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Empirical modeling of material composition and size in MOFs prepared with ligand mixtures

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Systematic analyses on the composition and size of metal-organic frameworks built with Zn₄O and terephthalic/amino-terephthalic acid mixtures, together with a kinetic assay, highlight how these ligands behave differently, which reveals the complexity of crystal growth in these frameworks and the ability to tune it on purpose.

Metal-organic frameworks (MOFs)¹ are porous crystalline materials with unique properties for gas storage,² separation,³ or catalysis.⁴ In addition, its porosity has been also exploited to develop molecular gates,⁵ encapsulate relevant biomolecules,⁶ or even perform chromatographic separations.⁷ The most common technique to obtain these structures consists in solvothermal crystal growth. MOF size is usually in the scale of micrometers; notwithstanding, some materials have been reported to grow up to the macroscopic scale (millimeters).^{7,8} This fact establishes a new difference between MOFs and further synthetic porous materials of wide use, such as zeolites or MCM-41⁹. Certainly, the ability to create macroscopic nanostructured materials is an important challenge that may boost novel applications.

However, the construction of such three-dimensional networks is an extremely complex process that depends on several parameters. The synthesis of **MOF-5** [Zn₄O(BDC)₃], also known as **IRMOF-1**, is prepared with 1,4-benzenedicarboxylic acid (BDC)¹⁰ —in the following ligand **1**— and usually performs with dimethyl formamide (DMF). This yields microcrystals (Fig. 1a), i.e., materials in the scale of micrometers. By contrast, the use of diethyl formamide (DEF), also acceptable in this case, leads to millimetric cubes.^{7,11} In addition to the medium, small chemical modifications of the ligand impact on the final size too. Previous work revealed the viability of obtaining **MOF-5**-like structures with up to 8 different ligands.¹¹ Interestingly, the use of 2-amino terephthalic acid —in the following ligand **2**— together with Zn₄O leads to crystals in the scale of millimetres with DMF (Fig. 1b), known as **IRMOF-3**.¹¹ Therefore, the ratio between the sizes of **IRMOF-3** and **MOF-5** appears to be larger than one order of magnitude with DMF.

Because **MOF-5** and **IRMOF-3** represent a pair of nanostructured materials with almost equal composition and

geometry, herein we explored the possibility of creating heterogeneous materials by employing mixtures of ligand **1** and **2**. Mixed-ligand MOFs have already been created and studied^{11c,12}, but the final composition and functionality of the material may result unpredictable. Through an experimental approach of systematic mixing, we wondered whether the resulting crystals span over a broad range in terms of size (functionality), trying to infer afterwards a simple, but predictive empirical model (Fig. 1c).

To shed light on how differently the two MOFs grow, we first performed a kinetic study. Despite their relevance to gain chemical insight, these studies are scarce in the field.¹³ **MOF-5** crystals started to be observable at 12–14 hours; however, it took more time (24–48 hours) for **IRMOF-3** crystals (Fig. 2 inset). More precisely, we measured with time the remaining amount of Zn(II) in solution during material formation (Fig. 2). Our data were roughly described with an exponential decay model (Eq. 1). In the case of **MOF-5**, we fitted $k = 0.092 \pm 0.004$, while in the case of **IRMOF-3**, $k = 0.082 \pm 0.014$ (k denotes the kinetic constant, in h⁻¹). Although the difference between both kinetics appears to be statistically non-significant following a Kolmogorov-Smirnov test, the faster assembly of Zn(II)–ligand **1** is supported by the higher Zn(II) consumption at 22 hours for **MOF-5** and the visual observation of these crystals already at that time. Arguably, **MOF-5** crystals are expected to be smaller than **IRMOF-3** crystals because, at least in part, many more macroscopic nucleation seeds appear, yielding a larger amount of **MOF-5** crystals, as observed.

Figure 1. Reaction schematics for material preparation, highlighting the macroscopic differences between a) **MOF-5** and b) **IRMOF-3**. c) Question addressed in this work.

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Figure 2. Kinetics of crystal formation with unique ligands. Time-dependent Zn(II) amount in solution during MOF growth. Points (circles or triangles) correspond to experimental data, while solid lines (black or blue) are fittings. All measurements were done by triplicate (errors bars correspond to standard deviations; ± 0.5 h has been applied in time for clarity). See ESI for exact ICP values. Inset: visual observation of crystal appearance (+ indicates qualitative observation, - no crystals).

