Faraday Discussions

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DISCUSSIONS

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New directions in gas sorption and separation with MOFs: general discussion

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Mircea Dincă opened a general discussion of the paper by Dmytro Denysenko: What are the thermodynamics of the NO + CO reaction?

Dmytro Denysenko responded: The overall transformation $CO + 2NO = CO_2 + N_2O$ is highly exothermic (-470 kJ mol^{-1}, as calculated from the tabulated standard enthalpy of formation values. The standard entropy for this reaction is -185.7 J mol^{-1} K^{-1}. From these data we can estimate that the process is thermodynamically favorable up to approximately 2500 K (as $\Delta G = \Delta H - T\Delta S$).

Mircea Dincă asked: Have you considered adding water to the reaction mixtures? What would this do to the thermodynamics and the products?

Dmytro Denysenko replied: So far we have always worked with dry gases and we have never tried adding water. If the overall reaction process $CO + 2NO = CO_2 + N_2O$ remains unchanged, there will be no change in the net thermodynamic parameters. However, water can, of course, have an influence on the reaction process, but we cannot easily predict which products might be formed in the presence of water — it has to be tested experimentally.

Laura Gagliardi asked: You showed some calculations, but they must be in the SI because they are not reported in the main paper. Did you model your system with a simplified model with 1 Ni atom? Do you know if your model is truly representative of the real system?

Dmytro Denysenko replied: Preliminary DFT calculations were performed in parallel and are not included in the manuscript. As a cluster model for Ni-MFU-4*l* derivatives, we often employ a scorpionate complex containing a single Ni metal centre. The validity of this approach has been demonstrated in previous reports by DFT calculations comprising several hetero-metal MFU-4*l* derivatives, in order to support experimental data and to predict the reactivity of metal sites towards binding of small molecules.[1–4] Test calculations have shown that scorpionate complexes give results very close to those from calculations on fully periodic MFU-4*l* structure models. In calculating full catalytic cycles, special care has to be taken with open-shell transition metal complexes which prefer a coordination environment different to that of the facial N-donor coordination of the metal by the scorpionate ligand (*e.g.* square planar d^8 electron configuration). In such cases, larger deviations between cluster and periodic models are sometimes observed, owing to the less rigid coordination of the scorpionate ligand when compared to the metal binding site in MFU-4*l* lattice models.

1 J. Jelic, D. Denysenko, D. Volkmer and K. Reuter, *New J. Phys.*, 2013, **15**, 115004.
2 D. Denysenko, M. Grzywa, J. Jelic, K. Reuter and D. Volkmer, *Angew. Chem. Int. Ed.*, 2014, **53**, 5832–5836.
3 D. Denysenko, J. Jelic, K. Reuter and D. Volkmer, *Chem. Eur. J.*, 2015, **21**, 8188–8199.
4 D. Denysenko, J. Jelic, O.V. Magdysyuk, K. Reuter and D. Volkmer, *Micropor. Mesopor. Mat.*, 2015, **216**, 146–150.

Connie Lu asked: The conversion of NO and CO to N_2O and CO_2 happens in two discrete steps. What happens if you co-feed NO and CO? Would you still obtain the same, expected products?

Dmytro Denysenko answered: We haven't yet tested the process with a gas mixture. As the two reaction steps proceed at completely different temperatures (40 °C for NO and 350 °C for CO), the stability of the MFU-4*l* framework towards NO (and N_2O, if it is being formed) at high temperature might be questionable, but it is certainly a good idea, to test the reaction with a gas mixture.

Connie Lu said: I enjoyed the mechanistic implications of your work, including the possible intermediacy of a high-valent Ni oxo complex. I also found it compelling that you compare the IR of the Ni nitrosyl intermediate to that of a well-defined molecular coordination complex. My question is regarding the Ni nitrite intermediate — what evidence do you have that the nitrite is bound in an η^2 O-coordinated fashion?

Dmytro Denysenko responded: Thank you for the nice comment. The evidence for the η^2 coordination of the nitrite ligands is given by UV-vis spectroscopy. There, tetrahedrally coordinated Ni^{2+} ions should show an intense absorption band centered at approximately 600 nm (similar to the band observed in a nickel nitrosyl complex). The experimentally observed spectrum with several weak absorption bands that are shifted towards lower energy corresponds, rather, to a five-fold coordinated Ni(II), as can be seen by comparing spectral data with those from literature-known Ni(II) complexes. Additional EXAFS measurements, as proposed by Prof. Carlo Lamberti, would definitely provide further evidence for this interpretation.

