ROYAL SOCIETY
OF CHEMISTRY

Check for updates

Complete twin suppression in oriented NH₂-MIL-125 film *via* facile coordination modulation†

Yanwei Sun,[a] Liangliang Liu,[a] Taotao Ji,[a] Jiahui Yan[a] and Yi Liu ✉ [iD] ⋆[ab]

Complete suppression of twin crystal formation in oriented metal–organic framework (MOF) film remains a great challenge. In this study, we successfully avoided the twin generation in *c*-oriented NH₂-MIL-125 film through simple competitive metal ion-based coordination modulation. Simultaneously, relevant mechanism associated with twin suppression was elucidated.

MOF films have found widespread applications in separation, catalysis, sensing, and adsorption.[1] Notably, their performance was anticipated to be further enhanced in the case that the preferred orientation could be precisely adjusted. For instance, Fischer *et al.* demonstrated that the $[Cu_2(NDC)_2(DABCO)]$ film with (100)-orientation favored a faster guest molecule uptake, resulting in a higher kinetic adsorption selectivity of benzene over toluene and *p*-xylene.[2] Heinke *et al.* prepared highly *a*-oriented HKUST-1 film showing much higher optical transparency than its randomly-oriented counterpart.[3] Our recent study further indicated that maintaining preferred (111)-orientation was beneficial for improving gas separation performance of UiO-66/NH₂-UiO-66 films due to significantly reduced density of grain boundary defects.[4]

Oriented seeded growth has been proven quite effective for oriented MOF film fabrication.[5] However, twin growth, which may lead to severe performance deterioration, is often an unavoidable consequence of direct epitaxial growth. Therefore, maintenance of preferred orientation derived from the seed layer during epitaxial growth has become indispensable. Previous studies indicated that random attachment of MOF nuclei formed in the bulk solution to the seed layer was the main cause of crystal twinning during epitaxial growth. A variety of approaches, such as the use of stable metal precursors and microwave-assisted heating, have been developed to suppress undesired twin growth.[6] Nonetheless, under most conditions suppression of twinning remains highly demanding in terms of reagents, apparatus, and expertise. Taking *c*-oriented NH₂-MIL-125 film as an example, our recent study indicated that concurrent employment of TiS_2/TiS_3 source and single-mode microwave heating was indispensable for reducing crystal twinning during epitaxial growth; even so, it remained impossible for their complete suppression.[7] It is therefore highly desirable to develop a facile method enabling complete twinning suppression during epitaxial growth.
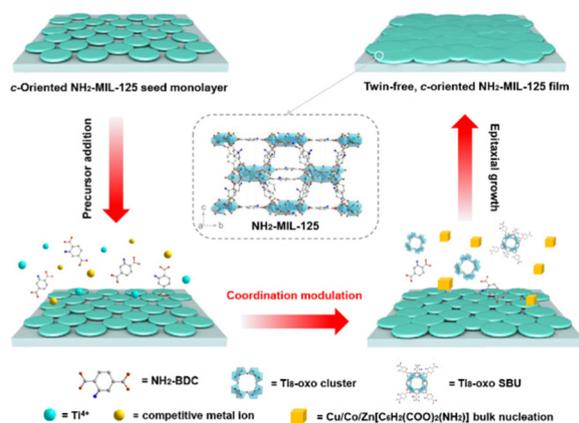
Coordination modulation, which refers to the adjustment of crystal nucleation and growth rates in the bulk solution by adding competitive coordinating modulators, has proven to be effective for optimizing the morphology and size of MOF crystals.[8] Nonbridging ligands, which bear the same coordinating functional group as organic linkers used to construct the framework, are commonly used as coordination modulators. Fischer *et al.* pioneered the coordination modulation strategy for microstructural control of MOF films. The addition of acetic acid modulator led to enhanced orientation and crystallinity of prepared $Zn_4O(L)_3$ film.[9] In contrast, the potential use of metal ions as coordination modulators in microstructural control (*e.g.*, preferred orientation control) of MOF films, which may be realized through competing with the metal ions employed to construct the framework, has never been explored before, although heterogeneous metal ions have been widely employed to tune the chemical composition, aperture size, framework flexibility, and hydrophobicity/hydrophilicity of MOF powders.[10]