To investigate the formation of mixed-ligand MOFs, we prepared under the same conditions a series of samples with different concentrations of ligand **1** and **2** (Table 1), maintaining constant the total ligand amount (in DMF, see ESI). Crystalline structure was verified for all engineered materials by PXRD (Fig. S15) after activation. The same pattern was observed in all cases, but with variations in intensity. Careful examination of PXRD indicated that interpenetration was present in samples containing more than 50% of ligand **2** (Fig. 3a). However, a sample with 20% presented distinctive relative heights of the peaks at 6.8° and 13.8° for an interpenetrated MOF (Fig. 3a).¹⁴ The quality of IRMOF-3 PXRD was low; a large-scale synthesis (10 fold) gave acceptable PXRD with reduced noise (Fig. S16). Moreover, we observed that the activation process broke the large crystals. To extract direct information, we decided to perform direct PXRD of MOFs immersed in DMF (after three rounds of solvent exchange). In Fig. 3c, PXRDs of MOF-5 (activated), MOF-5 calculated from cif file,¹⁰ and DMF-immersed MOF-5 are presented. As it was seen, the former pattern is the simplest. This experience was repeated for all samples and again similar spectra were obtained, confirming the constant structure. Only pure IRMOF-3 presented extra bands at 17° and 25° . Those differences might be induced by a specific phase growth, as already reported for other MOFs with large size (Fig. S17).¹⁵

Table 1 reports the ligand distribution employed in each of the 11 samples, together with the yield obtained. For each condition (a given ligand mixture, e.g., 20% of ligand **2**) was repeated 10 times. Those samples were employed for calculating the properties of the resulting material. The whole experience was repeated three times in independent days and with freshly prepared solutions. This allowed calculating an average and standard deviation for composition, size, and yield (e.g., size of 0.282 ± 0.096 mm and yield of $74.4 \pm 15.1\%$ for 20% of ligand **2**). We observed similar yields in all samples (around 50%). Of note, we found a distinctive ligand distribution within the crystals (measured by NMR, performed with 8 mg from the

samples employed for yield calculation), which did not correspond to the distribution of the reagent mixture. Indeed, following a plot comparing the initial and within-crystal concentration of ligand **2** (as a ratio, denoted by x_0 and x , respectively), we observed a clear deviation from linearity (Fig. 3b). To model this behavior, we introduced the incomplete beta function¹⁶ (β ; Eq. 2). Thus, we have $x = \beta(x_0|a,b)$, where a and b are two control parameters. We fitted $a = 0.991$ and $b = 0.744$ by nonlinear regression, obtaining a curve that described well our data (Fig. 3b). This model resulted statistically significant with respect to the null model $x = x_0$ (Snedecor's F -test, $P < 10^{-3}$). Being obtained under different growth conditions, this trend is in agreement with previous data.^{11c} The β function, which is very plastic, is still valid to capture other profiles by changing the parameter values (see section S11 in ESI).

Table 1. Reagent concentrations for crystal growth, yield of the process, ligand ratio, and resulting size (each condition was repeated 10 times and this was triplicated).

[Zn ²⁺] (μ M)	[1] (μ M)	[2] (μ M)	Yield ^[a] (%)	[2] / ([1]+[2]) (%)		Size ^[c] (mm)
				Initial	Within ^[b]	
100	78.3	0	66	0	0,00	0.11
100	70.5	7.8	70	10	6,33	0.11
100	62.6	15.7	74	20	15,33	0.28
100	54.8	23.5	72	30	23,67	0.44
100	47.0	31.3	68	40	34,33	1.74
100	39.2	39.2	61	50	39,33	1.24
100	31.3	47.0	59	60	49,67	1.17
100	23.5	54.8	55	70	60,33	1.24
100	15.7	62.6	52	80	67,33	1.21
100	7.8	70.5	55	90	83,67	1.19
100	0	78.3	49	100	100,00	1.32

[a] See Table S2 in ESI for all values in triplicate. [b] Ratio calculated experimentally by NMR from crystals (see Table S3 in ESI). [c] Edge size (see section S5 in ESI).

