. Zhang, T. Zhang, L. Long, J. Sun, W. Lin, *Angew. Chem. Int. Ed.* **2016**, *55*, 4962-4966; b) C. Hermosa, B. R. Horrocks, J. I. Martinez, F. Liscio, J. Gomez-Herrero, F. Zamora, *Chem. Sci.* **2015**, *6*, 2553-2558; c) Z. Kang, Y. Peng, Z. Hu, Y. Qian, C. Chi, L. Y. Yeo, L. Tee, D. Zhao, *J. Mater. Chem. A*, **2015**, *3*, 20801-20810; d) Y. Peng, Y. Li, Y. Ban, H. Jin, W. Jiao, X. Liu, W. Yang, *Science*, **2014**, *346*, 1356-1359.
- [9] a) P. J. Beldon, S. Tominaka, P. Singh, T. Saha Dasgupta, E. G. Bithell, A. K. Cheetham, *Chem. Commun.* **2014**, *50*, 3955-3957; b) T. Rodenas, I. Luz, G. Prieto, B. Seoane, H. Miro, A. Corma, F. Kapteijn, F. X. Llabrés i Xamena, J. Gascon, *Nat. Mater.* **2015**, *14*, 48-55; c) J.-C. Tan, P. J. Saines, E. G. Bithell, A. K. Cheetham, *ACS Nano*, **2012**, *6*, 615-621.
- a) F. Cao, M. Zhao, Y. Yu, B. Chen, Y. Huang, J. Yang, X. Cao, Q. Lu,
   X. Zhang, Z. Zhang, C. Tan, H. Zhang, *J. Am. Chem. Soc.* 2016, *138*, 6924-6927; b) K. Otsubo, H. Kitagawa, *APL Mater.* 2014, *2*, 124105; c)
   M.-H. Pham, G.-T. Vuong, F.-G. Fontaine, T.-O. Do, *Cryst. Growth* &

Des. 2012, 12, 3091-3095; d) X. Xi,Y. Fang,T. Dong, Y. Cui, Angew. Chem. Int. Ed. 2011, 50, 1154-1158.

- [11] a) S. P. Black, D. M. Wood, F. B. Schwarz, T. K. Ronson, J. J. Holstein, A. R. Stefankiewicz, C. A. Schalley, J. K. M. Sanders, J. R. Nitschke, *Chem. Sci.* 2016, 7, 2614-2620; b) B. Olenyuk, J. A. Whiteford, A. Fechtenkotter, P. J. Stang, *Nature*, 1999, 398, 796-799; c) J. Park, L.-B. Sun, Y.-P. Chen, Z. Perry, H.-C. Zhou, *Angew. Chem. Int. Ed.* 2014, 53, 5842-5846; d) Q.-F. Sun, S. Sato, M. Fujita, *Angew. Chem. Int. Ed.* 2014, 53, 13510-13513.
- a) A. Mallick, B. Garai, D. D. Díaz, R. Banerjee, *Angew. Chem. Int. Ed.* **2013**, *52*, 13755-13759; b) D. Rodríguez-San-Miguel, P. Amo-Ochoa and F. Zamora, *Chem. Commun.* **2016**, *52*, 4113-4127; c) J.-R. Li, D. J. Timmons, H.-C. Zhou, *J. Am. Chem. Soc.* **2009**, *131*, 6368-6369.
- a) M. Eddaoudi, J. Kim, J. B. Wachter, H. K. Chae, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* 2001, *123*, 4368-4369; b) H. Furukawa, J. Kim, K. E. Plass, O. M. Yaghi, *J. Am. Chem. Soc.* 2006, *128*, 8398-8399.
- [14] a) T.-F. Liu, Y.-P. Chen, A. A. Yakovenko, H.-C. Zhou, J. Am. Chem. Soc. 2012, 134, 17358-17361; b) Z. Lu, C. B. Knobler, H. Furukawa, B. Wang, G. Liu, O. M. Yaghi, J. Am. Chem. Soc. 2009, 131, 12532-12533; c) Z. Ni, A. Yassar, T. Antoun, O. M. Yaghi, J. Am. Chem. Soc. 2005, 127, 12752-12753; d) L.-B. Sun, J.-R. Li, W. Lu, Z.-Y. Gu, Z. Luo, H.-C. Zhou, J. Am. Chem. Soc. 2012, 134, 15923-15928; e) J. M. Teo, C. J. Coghlan, J. D. Evans, E. Tsivion, M. Head-Gordon, C. J. Sumby, C. J. Doonan, Chem. Commun. 2016, 52, 276-279.

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## FULL PAPER

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Two dimensional metal organic nanosheets with few nanometer thickness have been synthesized through a unique combination of topdown and bottom-up approaches using water assisted self-exfoliation of metal organic polyhedra.



Bikash Garai, Arijit Mallick, Anuja Das, Rabibrata Mukherjeee and Rahul Banerjee\*



Self-exfoliated two dimensional metal organic nanosheets *via* hydrolytic unfolding of metal organic polyhedra