In this study, we demonstrated a competitive metal ion-based coordination modulation strategy for complete suppression of twinning in oriented MOF film during epitaxial growth (shown in Scheme 1). To be specific, NH₂-MIL-125, constructed by $Ti_8(\mu_2\text{-O})_8(\mu_2\text{-OH})_4$ (Ti₈-oxo) clusters and 2-aminoterephthalic acid (NH₂-BDC) ligands, was chosen as a showcase for experimental verification of its feasibility and efficiency. Our research indicated

[a] *State Key Laboratory of Fine Chemicals, School of Chemical Engineering Dalian University of Technology Dalian, 116024, China. E-mail: diligenliu@dlut.edu.cn*
[b] *Dalian Key Laboratory of Membrane Materials and Membrane Processes Dalian University of Technology Dalian, 116024, China*

Scheme 1 Illustration of the preparation of twin-free and *c*-oriented NH$_2$-MIL-125 film *via* competitive metal ion-based coordination modulation strategy by epitaxial growth.

Fig. 1 SEM images of (a) Top view of the NH$_2$-MIL-125 seed monolayer. (b) Top and (c) cross-sectional views of the NH$_2$-MIL-125 film prepared by epitaxial growth with Cu(NO$_3$)$_2$ as growth modulator ([Cu^{2+}] = 4 mM). (d) XRD patterns of (i) NH$_2$-MIL-125 seeds, (ii) NH$_2$-MIL-125 seed monolayer, and (iii) NH$_2$-MIL-125 film.

that undesired crystal twinning during epitaxial growth of the NH$_2$-MIL-125 seed layer could be avoided by simple addition of a wide range of common metal salts (*e.g.*, Cu(NO$_3$)$_2$, Co(NO$_3$)$_2$, and Zn(NO$_3$)$_2$) in the precursor solution. The competitive coordination of NH$_2$-BDC ligands between competitive metal ions (*e.g.*, Cu^{2+}, Co^{2+}, and Zn^{2+}) and Ti$_8$-oxo clusters enabled moderate equilibrium concentration of NH$_2$-MIL-125 secondary building units, thereby inhibiting the bulk NH$_2$-MIL-125 nucleation with no compromise in lateral intergrowth of the seed layer. To the best of our knowledge, this represented the first report of highly oriented NH$_2$-MIL-125 film preparation under common solvothermal conditions.

The first step involved the preparation of NH$_2$-MIL-125 seeds. Disk-shaped NH$_2$-MIL-125 seeds with an average grain size of 750 nm and thickness of 170 nm were obtained after solvothermal crystallization (particle size distribution and size average were determined by particle counting as shown in Fig. S1, ESI†). Subsequently, a DALLAS method was employed for oriented deposition of NH$_2$-MIL-125 seeds on the substrate. A uniform and close-packed seed monolayer with a thickness of 170 nm could be obtained after deposition (Fig. 1a and Fig. S2, ESI†). The corresponding XRD pattern demonstrated the dominance of preferred *c*-orientation since only (002) and (004) diffraction peaks were clearly visible (Fig. 1d).

In the next step, epitaxial growth was carried out to seal intergranular gaps in the seed layer. However, owing to the excessively high nucleation rate of NH$_2$-MIL-125 crystals in the bulk solution as well as the relatively low epitaxial growth rate of the seed layer, it turned out to be very difficult to inhibit undesirable twin growth while simultaneously maintaining film continuity *via* simple reaction condition optimization. As shown in Fig. S3, (ESI†) substantial twin crystals were generated on the NH$_2$-MIL-125 film surface through epitaxial growth in the absence of any coordination modulators, which was in accordance with corresponding XRD results. Therefore, it became indispensable to suppress the bulk nucleation of NH$_2$-MIL-125 crystals while simultaneously enhancing the epitaxial growth of the seed layer. Considering its ability to regulate the coordination equilibria in the bulk solution, herein a
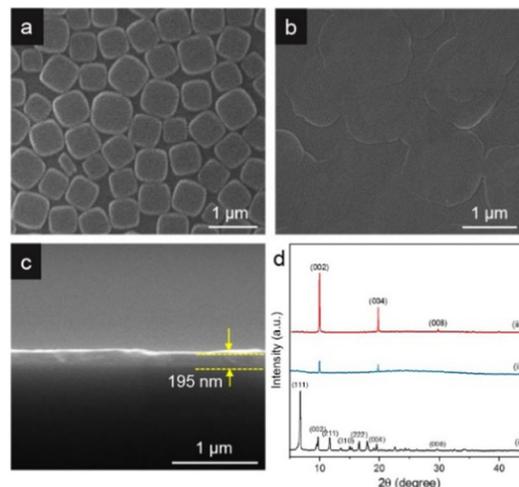
coordination modulation strategy was employed during epitaxial growth.

