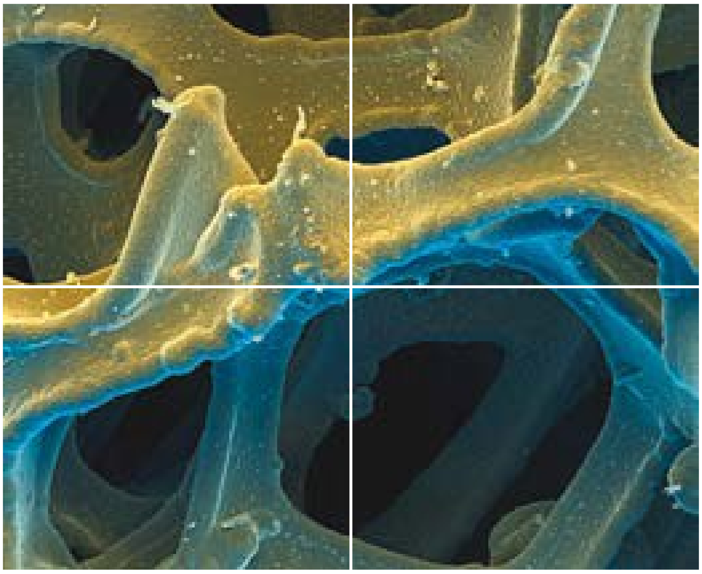
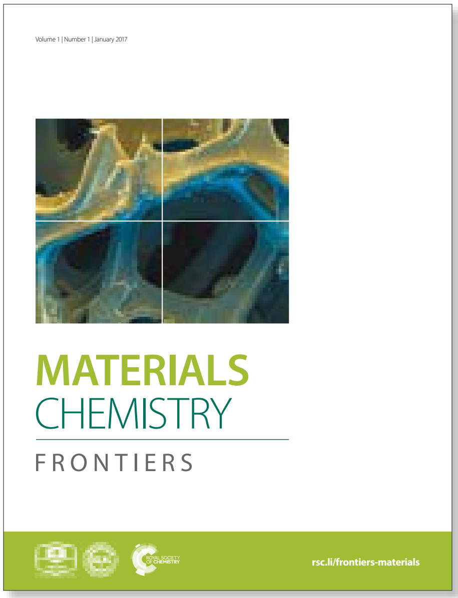
View Article Online
View Journal

MATERIALS
CHEMISTRY
FRONTIERS



Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: M. Rafti, E. Bindini, J. Giussi, J. S. Tuninetti, G. M. Segovia, J. A. Allegretto and O. Azzaroni, *Mater. Chem. Front.*, 2017, DOI: 10.1039/C7QM00235A.



Volume 1 | Number 1 | January 2017

MATERIALS
CHEMISTRY
FRONTIERS

rsc.li/frontiers-materials

View Article Online
DOI: 10.1039/C7QM00235A

Journal Name

COMMUNICATION

Metal-organic frameworks meet polymer brushes: enhanced crystalline film growth induced by macromolecular primers

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

M. Rafti,[a,*] J. A. Allegretto,[a,b] G. M. Segovia,[a,b] J. S. Tuninetti,[a] J. M. Giussi,[a] E. Bindini,[c] and O. Azzaroni [a,*]

We used of poly-(3-sulfopropylmethacrylate) brushes as macromolecular 3D primers to promote heterogeneous nucleation and growth of archetypal ZIF-8 MOF thin films. The enhancement can be understood in terms of a high preconcentration of Zn^{2+} ions in the polymer brush; that leads to a rapid increase of nucleation sites in the primer.