Xiaowei Liu addressed Dmytro Denysenko: Why did you choose 5% NO and 10% CO for the system? What would happen if you increased the concentration? Does the concentration affect the cyclic performance of your sample?

Dmytro Denysenko replied: We generally use diluted reactive gases, since they offer various experimental advantages. First, we can detect concentration changes when performing the reaction under gas flow. Second, we can use diluted gases for highly sensitive pulse chemisorption measurements. The usage of diluted toxic gases, in addition, is preferable for safety reasons. Generally we wouldn't expect the gas concentration to have a large influence on the cyclic performance.

Xiaowei Liu asked: Why do the TGA curves in Fig. 1 end at 400 °C? At this point, there is only ca. 12% weight loss.

Dmytro Denysenko answered: As the thermal stability of MFU-4*l* frameworks is limited to approximately 400 °C, we didn't measure up to higher temperature values. We are actually interested in stoichiometric or catalytic transformations of side-ligands coordinated to the peripheral metal centres in a Kuratowski-Type SBU, preferentially occurring at low temperature and, for that reason, we often stop the TGA measurement after the transformation is finished, but before the decomposition of the framework starts. In this case we can perform further analysis of the transformed sample (XRPD, IR *etc.*).

Marco Ranocchiari remarked: Is there any chemical reason why a co-feed of gases cannot be attempted?

Dmytro Denysenko responded: The problem is that the reaction with NO is performed at 40 °C, whereas for the reaction with CO 350 °C is required. The stability of the MFU-4*l* framework towards NO (and N_2O, if it is being formed) at 350 °C might be a problem. We also don't know whether the nitrite derivative in the presence of NO at 350 °C will still react with CO, or if it will react more rapidly with NO, thus forming different kinds of products. We didn't investigate these points, but it might be worth testing the reaction with a gas mixture.

Christopher Hendon addressed Laura Gagliardi and Dirk Volkmer: In both the presented calculations and in our own experience computing clusters of MFU-4*l*, we found that the equilibrium structures of Ni-substituted analogues allowed the Ni to oscillate between 2 and 3 coordinate in the molecular complex, whilst the MOF calculations featured no such effect. This could be because the Ni serves a structural role in the MOF, and a displacement of this nature would be costly. From my experience in cutting clusters from MOFs, I think the best method is to ensure that the ligand features the operative functionality such that the electron energies are relatively unperturbed by the decrease in symmetry and dimensionality. For example, the benzene dicarboxylate linker should be computed including the para-carboxylic acid as this motif is strongly electron withdrawing and hence stabilizes the π-system of the aromatic ring.

Dirk Volkmer replied: Thank you for the valuable comment. I should first apologize for displaying preliminary data from DFT calculations which are not contained in the manuscript or supporting information! I fully agree with the comment given above in the sense that metal coordination sites in molecular cluster models are expected to be considerably more flexible than their bond topological equivalents in the SBUs of MFU-4*l* frameworks. We have addressed this potential pitfall of modelling reactivity in some manuscripts covering a whole range of comparative DFT calculations on scorpionate-type or Kuratowski-type complexes *versus* fully periodic structure models of MFU-4*l*.[1–4]

For most electron configurations, the relative energy differences of intermediates occurring in catalytic cycles are within less than a few kJ mol^{-1} when cluster and periodic models are being directly compared. However, this might not necessarily be true when it comes to calculations on transition states, which are expected to depend far more critically on the structural flexibility or adaptability of a metal binding site.

Polynuclear Kuratowski complexes — instead of single -site scorpionate complexes — seem to provide a good compromise between both worlds, because the former is much more rigid than the latter, thus mimicking the coordination behaviour of peripherally coordinated metal ions within the SBUs of MFU-4*l*.

[1] J. Jelic, D. Denysenko, D. Volkmer and K. Reuter, *New J. Phys.*, 2013, **15**, 115004.
[2] D. Denysenko, M. Grzywa, J. Jelic, K. Reuter and D. Volkmer, *Angew. Chem. Int. Ed.*, 2014, **53**, 5832–5836.
[3] D. Denysenko, J. Jelic, K. Reuter and D. Volkmer, *Chem. Eur. J.*, 2015, **21**, 8188–8199.
[4] D. Denysenko, J. Jelic, O.V. Magdysyuk, K. Reuter and D. Volkmer, *Micropor. Mesopor. Mat.*, 2015, **216**, 146–150.