Initially, acetic acid, a typical monodentate carboxylic acid, was chosen as the coordination modulator. Nevertheless, substantial grain boundary defects remained in prepared NH$_2$-MIL-125 film (Fig. S4, ESI†), which could be ascribed to excessive high-affinity interaction between acetic acid and Ti species in the precursor solution, thereby leading to insufficient nutrient supply during epitaxial growth.

Instead of the addition of competitive monodentate carboxylic acid, herein a novel competitive metal ion-based coordination modulation strategy was developed for complete twin suppression. Since NH$_2$-MIL-125 is constructed by Ti$_8$-oxo clusters (hard acid) and NH$_2$-BDC ligands (hard base), we deduced that borderline acids (like Cu^{2+}, Co^{2+} and Zn^{2+}) could be more effective for hindering the quick and strong ligand-metal ion interaction with no compromise in chemical composition and crystallinity, according to Pearson's Hard-Soft Acid-Base (HSAB) theory.[11] To verify this deduction, given amount of Cu(NO$_3$)$_2$ was tentatively added to the precursor solution. SEM results indicated that after epitaxial growth, a smooth film with no discernable twin crystals was formed (Fig. 1b), thus demonstrating that the addition of Cu^{2+} effectively suppressed twin generation with no compromise in film continuity. Low-magnification SEM images in different regions further indicated that prepared film was uniform and continuous (Fig. S5, ESI†). Moreover, compared with *c*-oriented NH$_2$-MIL-125 film obtained through combining TiS$_2$/TiS$_3$ source and single-mode microwave heating, the twin density was significantly reduced (Fig. S6, ESI†). In addition, we noted that the NH$_2$-MIL-125 film thickness reached ~195 nm (Fig. 1c), which was only slightly larger than that of the seed layer, demonstrating that epitaxial growth in the vertical direction was largely restrained. To quantify the relative lateral epitaxial growth rate

($v_r = v_{lateral}/v_{vertical}$) during epitaxial growth, the ratio of lateral increasing length ($v_{lateral}$) to vertical increasing length ($v_{vertical}$) of c-oriented NH_2-MIL-125 film was calculated. Our results indicated that v_r of our NH_2-MIL-125 film (22.0) was much higher than the above film prepared through combining TiS_2/TiS_3 source with single-mode microwave heating (1.7/5.6), thereby confirming preferential epitaxial growth of the seed layer in the lateral direction through the addition of Cu^{2+} (Table S1). Corresponding XRD pattern (Fig. 1d) exhibited only characteristic diffraction peaks derived from (002), (004), and (006) planes, which confirmed that prepared NH_2-MIL-125 film remained dominantly c-oriented. In addition, The ATR-IR spectrum of prepared NH_2-MIL-125 film showed characteristic bands located in the range of 1200–1600 cm^{-1} and 600–800 cm^{-1}, which could be assigned to vibrations of benzene rings and O–Ti–O bonds in Ti_8-oxo clusters in NH_2-MIL-125 framework (Fig. S7, ESI†). In particular, the broad peaks centering at 1686 and 1110 cm^{-1}, which were ascribed to –NH_2 scissoring and rocking vibrations, exhibited weakened intensity, suggesting the existence of chelating interactions between Cu^{2+} ions and dangling –NH_2 groups. The content of Cu^{2+} ions in the sample was 0.85 wt% as determined by inductively coupled plasma atomic emission spectroscopy (ICP). EDS mappings of Cu and Ti elements convincingly demonstrated homogeneous distributions of Cu and Ti elements in the film (Fig. S8, ESI†). However, no new peaks assignable to the vibration of Cu–O bonds could be discerned, implying that Cu^{2+} ions were not incorporated in NH_2-MIL-125 framework.