MOFs (metal-organic frameworks) represent an emergent class of porous materials constituted of infinite ordered arrays of metal-ion-based nodes or clusters, coordinated with multidentate organic linkers.[1–3] Due to its straightforward synthesis and many interesting features, such as unusually large surface areas, tuneable pore sizes and shapes, and chemical versatility; MOFs find use in a growing number of applications such as sensors,[4,5] catalysis,[6–8] gas adsorption,[9,10] and separations.[11,12] The development of strategies for synthesizing MOF films has recently gained considerable attention[13–16] due to its importance for the fabrication of separation membranes, optical devices, and surface mounted sensors.[17–20] Different properties can be expected when considering polycrystalline films with thicknesses in the micrometre range as they can exhibit properties similar to bulk powders depending on the crystallite sizes. On the other hand, crystalline thin films (also known as SURMOFs) span over a few nm and can be regarded ideally as single-crystal domains with structures sometimes non-existing for its bulk counterpart.[17,21,22] It was recently demonstrated that SURMOFs growth can be highly dependent on the crystal orientation.[23] Moreover, selective adsorption or "breathing" transitions can be observed for certain MOFs that do not present such behaviour when used as bulk powders.[24,25]

MOF films can be synthesized using a number of different procedures such as direct growth,[4] layer-by-layer,[26] solvothermal,[27] colloidal,[28] or seeded growth.[29] In all of these cases, the choice of an adequate chemical primer represents a crucial step towards achieving high crystallinity, good mechanical stability and enhanced growth extent.[30] There are several examples of MOF films displaying a given preferential crystalline orientation obtained using this bottom-up assembly strategy; which ultimately relies in a careful election of monolayer primers exposing suitable chemical moieties.[25,31–34]

Up to date, the use of chemical primers to grow MOF thin films has been almost exclusively circumscribed to the use of self-assembled monolayers.[35] The versatility of these molecular systems offer a simple means of modifying surfaces with predefined functional groups, which ultimately act as nucleation sites. However, due to the "monolayer" character of these systems, the number of functional groups –or nucleation sites– that can be allocated on a particular substrate is limited. In recent years different authors started to explore the use of polymeric substrates as primers to grow MOF thin films. In a seminal work, Hatton and co-workers demonstrated that MIL-47 can be directly synthesized on polyacrylonitrile (PAN) substrates, providing thus evidence for the first time that MOFs can growth at the expense of an amorphous precursor phase.[36] More recently, Caro and co-workers further extended these notions by using polydopamine layers as platforms to grow ZIF-8 thin films showing that macromolecular surfaces can promote the heterogeneous nucleation of MOF crystals.[37,38]

Inspired by the above described attempts directed to the creation of hybrid polymer-MOFs materials,[39] which would certainly help broadening the range of possible applications by circumventing common limitations (e.g., organic phase immiscibility or sensitivity towards hydrolysis);[40,41] we have explored the use of polymer brushes as macromolecular primers to promote the heterogeneous nucleation and growth of ZIF-8 thin films. Polymer brushes refer to assemblies of macromolecules that are tethered by one end to a surface or

---

[a] *Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata – CONICET, Diagonal 113 y 64 (1900) La Plata – Argentina.*
[b] *Universidad Nacional de San Martín (UNSAM), San Martín – Argentina.*
[c] *Laboratoire Chimie de la Matière Condensée de Paris, UMR UPMC-CNRS 7574, Université Pierre et Marie Curie (Paris 6), 4 Place Jussieu 75252 Paris, France.*

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C7QM00235A

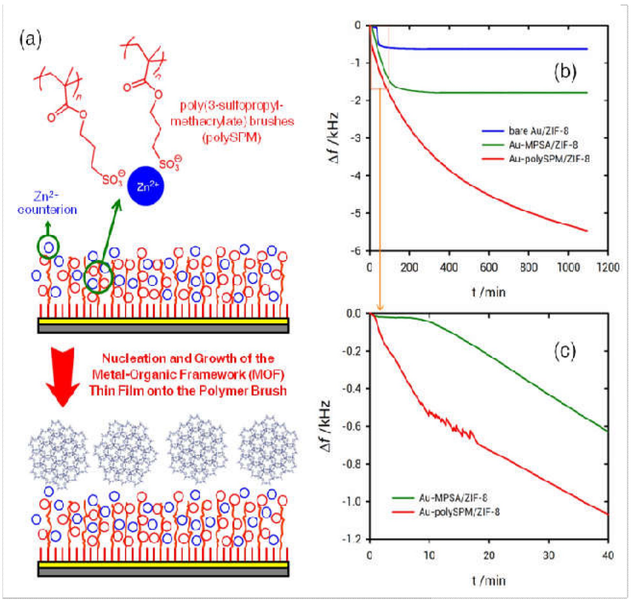


Figure 1. **(a)** Schematic representation of the fabrication of ZIF-8 thin films on poly-SPM brushes. **(b)** Deposition of ZIF-8 films on different surfaces, as detected by QCM: (blue) bare gold, (green) MPSA modified-gold, and (red) poly-SPM-modified gold. The deposited mass of MOF is directly proportional to the frequency change. **(c)** Early stages of time evolution in panel **(b)**.