Mircea Dincă asked: Does the MOF do disproportionation of NO itself? This may happen directly from the Ni(II) rather than having to get to Ni(I) first. This may also inform the mechanism of the Co + NO reaction

Dmytro Denysenko responded: We didn't test the disproportionation of NO directly on Ni-MFU-4*l*-nitrite, but it might be worth a try. However, our feeling is that it might not work, since the reaction must involve the formation of a rather unfavorable Ni(III) nitrite species. Co(II) sites should be definitely more suitable for NO disproportionation.

Carlo Lamberti commented: Concerning the monodentate or bidentate coordination of the NO_2 on the metal center of the MOF, EXAFS spectroscopy will probably be the best to discriminate between the two possible coordinations.[1]

[1] C. Tyrsted, E. Borfecchia, T. V. W. Janssens, G. Berlier, K. A. Lomachenko, C. Lamberti, P. N. R. Vennestrøm, S. Bordiga, H. Falsig, P. Beato and A. Puig-Molina, *Catal. Sci. Technol.*, 2016, **6**, 8314–8324.

Dmytro Denysenko responded: Thank you for your comment. Indeed, EXAFS spectroscopy would provide additional information about the coordination environment of Ni(II), such as bond length values which cannot be obtained from UV-vis spectroscopic data. However, since this requires X-ray absorption experiments to be performed at a dedicated synchrotron beamline, we haven't carried out such measurements yet.

Huan Doan opened a general discussion of the paper by S. Hindocha: What are the synthesis yields of CuBTC? How can you upscale your synthesis to kilograms, and how are your yields determined? What temperature do you use for synthesising Cu-BTC?

Sheena Hindocha responded: The synthesis of Cu-BTC is detailed within the paper and is completed at room temperature. All our synthesis methods are designed to be scaleable.

Huan Doan asked: These MOFs are sensitive to water. How do you use them in that application?

Sheena Hindocha answered: The paper shows not all the MOFs tested are moisture sensitive and, more importantly, they have been aged using application specific conditions.

Gareth Lloyd asked: Are kinetics of the sorption more important than the equilibrium state (normally observed in sorption isotherms) in relation to this system of the porous material in a breathing mask? And have the kinetics been determined?

Sheena Hindocha responded: The key performance indicator is the breakthrough time under the specific application test conditions as that is what the material will be specified to. It is likely that kinetics will be important. The kinetics are reflected in the test conditions we employ but not in adsorption isotherms.

Jing Li enquired: It was observed that adsorption kinetics was affected by aging. How was it affected and what is the main reason for such an effect?

Sheena Hindocha stated: This has not yet been studied in detail.

Jing Li remarked: Did the aging effect on the adsorption kinetics show any trend? For example, did it normally slow down the adsorption rate?

Sheena Hindocha responded: This has not yet been studied in detail.

Thomas Bennett said: Have you tried compacting combinations of the MOFs mentioned in this paper together? Is that of any interest as a strategy?

Sheena Hindocha answered: This has not been attempted but is certainly something that would be interesting to consider.

Valeska Ting asked: If you're looking at respiratory applications then pressure drop in powders will be an issue. Have you considered using MOF foams or aerogels?

Sheena Hindocha explained: The reason for using pellets within the size range specified is to achieve an acceptable pressure drop.

Carlo Lamberti said: Some years ago, we investigated the interaction of ammonia on HKUST-1.[1] We found that NH_3 is strongly adsorbed on the Cu(II) centers of anhydrous HKUST-1 and we agree with your findings that the MOF's stability is compromised if ammonia is dosed HKUST-1 in the presence of water. However, we found that the framework is stable (on the few days-long time scale investigated by us) if water is present on HKUST-1 after ammonia adsorption. Did you confirm this evidence in your studies?

[1] E. Borfecchia, S. Maurelli, D. Gianolio, E. Groppo, M. Chiesa, F. Bonino and C. Lamberti, *J. Phys. Chem. C*, 2012, **116**, 19839–19850

Sheena Hindocha said: This is an interesting point and not something that has been investigated in the scope of this work.

Miguel Jorge asked: The results for CPO-27(Ni) show that, when wet granulation is applied (to sample 3), the surface area mysteriously increases (Table 2) while ammonia capacity and breakthrough time both decrease (Table 3). This suggests a change in the adsorption mechanism relative to the pristine and dry compacted material. Could this be related to inaccessibility of the open metal sites of the MOF, given that those are the primary adsorption sites for ammonia?