Figure 3. a) PXRD patterns of selected materials (80%, 20% and MOF-5). b) Within-crystal vs. initial concentration of ligand **2** (as a ratio, open circles). Solid line fits data, while dashed line is the linear trend. c) PXRD of activated MOF-5 (blue), calculated from MOF-5 cif (black), and DMF-immersed MOF-5 (red).

At this point, it is important to note that MOFs grow distinctively.^{11,13} In first place, different metal-organic aggregates are created to form nanostructures^{13b} and, in second place, these nanostructures combine each other, in addition to layered growth,^{13a} to end with macroscopic crystals. According to our data, the amount of ligand **2** within the materials is always lower than its initial amount in the preparation. Arguably, the small difference observed in growth kinetics (Fig. 2) may be on the basis of this behavior. In addition, the difference in pKa (pKa(**1**) = 3.5; pKa(**2**) = 4.6)¹⁷ may also contribute to a more favorable formation of MOF-5, as ligand **1** is slightly more acidic. By means of a rough theoretical model and calculations (section S9 in ESI), both processes revealed similar energies (1 Kcal/mol difference, see Fig. S21), which indicates that both can take place at the same time. This is in tune with the observed results.

Subsequently, samples were examined by optical microscopy to obtain images of the resulting materials, finding that size changes with the ligand ratio. We measured the edge sizes of the different crystalline cubes (values summarized in Table 1 and section S5 in ESI). Again, the preparations were repeated three times in independent days. In our hands and in agreement with previous observations, MOF-5 grew to form transparent cubes of 0.1 mm edge (only ligand **1**). IRMOF-3 grew, by contrast, to form yellowish cubes of 1.1–1.7 mm edge (only ligand **2**). With ligand mixtures, we found intermediate sizes of the resulting cubes. Crystal edge size (y) was plotted against ligand ratio (x), revealing a logistic trend (Eq. 3), spanning over one order of magnitude (Fig. 4a). Indeed, this was statistically significant (Snedecor's F -test, $P < 10^{-3}$) with respect to a null linear model, $y = y_{\min} + (y_{\max} - y_{\min})x$. In our case, we fitted by least squares $x_{50} = 36.8\%$ and $n = 15.1$ over average values, with $y_{\min} = 0.128$ mm and $y_{\max} = 1.249$ mm. Parameter x_{50} describes the transition between crystals of small size and crystals of large size. In materials in which ligand **2** satisfies $x < x_{50}$ (in the reaction mixture), edge size was smaller than 0.5 mm. When ligand **2** was very low ($< 20\%$), the resulting cubes were totally transparent. In addition, when $x \gg x_{50}$ (60–100%), we observed transparent yellowish cubes with edge size larger than 1 mm, although with high variability. It is worth mentioning that non-interpenetrated materials are also obtained after this point. This result is suggesting that the amino group of ligand **2** is playing a major role in terms of avoiding interpenetration. However, in the transition range (i.e., from 30 to 50%, when x is around x_{50}), heterogeneous crystals in terms of transparency were observed systematically. We hypothesized that the existence of clusters, as previously reported for similar systems,^{11c} might explain this. Furthermore, similar to modulators employed to enhance crystal size by slowing the reaction rate,¹⁸ ligand **2** may act as such through N coordination to the metal cluster. For illustrative purposes, Fig. 4b shows representative images of materials with larger size. See also Fig. S26 in ESI for a fitted trend between size and ligand **2** amount within materials.

Figure 4. a) Crystal edge size vs. initial concentration of ligand **2** (as a ratio). Solid line fits data (average values), while dashed line is the linear trend. Error bars correspond to standard deviations and indicate size dispersion of each sample. b) Representative images of materials containing 61.5% (top), 72.2%, 83.3%, and 100% (bottom) of ligand **2** within crystals. Scale bar of 2 mm.

In conclusion, the studies carried out in this work (with **MOF-5/IRMOF-3**) clearly indicate that material size is a functional property that can vary with ligand ratio. Moreover, the resulting distribution of size can be well explained with a logistic model. As a consequence, this empirical model could be used as a computational tool to guide the chemical reaction design to obtain materials of a given size. We envision that these materials, especially those bigger, might be exploited as nanostructured containers to be loaded with specific compounds (e.g., pharmacological drugs) affording long-time release. In addition, material composition can also vary in a non-linear way. In this case, this can be modeled with an incomplete beta function. Notably, both empirical models only require two independent parameters that need to be adjusted, which stresses the applicability of these models. Here, we reported data of growth formation and ligand assembly. The incomplete beta function can be parameterized to describe multiple scenarios, including these two. We also anticipate its relevance to describe reactivities between molecules in other scenarios involving pairs of related molecules that work together (e.g., copolymerization^{19a} or processes involving enantiomers^{19b}). All in all, as different mathematical models start to emerge to describe MOFs,²⁰ our ability to engineer these materials on purpose increases.