Our results revealed that the molar ratio of Cu^{2+}/Ti^{4+} in the precursor solution exerted a significant influence on final morphology of the NH_2-MIL-125 film. To elucidate this issue, the molar ratio of Cu^{2+}/Ti^{4+} was deliberately varied in the range of 0.25–1.5 while keeping other synthetic conditions unchanged. As shown in Fig. 2a and b, twin crystals could not be effectively suppressed by maintaining Cu^{2+}/Ti^{4+} at 0.25. Upon further increasing Cu^{2+}/Ti^{4+} to 0.5, twin crystals still could not be completely suppressed despite having been largely alleviated (Fig. 2c and d). The generation of twin crystals could be avoided upon further increasing Cu^{2+}/Ti^{4+} to 1.0. Nevertheless, in the case that Cu^{2+}/Ti^{4+} was further increased to 1.5, substantial intercrystalline defects were simultaneously generated in the film, although crystal twinning could be effectively suppressed (Fig. 2e and f). This could be attributed to excessive consumption of NH_2-BDC ligands, which led to insufficient nutrient supply.

Additionally, precipitates sedimented from the bulk solution after epitaxial growth were collected and subjected to further characterization. As confirmed by XRD patterns (Fig. S9, ESI†), substantial NH_2-MIL-125 crystals were formed in the bulk solution in the case that the molar ratio of Cu^{2+}/Ti^{4+} fell below 1, which inevitably led to their random sedimentation on the seed layer and therefore, twin formation in the NH_2-MIL-125 film. In contrast, As the molar ratio of Cu^{2+}/Ti^{4+} was equivalent to or higher than 1, instead of NH_2-MIL-125 crystals, a large amount of $Cu[C_6H_2(COO)_2(NH_2)]$ crystals were generated in the bulk solution instead,[12] which further demonstrated that NH_2-BDC ligands were largely consumed due to the presence of Cu^{2+} so that NH_2-MIL-125 nucleation in the bulk solution could be effectively inhibited.
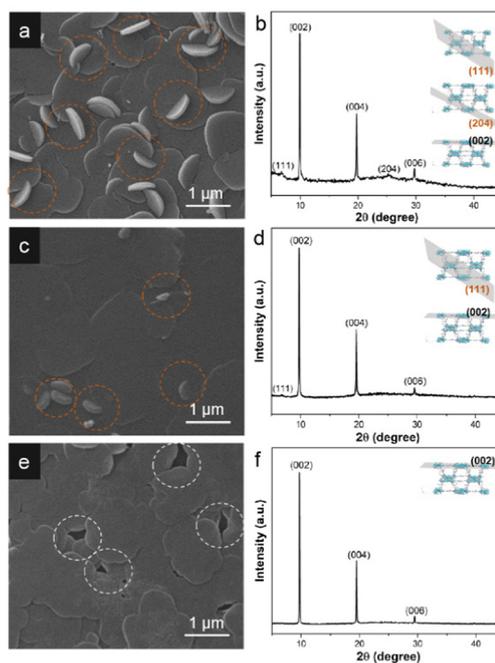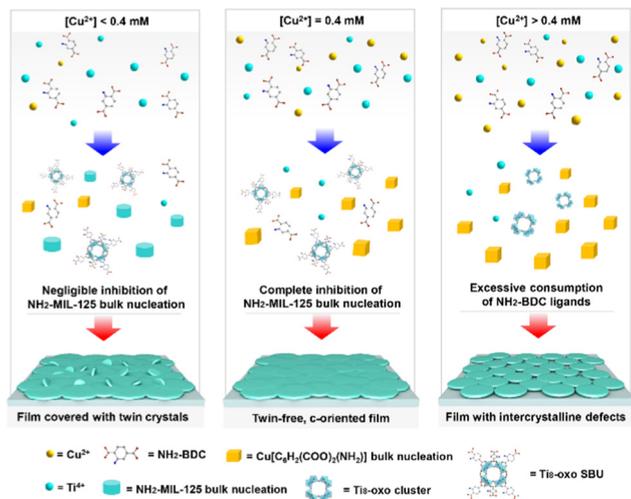

Fig. 2 SEM images and XRD patterns of NH_2-MIL-125 films prepared by epitaxial growth with different [Cu^{2+}] in the precursor solution: (a and b) 1 mM, (c and d) 2 mM, and (e and f) 6 mM. Inset: Lattice planes with different Miller indices in NH_2-MIL-125 framework.