Sheena Hindocha responded: Yes the this could be the reason the performance of the MOF decreases, however this doesn't explain the increase in surface area. Work is ongoing to understand this further.

Omar Farha asked: In a mask, the volumetric uptake is important and may be more important than gravimetric uptake. Have you compared the volumetric uptake of your materials against what is published?

Sheena Hindocha answered: Our test is completed at a set volume and we have benchmarked the materials.

Omar Farha commented: If the MOF degrades, but doesn't let ammonia break through and the filter is disposable, is that a problem?

Sheena Hindocha responded: Not necessarily, though the full product specification will depend on the application.

Mircea Dincă stated: We have seen that if we do ammonia cycling, even though the crystallinity and N_2 BET surface area decreased, ammonia sorption is not affected. Do you have any ideas as to why the ammonia sorption is not affected?

Sheena Hindocha responded: We have not investigated ammonia cycling so are unable to comment on your findings.

Mircea Dincă asked: In evaluating these ammonia adsorbents, how do you assess whether to focus on cost, performance, *etc.*?

Sheena Hindocha answered: This is a market question and is dependent on a range of different factors including performance, cost and stability. All need to be considered.

Omar M. Yaghi remarked: Johnson Matthey and Industry serve as an outlet for MOF research in terms of applications, so how do you go about choosing the appropriate MOF? How much thought goes into the MOFs you choose? Out of the thousands of MOFs there are, as industry, how do you go about choosing which one to use?

Sheena Hindocha responded: Currently we focus on understanding the application problem and using the literature to evaluate the best materials to test.

Nathaniel Rosi asked: The binder used could potentially affect the performance/adsorption properties of the material, as you have shown. What other binders have you used, and have systematic studies been performed to determine how binder identity affects performance?

Sheena Hindocha explained: There are a range of different binders available, all of which could influence the properties of the material. A systematic investigation is currently ongoing.

Jet-Sing Lee commented: One of the main problems with MOFs is their sensitivities to moisture which affects their stabilities. Have you considered using more moisture-stable porous materials, such as porous polymers, which could contain groups that are tuned for NH_3 capture, such as Brønsted acid groups?

Sheena Hindocha answered: A range of different materials are being investigated for this application.

Thomas Bennett enquired: The degradation of Cu-BTC is detrimental to NH_3 adsorption in this case, but have you witnessed framework degradation/loss of crystallinity to be favourable for any application?

Sheena Hindocha responded: This is an interesting point and not something that has been investigated in the scope of this work.

Omar Farha asked: You said it's not important to know the structure of the product, but is that actually correct? How can you protect it (*e.g.* by patent)?

Sheena Hindocha responded: In the wider chemical industry there are many patents protecting products where the structure is not known.

Mohamed Eddaoudi remarked: What is the main objective of your targeted end product? Is it just for ammonia capture? Is it disposable or recyclable?

Sheena Hindocha answered: The MOFs detailed in the paper could be used for ammonia capture in respiratory protection devices as single use materials.

Simon Vornholt asked: You pointed out that the surface area is not necessarily the key factor you are looking for in your materials, as long as they perform. Hence, a high crystallinity is desired. Have you tested and analysed materials, obtained from different synthetic methods, which might have a high(er) crystallinity but are known to have a low(er) surface area?

Sheena Hindocha responded: We have tested a range of different materials with varying surface areas and crystallinity.

Timothy Easun commented: Did you try any very hydrophobic binders and did these reduce water-induced degradation?

Sheena Hindocha answered: There are a range of different binders available, all of which could influence the properties of the material. A systematic investigation is currently ongoing.

Monique van der Veen said: You are proposing these materials for single-use applications. However, you are using nickel and copper in the disposable materials, isn't that a waste that one would rather prefer not to have?

Sheena Hindocha explained: These metals are relatively cheap and can be recycled if required.

Omar M. Yaghi remarked: To save someone's life, it is worth it

Christophe M. L. Vande Velde asked: How mechanically stable are the granules that were prepared? It would be problematic to the user of the mask if there is a risk of inhalation of a finely powdered Cu- or Ni-containing MOF.

Sheena Hindocha responded: The mechanical stability of the granules is tested during the attrition test, and the results are detailed within the paper.