Notes and references

Material preparation

Reagents were mixed and dissolved in 2 mL of freshly distilled DMF into a glass flask with Teflon cap at 80 °C for 72 h. 11 mixture conditions were assayed. Each experiment was repeated 10 times (all 110 vials were prepared simultaneously to ensure equal conditions). After 3x washing with DMF and 3x washing with CHCl₃, MOFs were activated under vacuum at 120 °C for 50 h. This was repeated three times.

Analytical techniques

Yield calculated from activated MOFs (pooling 5 of the 10 samples to obtain one estimation). Material composition calculated by $^1\text{H-NMR}$. Digestion of evacuated and activated MOFs performed by sonicating 8 mg of sample (activated for yield calculation) in 1 mL 4% NaOD/ D_2O . Zn(II) in solution was measured by ICP. Material size calculated through representative images acquired with a Leica microscope (measuring multiple samples per replicate) with remaining DMF exchanged samples (non activated).

Mathematical modeling

To model the incorporation of Zn(II) into the material (z) with time (t), we followed an exponential decay model, which reads

$$z = z_{\min} + (z_{\max} - z_{\min})e^{-kt}, \quad (1)$$

where k is the observed kinetic constant, and $z_{\min}/z_{\max}$ the minimal/maximal concentration of metal. In addition, to model the concentration of one ligand (x) in mixed-ligand materials, we used the incomplete beta function, given by

$$\beta(x|a,b) = \frac{\int_0^x p^{a-1}(1-p)^{b-1}dp}{\int_0^1 p^{a-1}(1-p)^{b-1}dp}, \quad (2)$$

where a and b are two parameters that determine the shape of the function. Finally, to quantitatively describe material size (y), we made use of a logistic function, given by

$$y = y_{\min} + \frac{y_{\max} - y_{\min}}{1 + \exp(-n(x - x_{50}))}, \quad (3)$$

where x_{50} represents the concentration of input molecule (ligand **2**) at which the system reaches half of its upper bound, n is a parameter that encapsulates the non-linearity of the system, and $y_{\min}/y_{\max}$ the lower/upper bound of the property measured.