Based on the above results, we proposed that the presence of Cu^{2+} ions in the precursor solution had significantly altered epitaxial growth kinetics of NH_2-MIL-125 films (shown in Scheme 2 and Fig. S10, ESI†). Based on LaMer's model, "burst nucleation", a kinetic pathway towards assembly or crystallization which simultaneously yields a mass of nucleation, could be precisely and reliably regulated by the rates of solute supply (e.g., by tunning the concentration of building units).[13] Specifically, when the concentration of building units fell in the range of concentrations of solubility (C_s) and nucleation (C_n), excessive nucleation in the bulk solution could be largely suppressed so that twin suppression during epitaxial growth could be realized. In this study, Cu^{2+} and Ti^{4+} were in a competitive relationship in terms of coordination with NH_2-BDC ligands. Therefore, the addition of Cu^{2+} in the precursor solution equivalently decreased the concentrations of NH_2-BDC ligands and $Ti_8O_8(OH)_4(COO)_{12}(NH_2)_6$ secondary building units (denoted as Ti_8-oxo SBU). When an appropriate amount of Cu^{2+} ions ([Cu^{2+}] ≥ 4 mM) was added to the precursor solution, the equilibrium concentration of Ti_8-oxo SBU was maintained at a value below the nucleation threshold (i.e., ≤C_n), thus prohibiting NH_2-MIL-125 nucleation in the bulk solution. Nonetheless, the addition of an excessive amount of Cu^{2+} ions (the molar ratio of Cu^{2+}/Ti^{4+} ≥ 1.5) led to excessive consumption of NH_2-BDC ligands and a Ti_8-oxo SBU concentration below C_s, resulting in insufficient nutrient supply.

It should be emphasized that the type of metal salts enabling effective twin suppression was not limited to $Cu(NO_3)_2$. Our study indicated that a variety of common metal sources, such as copper

Scheme 2 Representations of the processes of NH₂-MIL-125 epitaxial growth and twin crystal formation with various [Cu²⁺].

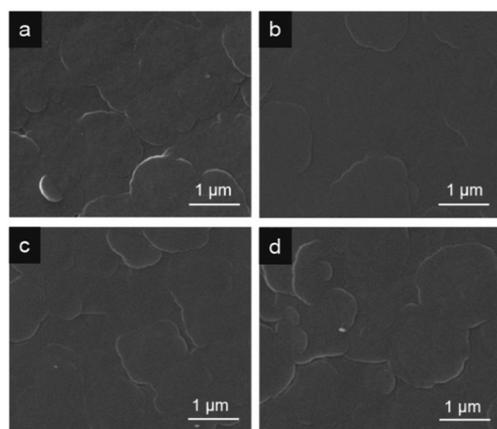**Fig. 3** SEM images of c-oriented NH₂-MIL-125 films prepared with (a) Cu(oAC)₂ ([Cu²⁺] = 4 mM), (b) Cu₃(C₆H₅O₇)₂ ([Cu²⁺] = 4 mM), (c) Co(NO₃)₂ ([Co²⁺] = 4 mM), and (d) Zn(NO₃)₂ ([Zn²⁺] = 4 mM) as growth modulators in the precursor solution.

salts (*e.g.*, Cu₃(C₆H₅O₇)₂, Cu(OAc)₂), cobalt salts (*e.g.*, Co(NO₃)₂), and zinc salts (*e.g.*, Zn(NO₃)₂) were all competent coordination modulators for effective twin suppression (Fig. 3). It was worth mentioning that the optimum molar ratios of Zn²⁺/Ti⁴⁺ and Co²⁺/Ti⁴⁺ for effective twin suppression were both equal to 1.0 as in the case of Cu²⁺ ions (Fig. S11, ESI†). The above results convincingly demonstrated that twin growth could be effectively suppressed as long as appropriate borderline acids were added to the precursor solution. In contrast, hard acid salts (*e.g.*, ZrCl₄) and soft acid salts (*e.g.*, CuCl) were not capable of preventing twin formation (Fig. S12 and S13, ESI†), owing to their insufficient or excessive competitive interaction with Ti⁴⁺ ions.