Marco Ranocchiari asked: What are the parameters that determine how you decide which materials will be tested for your application? Do you benchmark by application or by property?

Sheena Hindocha answered: We benchmark materials against the current commercial product. As mentioned in the paper there is always a balance between performance, cost and stability.

Simon Vornholt remarked: In your paper and presentation, you showed us breakthrough experiments of your materials for ammonia. Have you compared these results to adsorption isotherms of these materials, to get a benchmark value (*i.e.* maximum uptake)?

Sheena Hindocha responded: We don't evaluate materials using adsorption isotherms as breakthrough testing is more relevant to the application.

Carlo Lamberti opened a general discussion of the paper by Mohamed Eddaoudi: Your approach represents a very nice example whereby mathematical topological approaches are combined with reticular chemistry. Is the algorithm able to predict all of the topologies that are possible?

Mohamed Eddaoudi responded: As you know, various approaches such as net tilling were employed to enumerate edge-transitive nets (one kind of edge). Edge-transitive nets are suitable (ideal) targets in MOF chemistry. In this paper, we introduce various suitable targets in crystal chemistry based on minimal-edge-transitive nets, namely based on what we call a double six-membered ring as net-coded building units for the sole edge-transitive nets based on d6R, namely **shp** and **alb**. In the presented Faraday Discussions paper, we reported all the enumerated minimal edge transitive nets derived from the **shp** and **alb** nets.

Matthew Addicoat asked: Your approach is to synthesise large building blocks specifically to occupy a given solid shape (in the augmented net). Can you comment on the forgivability/flexibility of a particular shape? For example, a square in a **sql** net is quite forgiving of what you put in it – you can put a rectangle or even a tetrahedron and **sql** will still happily form. On the other hand, the square in **soc** is quite constrained – you won't form that net if the dimensions of your square are out of tolerance.[1]

So can you comment on how forgiving the double six-member ring in both the **shp** and **alb** nets? So if you were to synthesise something less symmetric, would the net still form? How much less symmetric can it be?

In general can you comment on quantifying this "forgivability" for different shapes in different nets?

[1] M. Addicoat, D. E. Coupry and T. Haine, *J. Phys. Chem. A*, 2014, **118**, 9607–9614.

Mohamed Eddaoudi answered: As you stated the presented strategy in this paper, for the deliberate construction of MOFs, is based on the employment of highly-connected building blocks. In this case, a double six-membered (6dR) ring as a net-coded building unit for the **shp** and **alb** nets, the sole edge-transitive nets based on 6dR. Accordingly, we derived minimal edge transitive nets from **shp** and **alb** nets. The derived nets have now 3 vertices and 2 edges. The ones we enumerated are based on the derived nodes from the fully symmetrical double six-membered ring. In other words, we haven't enumerated the other possible nets with a lower symmetry yet as they will possess more than 3 vertices and more than 2 edges and are thus very difficult to use as blueprints for the design, and as suitable targets at this stage. It is also worth stating that both structures, **alb**-MOFs and **shp**-MOFs, can be regarded as being based on pillaring and are thus easily amenable to isoreticular chemistry with less constraint, in contrast to the imposed restriction in the case of **soc**-MOF as you alluded to.

Matthew Addicoat followed up: Have you synthesised any other double six-member rings that are either less symmetric or more conformationally flexible and used them to make MOFs? Could you create a double six-membered ring where the two rings were rotated relative to each other?

Mohamed Eddaoudi replied: That is another excellent question. However as I stated earlier, at this stage we targeted symmetrical ligands in order to direct the assembly and promote the construction of the first **alb**-MOFs and **shp**-MOFs. Definitely, we will explore less symmetrical ligands mimicking a less symmetrical double six-member ring or with eclipsed rings as stated, if the organic synthesis permits a relatively straightforward access to such intricate ligands bearing 12-carboxylate moieties.

Omar M. Yaghi asked: Regarding the design of frameworks, I have two questions. First, look at structures — they all seem the same! What is the next step? When you design these structures, are you stopping nature from teaching you? What is different about them and what properties do they have?