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- (a) M. Eddaoudi, D.B. Moler, H.L. Li, B.L. Chen, T.M. Reineke, M. O'Keeffe, and O.M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319–330. (b) G. Ferey, *Chem. Soc. Rev.*, 2008, **37**, 191–214. (c) S. Kitagawa, R. Kitaura, and S. Noro, *Angew. Chem. Int. Ed.*, 2004, **43**, 2334–2375. (d) O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, and J. Kim, *Nature*, 2003, **423**, 705–714. (e) M. O'Keeffe and O.M. Yaghi, *Chem. Rev.*, 2012, **112**, 675–702.
- (a) K. Sumida, D.L. Rogow, J.A. Mason, T.M. McDonald, E.D. Bloch, Z.R. Herm, T.-H. Bae, and J.R. Long, *Chem. Rev.*, 2012, **112**, 724–781. (b) M.P. Suh, H.J. Park, T.K. Prasad, and D.-W. Lim, *Chem. Rev.*, 2012, **112**, 782–835. (c) Y. He, W. Zhou, G. Qian, and B. Chen, *Chem. Soc. Rev.*, 2014, **43**, 5657–5678.
- (a) Z. Kang, L. Fana, and D. Sun, *J. Mater. Chem. A*, 2017, **5**, 10073–10091. (b) Z. Xhao, X. Ma, A. Kasik, Z. Li, and Y.S. Lin, *Ind. Eng. Chem. Res.*, 2013, **52**, 1102–1108.
- (a) J.Y. Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S.B.T. Nguyen, and J.T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450–1459. (b) A. Dhakshinamoorthy and H. Garcia, *Chem. Soc. Rev.*, 2014, **43**, 5750–5765.
- (a) B. Tam and O. Yazaydin, *J. Mater. Chem. A*, 2017, **5**, 8690–8696. (b) S.-M. Hyun, J.H. Lee, G.Y. Jung, Y.K. Kim, T.K. Kim, S. Jeoung, S.K. Kwak, D. Moon, and H.R. Moon, *Inorg. Chem.*, 2016, **55**, 1920–1925.
- (a) H.K. Chae, D.Y. Siberio-Pérez, J. Kim, Y. Go, M. Eddaoudi, A.J. Matzger, M. O'Keeffe, and O.M. Yaghi, *Nature*, 2004, **427**, 523–527. (b) M.J. Dong, M. Zhao, S. Ou, C. Zou, and C.D. Wu, *Angew. Chem. Int. Ed.*, 2014, **53**, 1575–1579. (c) J. Yu, Y. Cui, C. Wu, Y. Yang, Z. Wang, M. O'Keeffe, B. Chen, and Q. Guodong, *Angew. Chem. Int. Ed.*, 2012, **51**, 10542–10545. (d) H. Deng, S. Grunder, K.E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gándara, A.C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O'Keeffe, O. Terasaki, J.F. Stoddart, and O.M. Yaghi, *Science*, 2012, **336**, 1018–1023.
- S. Han, Y. Wei, C. Valente, I. Lagzi, J.J. Gassensmith, A. Coskun, J.F. Stoddart, and B.A. Grzybowski, *J. Am. Chem. Soc.*, 2010, **132**, 16358–16361.
- (a) R.A. Smaldone, R.S. Forgan, H. Furukawa, J.J. Gassensmith, A.M.Z. Slawin, O.M. Yaghi, and J.F. Stoddart, *Angew. Chem. Int. Ed.*, 2010, **49**, 8630–8634. (b) L. Li, F. Sun, J. Jia, T. Borjigina, and G. Zhu, *CrystEngComm*, 2013, **15**, 4094–4098. (c) C.A. Trickett, K.J. Gagnon, S. Lee, F. Gándara, H.B. Bürgi, and O.M. Yaghi, *Angew. Chem. Int. Ed.*, 2015, **54**, 11162–11167. (d) D. Rankine, A. Avellaneda, M.R. Hill, C.J. Doonan, and C.J. Sumby, *Chem. Commun.*, 2012, **48**, 10328–10330. (e) S. Furukawa, K. Hirai, K. Nakagawa, Y. Takashima, R. Matsuda, T. Tsuruoka, M. Kondo, R. Haruki, D. Tanaka, H. Sakamoto, S. Shimomura, O. Sakata, and S. Kitagawa, *Angew. Chem. Int. Ed.*, 2009, **121**, 1798–1802. (f) K. Koh, A.G. Wong-Foy, and A.J. Matzger, *Chem. Commun.*, 2009, **41**, 6162–6164. (g) S. Furukawa, K. Hirai, Y. Takashima, K. Nakagawa, M. Kondo, T. Tsuruoka, O. Sakata, and S. Kitagawa, *Chem. Commun.*, 2009, **34**, 5097–5099.
- (a) A. Corma, *Chem. Rev.*, 1997, **97**, 2373–2420. (b) A. Corma, *J. Catal.*, 2003, **216**, 298–312. (c) M. Kruk, M. Jaroniec, and A. Sayari, *J. Phys. Chem. B*, 1997, **101**, 583–589.
- H. Li, M. Eddaoudi, M. O'Keeffe, and O.M. Yaghi, *Nature*, 1999, **402**, 276–279.
- (a) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, and O.M. Yaghi, *Science*, 2002, **295**, 469–472. (b) H. Deng, C.J. Doonan, H. Furukawa, R.B. Ferreira, J. Towne, C.B. Knobler, B. Wang, and O.M. Yaghi, *Science*, 2010, **327**, 846–850. (c) X. Kong, H. Deng, F. Yan, J. Kim, J.A. Swisher, B. Smit, O.M. Yaghi, and J.A. Reimer, *Science*, 2013, **341**, 882–885.
- (a) A.F. Gross, E. Sherman, S.L. Mahoney, and J.J. Vajo, *J. Phys. Chem. A*, 2013, **117**, 3771–3776. (b) M. Du, X.J. Jiang, and X.J. Zhao, *Inorg. Chem.*, 2007, **46**, 3984–3995. (c) Z. Yin, Y.L. Zhou, M.H. Zeng, and M. Kurmoo, *Dalton Transact.*, 2015, **44**, 5258–5275. (c) P. Wang, K. Chen, Q. Liu, H.-W. Wang, M. Azam, S. I. Al-Resayesb Y. Lu, W.-Y. Sun, *Dalton Trans.*, 2017, **46**, 11425–11430. (d) P.-P. Cui, X.-D. Zhang, P. Wang, Y. Zhao, M. Azam, S. I. Al-Resayes, W.-Y. Sun, *Inorg. Chem.*, 2017, **56**, 14157–14163.
- (a) P. Cubillas, K. Etherington, M.W. Anderson, and M.P. Attfie, *CrystEngComm*, 2014, **16**, 9834–9841. (b) C. Zheng, H. F. Greer, C.Y. Chiang, and W. Zhou, *CrystEngComm*, 2014, **16**, 1064–1070. (c) J.P. Patterson, P. Abellan, M.S. Denny Jr., C. Park, N.D. Browning, S.M. Cohen, J.E. Evans, and N.C. Gianneschi, *J. Am. Chem. Soc.*, 2015, **137**, 7322–7328.
- B. Chen, X. Wang, Q. Zhang, X. Xi, J. Cai, H. Qi, S. Shi, J. Wang, D. Yuana, M. Fang, *J. Mater. Chem.*, 2010, **20**, 3758–3767.
- A.K. Gupta and S. Nadarajah, *Handbook of beta distribution and its applications*. CRC press, 2004.
- (a) S. Rostamnia, H. Xin, *Appl. Organometal. Chem.*, 2014, **28**, 359–363. (b) J.-M. Yang, Q. Liu, Y.-S. Kang, W.-Y. Sun, *Dalton Trans.*, 2014, **43**, 16707–16712. (c) L. Li, F. Sun, J. Jia, T. Borjigina, G. Zhu, *CrystEngComm*, 2013, **15**, 4094–4098.
- J.M. Chin, E.Y. Chen, A.G. Menon, H.Y. Tan, A.T.S. Hor, M.K. Schreyer and J. Xu, *CrystEngComm*, 2013, **15**, 654–657.
- (a) R.J. Marshall, C.L. Hobday, C.F. Murphie, S.L. Griffin, C.A. Morrison, S.A. Moggach, and R.S. Forgan, *J. Mater. Chem. A*, 2016, **4**, 6955–6963. (b) B. Van de Voorde, I. Stassen, B. Bueken, F. Vermoortele, D. De Vos, R. Ameloot, J.C. Tan, and T.D. Bennett, *J. Mater. Chem. A*, 2015, **3**, 1737–1742. (c) Z. Hu