interface in which chemical groups all along the polymer backbone can be placed in pseudo-3D spatial arrangements. Polymer brushes provide a complementary perspective from which to consider the manipulation of the heterogeneous nucleation of MOF thin films as they expose a high density of moieties interacting with the precursors in solution.[42] Despite all the efforts made to optimize the heterogeneous nucleation of MOF thin films, little –or none– is known about the effect of exposing specific primers or functional groups in "polymeric" formats rather than in "monolayer" configurations. As such, this work aimed to address how the heterogeneous nucleation of MOF thin films is affected when the same functional group is introduced in the substrate as a "polymer brush" rather than as a self-assembled monolayer. Our proof-of-concept consists of employing densely grafted poly-(3-sulfopropyl-methacrylate) or polySMP brushes in order to explore the capabilities of this macromolecular primer to enhance the crystalline growth of ZIF-8 films.[43]

ZIF-8 (a member of the MOF subclass known as zeolitic imidazolate frameworks, with sodalite (SOD) zeolite-type structure widely used as prototype material in the literature)[44,45] is a MOF constituted by tetrahedrally coordinated Zn^{2+} metal ions with bidentate 2-methylimidazolate (2-mIm) organic linkers. Aside from its reproducible straightforward synthesis and robustness, ZIF-8 was selected as suitable candidate to explore the effect of multiple sulfonate moieties present on the brush, due to the already reported enhancement effect on nucleation caused by sulfonate-decorated surfaces.[30,46,47] Our research demonstrates that in the presence of polymer brushes, the heterogeneous nucleation and growth of MOF thin films is promoted greatly; meanwhile, the resulting films still exhibit a smooth and homogeneous surface. As far as we know, this work constitutes the first systematic examination of "polymer brushes" as macromolecular primers to induce and enhance MOF thin film growth.

The preparation of poly-SPM brushes was carried using aqueous, surface-initiated, atom transfer radical polymerization (SI-ATRP) of the SPM monomers following a previously reported procedure.[43] The assembly procedure of ZIF-8 MOF on poly-SPM modified surface is shown schematically in Figure 1. Polymer brushes synthesized through overnight polymerization were characterized by FTIR, AFM and ellipsometry corroborating the presence of smooth polymer layers, with an average thickness of ≈ 250 nm (see ESI for characterization and synthesis details).

The SPM monomer was in the form of a potassium salt, and hence, the synthesized polymer brush is mainly coordinated with potassium ions as counter-ions. The large content of sulfonate groups in the polymer brush provide a great capacity for uptake and exchange of metal ions.[48] This is one of the essential aspects of polymer brushes as primers for the nucleation of MOF thin films. Polyanionic polymer brushes can act as surface-confined nanoreservoirs for cations, such as Zn^{2+}, that subsequently will play a decisive role as nucleation sites for the ZIF-8 film. In addition, the great advantage of polymer brushes is the enhanced accessibility between the functional groups and the solution given by the stretched conformation of the surface-grafted chains. In this way, species dissolved in solution can interact more freely with functional groups on the brush layer compared to chemical moieties confined inside a compact polymeric substrate.

In order to demonstrate the ability of poly-SPM brushes to coordinate Zn^{2+} ions available from solution, XPS experiments were conducted. XPS characterization confirmed the presence of Zn^{2+} in the brush layer after soaking the as-synthesized, K^+-coordinated poly-SPM brushes during 20 seconds in a 50 mM $Zn(NO_3)_2$ methanolic solution (Fig. 2). This indicates that, even in the case of short immersion times, in the presence of Zn^{2+} ion-rich solutions, ion exchange takes place. As a result, K^+ ions are removed from the macromolecular environment of the polymer brush and subsequently replaced by Zn^{2+} ions.