In summary, herein we developed a facile competitive metal ion-based coordination modulation strategy for preparing highly c-oriented NH₂-MIL-125 film through introducing metal salts as coordination modulators during epitaxial growth. The addition of borderline acids (*e.g.*, Cu²⁺, Co²⁺, and Zn²⁺) not only completely suppressed twin growth but also significantly enhanced relative lateral epitaxial growth rate of NH₂-MIL-125 seeds, which could be ascribed to competitive coordination of NH₂-BDC ligands between competitive metal ions and Ti₈-oxo clusters. The new strategy developed here might be useful for the growth of diverse twin-free oriented high-valence MOF films in the case that crystal twinning is unavoidable under conventional synthesis conditions.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 (*a*) M. S. Yao, W. X. Tang, G. E. Wang, B. Nath and G. Xu, *Adv. Mater.*, 2016, **28**, 5229–5234; (*b*) S. R. Ahrenholtz, C. C. Epley and A. J. Morris, *J. Am. Chem. Soc.*, 2014, **136**, 2464–2472.
2 B. Liu, M. Tu and R. A. Fischer, *Angew. Chem., Int. Ed.*, 2013, **52**, 3402–3405.
3 Z.-G. Gu, A. Pfriem, S. Hamsch, H. Breitwieser, J. Wohlgemuth, L. Heinke, H. Gliemann and C. Wöll, *Microporous Mesoporous Mater.*, 2015, **211**, 82–87.
4 (*a*) Y. Sun, C. Song, X. Guo and Y. Liu, *ACS Appl. Mater. Interfaces*, 2019, **12**, 4494–4500; (*b*) J. Yan, Y. Sun, T. Ji, L. Liu, M. Zhang and Y. Liu, *J. Membr. Sci.*, 2021, **635**, 119515.
5 (*a*) Y. S. Li, H. Bux, A. Feldhoff, G. L. Li, W. S. Yang and J. Caro, *Adv. Mater.*, 2010, **22**, 3322–3326; (*b*) Y. Yoo, Z. Lai and H.-K. Jeong, *Microporous Mesoporous Mater.*, 2009, **123**, 100–106.
6 (*a*) R. Rong, Y. Sun, T. Ji and Y. Liu, *J. Membr. Sci.*, 2020, **610**, 118275; (*b*) S. Chen, Y. Liu, Y. Sun, G. Xu, T. Ji, X. Zhang and F. Wang, *J. Membr. Sci.*, 2022, **643**, 120064.
7 (*a*) Y. Sun, Y. Liu, J. Caro, X. Guo, C. Song and Y. Liu, *Angew. Chem., Int. Ed.*, 2018, **130**, 16320–16325; (*b*) Y. Sun, D. Yan, Y. Wu, F.-Y. Shih, C. Zhang, H. Luo, S.-H. Lin and Y. Liu, *ACS Mater. Lett.*, 2021, **4**, 55–60.
8 (*a*) A. Umemura, S. Diring, S. Furukawa, H. Uehara, T. Tsuruoka and S. Kitagawa, *J. Am. Chem. Soc.*, 2011, **133**, 15506–15513; (*b*) F. Wang, H. Guo, Y. Chai, Y. Li and C. Liu, *Microporous Mesoporous Mater.*, 2013, **173**, 181–188.
9 S. Wannapaiboon, K. Sumida, K. Dilchert, M. Tu, S. Kitagawa, S. Furukawa and R. A. Fischer, *J. Mater. Chem. A*, 2017, **5**, 13665–13673.
10 S. Abednatanzi, P. G. Derakhshandeh, H. Depauw, F.-X. Coudert, H. Vrielinck, P. Van Der Voort and K. Leus, *Chem. Soc. Rev.*, 2019, **48**, 2535–2565.
11 R. G. Pearson, *Inorg. Chim. Acta*, 1995, **240**, 93–98.
12 (*a*) G. Gumilar, Y. V. Kaneti, J. Henzie, S. Chatterjee, J. Na, B. Yuliarto, N. Nugraha, A. Patah, A. Bhaumik and Y. Yamauchi, *Chem. Sci.*, 2020, **11**, 3644–3655; (*b*) T. Rodenas, I. Luz, G. Prieto, B. Seoane, H. Miro, A. Corma, F. Kapteijn, F. X. Llabresi Xamena and J. Gascon, *Nat. Mater.*, 2015, **14**, 48–55.
13 (*a*) X. G. Wang, Q. Cheng, Y. Yu and X. Z. Zhang, *Angew. Chem., Int. Ed.*, 2018, **57**, 7836–7840; (*b*) Y. Luo, M. Ahmad, A. Schugan and M. Tsotsalas, *Adv. Mater.*, 2019, **31**, 1901744.