- and D. Zhao, *Dalton Transact.*, 2015, **44**, 19018–19040. (d) O.V. Gutov, S. Molina, E.C. Escudero-Adán, and A. Shafir, *Chem. Eur. J.*, 2016, **22**, 13582–13587. (e) C.V. McGuire and R.S. Forgan, *Chem. Commun.*, 2015, **51**, 5199–5217.
- 19 (a) K.R. Sharma, *J. Encapsul. Adsor. Sci.*, 2013, **3**, 77–92. (b) C.T. Yeung, K.H. Yim, H.Y. Wong, R. Pal, W.S. Lo, S.C. Yan, M.Y.-M. Wong, D. Yufit, D.E. Smiles, L.J. McCormick, S.J. Teat, D.K. Shuh, W.T. Wong, and G.L. Law, *Nat. Commun.*, 2017, **8**, 1128.
- 20 (a) T. Titze, A. Lauerer, L. Heinke, C. Chmelik, N.E. Zimmermann, F.J. Keil, D.M. Ruthven, and J. Kärger, *Angew. Chem. Int. Ed.*, 2015, **54**, 14580–14583. (b) S. Han, T.M. Hermans, P.E. Fuller, Y. Wei, and B.A. Grzybowski, *Angew. Chem. Int. Ed.*, 2012, **124**, 2716–2720. (c) R. Sabouni, H. Kazemian, and S. Rohani, *Environ. Sci. Technol.*, 2013, **47**, 9372–9380. (d) F.-X. Coudert and A.H. Fuchs, *Coord. Chem. Rev.*, 2016, **307**, 211–236.