Once demonstrated that poly-SPM brushes can act as Zn^{2+} ions nanoreservoirs we proceeded with the synthesis of ZIF-8 films using poly-SPM as macromolecular primers. As stated above, the main aim of our work is to address how the growth of MOF thin films is affected when the heterogeneous nucleation takes place on a "macromolecular" or a "monomolecular" priming layer. To this end, we tracked the nucleation and growth of ZIF-8 films by performing in situ quartz crystal microbalance (QCM) experiments using Au-coated sensors modified with poly-SPM brushes. For the sake of comparison, similar experiments were performed using Au-coated sensors modified with a sodium 3-mercapto-1-propanesulfonate (MPSA) self-assembled monolayer. We have recently reported that sulfonate-bearing self-assembled monolayers are very efficient primers for nucleation and growth of ZIF-8 films.[30] In essence, the comparison of QCM traces describing ZIF-8

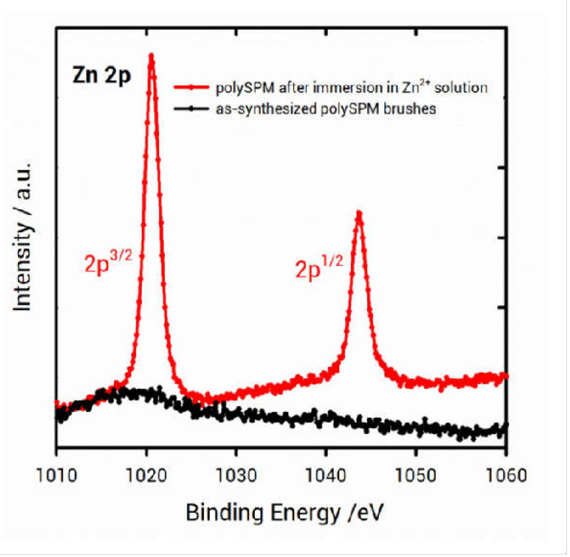


Figure 2. XPS spectra of a poly-SPM sample prior to (black trace) and after (red trace) immersion in a 50 mM Zn(NO3)2 methanolic solution during 20 seconds. The binding energies of the Zn 2p3/2 and 2p1/2 peaks are 1021 eV and 1044 eV, respectively.

growth on poly-SPM brushes, and MPSA monolayers refers to the heterogeneous nucleation of the MOF layer at interfaces exposing sulfonate groups in “polymeric” and “monomolecular” configurations.

To evaluate influence of sulfonate moieties “interfacial configuration” on ZIF-8 film growth, in situ monitoring of growth kinetics using quartz crystal microbalance (QCM) was carried out, as can be observed in Figure 1. QCM experiments show time evolution of frequency change (Δf) for films grown on QCM sensors modified with MPSA monolayers and poly-SPM brushes, respectively, after direct mixing of methanolic solutions of precursors at stoichiometric metal:linker (1:2) molar ratio (see ESI for further details).

Remarkable differences can be observed, not only in terms of the mass/thickness of ZIF-8 films grown on both sensor surfaces, but also regarding the early stages of film growth. QCM data indicates that induction times, *i.e.*: the time required to the start of film growth after mixing the precursor solutions, for surfaces modified with poly-SPM brushes and MPSA monolayers are 50 seconds and 9 minutes, respectively. In addition, it is observed that long-time mass limit for ZIF-8 films grown on poly-SPM brushes is significantly higher than those grown on MPSA modified surfaces. Microgravimetric experiments show striking differences between both platforms after ≈ 150 min of film growth. The growth rate of ZIF-8 films for MPSA modified sensors is 370 ng cm^{-2} min^{-1} during the first 120 min, and then film growth stops. However, when using poly-SPM, the initial growth rate determined by the QCM is 940 ng cm^{-2} min^{-1}. Then, the growth process spans far beyond the first 120 min whereas the growth rate gradually changes from 370 to 25 ng cm^{-2} min^{-1} during a 16-hour period. Compared to MPSA 2D-primers, the still high value of growth rate even after initial stages have passed (370 ng cm^{-2} min^{-1}), suggests that poly-SPM 3D-primer influence spans beyond the obvious nucleation enhancement observed for early stages of film growth. As is well known, the induction period is influenced by supersaturation, *i.e.*; the driving force necessary for the nucleation and growth of crystalline phase. This induction time involves not only the time required for the formation of nuclei, but also the time needed for nuclei formed to attain detectable size.[49] If we consider that poly-SPM brushes efficiently pre-concentrate Zn^{2+} ions, it is plausible to consider that the high concentration of nucleation sites hosted in the macromolecular layer will speed up the appearance of stable growing nuclei.[50] Then, these nuclei will grow, spread, and coalesce forming the MOF layer through a mechanism resembling the multinucleation-multilayer growth.[51]

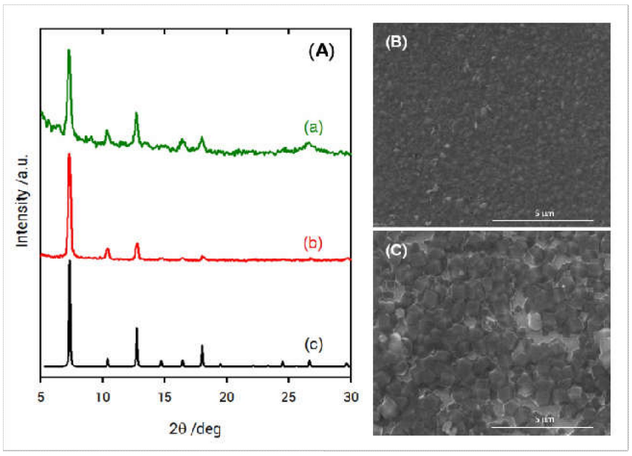


Figure 3. **(A)** XRD patterns corresponding to: **(a)** ZIF-8 films grown on MPSA self-assembled monolayers (green), **(b)** poly-SPM brushes (red), and **(c)** Calculated diffraction pattern (black). **(B)** SEM top view of a ZIF-8 film prepared on poly-SPM-modified substrate. **(C)** SEM top view of a ZIF-8 film prepared on MPSA-modified substrate.

X-ray diffraction (XRD) measurements of ZIF-8 films grown on poly-SPM brushes were used to establish the crystallinity of the obtained material. Figure 3 shows XRD patterns collected for ZIF-8 thin films grown on poly-SPM- and MPSA-modified QCM substrates corresponding to experiments presented in Fig. 1. XRD patterns of the as-obtained films agree well with the expected patterns in terms of peak positions, thus confirming that ZIF-8 was present in both platforms, and providing strong evidence that the use of an amorphous polyelectrolyte brush as a priming layer has no detrimental effects on MOF crystallinity. Moreover, the noise-to-signal ratio is improved when using the poly-SPM primer. Further examination of SEM experiments showed noticeable morphological differences between ZIF-8 films when grown on poly-SPM- or MPSA-modified substrates. SEM imaging corresponding to final state achieved in QCM experiments from Fig. 1 (b), are presented in Fig. 3 (A). It can be observed that when poly-SPM brushes were used as primer, well-intergrown films were obtained (see ellipsometry results in the ESI for additional evidence of smoothness achieved). The merged grains constituting the film have a relatively uniform, homogeneous size around 100-200 nm. On the contrary, a rough and poorly intergrown ZIF-8 film, rather than a

View Article Online
DOI: 10.1039/C7QM00235A

continuous and smooth layer, was formed on MPSA-functionalized substrates, as displayed in Fig. 3 (C). This can be rationalized by assuming that the heterogeneous nucleation of ZIF-8 crystals on MPSA is relatively poor compared with poly-SPM surfaces. Once again, this observation can be rationalized if we consider that poly-SPM brushes act as interfacial preconcentrator of Zn^{2+} species. The preconcentration of species that trigger the formation of nucleation sites shifts the system to a low supersaturation condition[52] which; in turn, leads to a smoother film. Or, in other words, the preconcentration of Zn2+ ions within the polymer brush helps the system reach a critical interfacial supersaturation for nucleation and growth of the MOF crystalline phase.[53] It could be argued that polymer brushes would adopt partially collapsed configurations due to moderate polar environment of solvent used for synthesis, thus reducing the effective number of $–SO_3^-$ moieties exposed to the solution. However, due to the roughness of brush—solution interface, the comparison hereby presented with MPSA SAMs still allows for a good qualitative comparison between a 2D primer and an eminently 3D primer, such as the hypothetically partially-collapsed poly-SPM brush. Once grown the ZIF-8 layer on the polyelectrolyte brush, we explored the subsequent growth of MOF multilayers by sequential crystallization processes. This strategy directed towards growth of thick MOF films was referred before as "*sequential one-pot*" (SOP)[18,54] synthesis, and consists in simply dipping the substrate in a freshly prepared solution of precursors during a preset growth time (for the experiments showed in Fig. 4, 10 min). Homogeneous and heterogeneous nucleation processes occur simultaneously, and the (maximum) film thickness can be controlled by the number of SOP cycles performed. The multi-layer growth of ZIF-8 films on poly-SPM brushes was monitored by spectroscopic ellipsometry (see ESI file for further details). Figure 4 shows successful "*nanolayer-by-nanolayer*" (NbN) film deposition[55–58] with linear growth (≈ 70 nm/cycle), thus demonstrating that each crystallization cycle resulted in deposition of nearly same amount of material. Compared with the traditional methods for preparing MOF thin films, our "*nanolayer-by-nanolayer*" strategy implemented on poly-SPM brushes achieved highly crystalline, thick films at high deposition rates in a rather controllable manner (e.g., it was previously reported that ≈ 30 min where needed to achieve similar thickness increase, with poorer control on surface rugosity).[59]

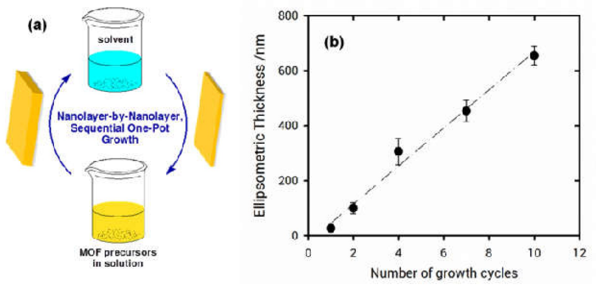


Figure 4. **(a)** Schematic illustration of the multilayer fabrication method. **(b)** *Nanolayer-by-nanolayer* (NbN), sequential one-pot growth of a ZIF-8 film onto a poly-SPM-modified Si/SiO_2 substrate, as observed by spectroscopic ellipsometry (see Suppl. Inf. for details on modelling of layers present).

Conclusions

To control growth, crystallinity and morphology of Metal Organic Frameworks (MOFs) films is a challenging and highly desirable task due to the many applications discovered in the last few years. We hereby proposed for the first time the use of a 3D polymeric primer, with pre-defined multiple chemical moieties exposed. Taking advantage of the already demonstrated affinity of Zn^{2+} ions for the multiple sulfonate exposed moieties; we explored the possibility of an enhancement on heterogeneous nucleation. XPS characterization supports our working hypothesis; i.e., poly-SPM brushes can act as efficient interfacial preconcentrators of Zn^{2+} species. The preconcentration triggers the formation of nucleation sites, thus shifting the system to a low supersaturation condition. Using this approach, we were able to synthesize highly inter-grown, controlled thickness, smooth ZIF-8 films. A notorious enhancement on growth kinetics, and extent (3-fold increase versus 2D primer MPSA SAMs) was obtained as evidenced *via* QCM in-situ measurements. We foresee that this novel strategy with high versatility could be applied with little modification for creating tailored polymeric 3D primers exposing virtually any desired moiety suitable for growth of a wide range of MOFs.

Notes and references

1 H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science (80-.).*, 2013, **341**, 1230444–1230444.
2 J. R. Long and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1213.
3 J. Jiang and O. M. Yaghi, *Chem. Rev.*, 2015, **115**, 6966–6997.
4 G. Lu and J. T. Hupp, *J. Am. Chem. Soc.*, 2010, **132**, 7832–7833.
5 Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815–5840.
6 D. Farrusseng, S. Aguado and C. Pinel, *Angew. Chemie Int. Ed.*, 2009, **48**, 7502–7513.
7 J. Chen, R. Liu, Y. Guo, L. Chen and H. Gao, *ACS Catal.*, 2015, **5**, 722–733.
8 J. Gascon, A. Corma, F. Kapteijn and F. X. Llabrés i Xamena, *ACS Catal.*, 2014, **4**, 361–378.
9 J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477.
10 J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2012, **112**, 869–932.
11 K. A. Cychosz and A. J. Matzger, *Langmuir*, 2010, **26**, 17198–17202.
12 B. Van de Voorde, B. Bueken, J. Denayer and D. De Vos, *Chem. Soc. Rev.*, 2014, **43**, 5766–5788.
13 S. Furukawa, J. Reboul, S. Diring, K. Sumida and S. Kitagawa, *Chem. Soc. Rev.*, 2014, 5700–5734.
14 K. Otsubo, T. Haraguchi, O. Sakata, A. Fujiwara and H.

Kitagawa, *J. Am. Chem. Soc.*, 2012, **134**, 9605–9608.

15 G. Xu, T. Yamada, K. Otsubo, S. Sakaida and H. Kitagawa, *J. Am. Chem. Soc.*, 2012, **134**, 16524–16527.

16 H. K. Arslan, O. Shekhah, J. Wohlgemuth, M. Franzreb, R. A. Fischer and C. Wöll, *Adv. Funct. Mater.*, 2011, **21**, 4228–4231.

17 A. Bétard and R. a. Fischer, *Chem. Rev.*, 2012, **112**, 1055–1083.

18 O. Shekhah, J. Liu, R. a Fischer and C. Wöll, *Chem. Soc. Rev.*, 2011, **40**, 1081–1106.

19 A. Huang, H. Bux, F. Steinbach and J. Caro, *Angew. Chemie Int. Ed.*, 2010, **49**, 4958–4961.

20 A. L. Robinson, V. Stavila, T. R. Zeitler, M. I. White, S. M. Thornberg, J. A. Greathouse and M. D. Allendorf, *Anal. Chem.*, 2012, **84**, 7043–7051.

21 P. Falcaro, D. Buso, A. J. Hill and C. M. Doherty, *Adv. Mater.*, 2012, **24**, 3153–3168.

22 H. Gliemann and C. Wöll, *Mater. Today*, 2012, **15**, 110–116.

23 O. Shekhah, H. Wang, D. Zacher, R. A. Fischer and C. Wöll, *Angew. Chemie Int. Ed.*, 2009, **48**, 5038–5041.

24 S. Sakaida, K. Otsubo, O. Sakata, C. Song, A. Fujiwara, M. Takata and H. Kitagawa, *Nat. Chem.*, 2016, **8**, 377–383.

25 B. Liu, M. Tu and R. a. Fischer, *Angew. Chemie Int. Ed.*, 2013, **52**, 3402–3405.

26 O. Shekhah and M. Eddaoudi, *Chem. Commun. (Camb).*, 2013, **49**, 10079–81.

27 X. Zhang, Y. Liu, S. Li, L. Kong, H. Liu, Y. Li, W. Han, K. L. Yeung, W. Zhu, W. Yang and J. Qiu, *Chem. Mater.*, 2014, **26**, 1975–1981.

28 P. Horcajada, C. Serre, D. Grosso, C. Boissière, S. Perruchas, C. Sanchez and G. Férey, *Adv. Mater.*, 2009, **21**, 1931–1935.

29 Y. S. Li, H. Bux, A. Feldhoff, G. N. Li, W. S. Yang and J. Caro, *Adv. Mater.*, 2010, **22**, 3322–3326.

30 J. S. Tuninetti, M. M. Rafti and O. Azzaroni, *RSC Adv.*, 2015, **5**, 73958–73962.

31 S. Hermes, F. Schröder, R. Chelmowski, C. Wöll and R. A. Fischer, *J. Am. Chem. Soc.*, 2005, **127**, 13744–13745.

32 S. Li, W. Shi, G. Lu, S. Li, S. C. J. Loo and F. Huo, *Adv. Mater.*, 2012, **24**, 5954–5958.

33 E. Biemmi, C. Scherb and T. Bein, *J. Am. Chem. Soc.*, 2007, **129**, 8054–8055.

34 P. Falcaro, K. Okada, T. Hara, K. Ikigaki, Y. Tokudome, A. W. W. Thornton, A. J. J. Hill, T. Williams, C. Doonan and M. Takahashi, *Nat. Mater.*, , DOI:10.1038/NMAT4815.

35 D. Zacher, O. Shekhah, C. Wöll and R. a Fischer, *Chem. Soc. Rev.*, 2009, **38**, 1418–1429.

36 A. Centrone, Y. Yang, S. Speakman, L. Bromberg, G. C. Rutledge and T. A. Hatton, *J. Am. Chem. Soc.*, 2010, **132**, 15687–15691.

37 A. Huang, Q. Liu, N. Wang, Y. Zhu and J. Caro, *J. Am. Chem. Soc.*, 2014, **136**, 14686–14689.

38 Q. Liu, N. Wang, J. Caro and A. Huang, *J. Am. Chem. Soc.*, 2013, **135**, 17679–17682.

39 M. Rafti, W. A. Marmisollé and O. Azzaroni, *Adv. Mater. Interfaces*, 2016, **3**, 1600047.

40 K. A. McDonald, J. I. Feldblyum, K. Koh, A. G. Wong-Foy and A. J. Matzger, *Chem. Commun.*, 2015, **51**, 11994–11996.

41 W. Zhang, Y. Hu, J. Ge, H. Jiang and S. Yu, *J. Am. Chem. Soc.*, 2014, **136**, 16978–16981.

42 O. Azzaroni, S. E. Moya, A. a. Brown, Z. Zheng, E. Donath and W. T. S. Huck, *Adv. Funct. Mater.*, 2006, **16**, 1037–1042.

43 M. Ramstedt, N. Cheng, O. Azzaroni, D. Mossialos, H. J. Mathieu and W. T. S. Huck, *Langmuir*, 2007, **23**, 3314–3321.

44 B. Wang, A. P. Côté, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Nature*, 2008, **453**, 207–211.

45 K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 10186–10191.

46 R. Zhang, S. Ji, N. Wang, L. Wang, G. Zhang and J.-R. Li, *Angew. Chemie Int. Ed.*, 2014, **53**, 9775–9779.

47 S. Bhattacharyya, S. H. Pang, M. R. Dutzer, R. P. Lively, K. S. Walton, D. S. Sholl and S. Nair, *J. Phys. Chem. C*, 2016, **120**, 2–10.

48 E. Choi, O. Azzaroni, N. Cheng, F. Zhou, T. Kelby and W. T. S. Huck, *Langmuir*.

49 J. W. Mullin, *Crystallization*, Butterworth-Heinemann, Oxford, 4th edn., 2001.

50 C. G. Pope, *Microporous Mesoporous Mater.*, 1998, **21**, 333–336.

51 M. Ohara and R. C. Reid, *Prentice-Hall International Series in the Physical and Chemical Engineering Sciences: Modeling Crystal Growth Rates from Solution*, Prentice-Hall, New Jersey, 1973.

52 D. Kashchiev and G. M. van Rosmalen, *Cryst. Res. Technol.*, 2003, **38**, 555–574.

53 P. Cubillas and M. W. Anderson, *Zeolites and Catalysis*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2010.

54 J. S. Tuninetti, M. Rafti, A. Andrieu-Brunsen and O. Azzaroni, *Microporous Mesoporous Mater.*, 2016, **220**, 253–257.

55 K. Ariga, Y. Yamauchi, G. Rydzek, Q. Ji, Y. Yonamine, K. C.-W. Wu and J. P. Hill, *Chem. Lett.*, 2014, **43**, 36–68.

56 K. Ariga, Q. Ji, W. Nakanishi, J. P. Hill and M. Aono, *Mater. Horiz.*, 2015, **2**, 406–413.

57 K. Ariga, M. V. Lee, T. Mori, X.-Y. Yu and J. P. Hill, *Adv. Colloid Interface Sci.*, 2010, **154**, 20–29.

58 M. Aono, Y. Bando and K. Ariga, *Adv. Mater.*, 2012, **24**, 150–151.

59 C. Hou, Q. Xu, J. Peng, Z. Ji and X. Hu, *ChemPhysChem*, 2013, **14**, 140–144.