Mohamed Eddaoudi replied: First, thank you for raising this very inspiring question. As stated in the opening lecture of this conference "not all MOFs are made equal". It is not surprising, at first glance, that most MOF structures look the same but the truth is that they are very different on many levels. It will be difficult to elaborate in detail about these various distinct differences between MOFs but I will try to state a few:

(i) Regarding the design there are various levels of design difficulties. For example, constructing MOFs with intricate topologies, such the **pbz** topology, is a challenge and requires a clear understanding of this net underlying topology and the non-obvious relationship between its nodes and edge metrics prior its reticulation in MOF chemistry; in brief, an elaborate design of the organic and inorganic building blocks is needed in order to construct such a **pbz**-MOF. In other words, the **pbz**-MOF cannot be readily achieved by relying on luck (although it is possible as Mother Nature is always here to unveil/teach us new things). Such an intricate **pbz**-MOF was recently introduced by our group and reported in a JACS paper,[1] illustrating the deliberate choice of the right building blocks with the ideal shape, size and connectivity to achieve this high level of design complexity.

(ii) From the properties perspective, each MOF has unique structural features and, for now, let us limit this discussion just to the MOF associated pore system and pore-aperture size: for example if we elect to use the **fcu** topology as a blueprint for the construction of MOFs, we can construct various isoreticular **fcu**-MOFs with various degrees of porosity and distinct properties. It is worth noting that the sole entrance to the pore system of the **fcu**-MOFs is the triangular window, delimiting the tetrahedral and octahedral cages. Accordingly, the employment of a shorter ditopic linker, such as fumaric acid, enables deliberate contraction of the triangular window and thus affords, for the first time, the realization of an **fcu**-MOF with unique sieving properties where *n*-butane is adsorbed but iso-butane is excluded.[2]

(iii) The ability to develop new strategies to design (direct the assembly of) MOFs does not, by any means, prohibit nature from teaching us. On the contrary, it allows us to deploy new tools that will permit us to access what nature is offering us, such as making the **pbz**-MOFs, **rht**-MOFs, **shp**-MOFs, **alb**-MOFs *etc.*[3] Nature has revealed these nets to us as unique blueprints, and ongoing progress in reticular chemistry over the past two decades permitted us to answer Mother Nature's propositions about the uniqueness of these nets as ideal blueprints for true design of MOFs. In summary, MOF chemistry associated with the power of reticular chemistry offers new chemistry and an unparalleled library of materials (either which have been made or are to be made) that can address various enduring challenges facing our society. Prominently, reticular chemistry paves the way for a new era of developing and deploying new solid-state materials where a solid-state material can, indeed, be designed to address a given challenge where scientists' imagination and perseverance are the key determining factors.

1 D. Alezi, I. Ioannis Spanopoulos, C. Tsangarakis, A. Shkurenko, A. Karim, Y. Belmabkhout, M. O'Keeffe, M. Eddaoudi, P. N. Trikalitis, Reticular Chemistry at Its Best: Directed Assembly of Hexagonal Building Units into the Awaited Metal-Organic Framework with the Intricate Polybenzene Topology, pbz-MOF, *J. Am. Chem. Soc.*, 2016, **138**(39), 12767–12770.
2 A. H. Assen, Y. Belmabkhout, K. Adil, P. M. Bhatt, D.-X. Xue, H. Jiang, M. Eddaoudi, Ultra-tuning of the rare-earth fcu-MOF aperture size for selective molecular exclusion of branched paraffins, *Angew. Chem., Int. Ed.*, 2015, **54**, 14353–14358.
3 Z. Chen, L. J. Weseliński, K. Adil, Y. Belmabkhout, A. Shkurenko, H. Jiang, P. M. Bhatt, V. Guillerm, E. Dauzon, D. Xue, M. O'Keeffe, M. Eddaoudi, Applying the Power of Reticular Chemistry to Finding the Missing alb-MOF Platform Based on the (6,12)-Coordinated Edge-Transitive Net, *J. Am. Chem. Soc.*, 2017, **139**(8), 3265–3274.

Omar Farha asked: Since the nets were enumerated a while ago, why has it taken this long to make?

Mohamed Eddaoudi replied: As stated in my short presentation and clearly illustrated in our Faraday discussions manuscript, there are special nets that are ideal for the successful practice of reticular chemistry: generally edge-transitive nets (nets with one kind of edge) and, of particular interest in MOF chemistry, edge-transitive nets based on highly-connected nodes (≥8). The employment of highly-connected nets as blueprints for the design of MOFs is a powerful strategy as these special nets are unique for the assembly of precise and well-defined highly-connected building blocks. The two examples presented in this manuscript attest to the uniqueness of the highly-connected nets for the deliberate design and construction of MOFs; namely the **shp** and **alb** nets are the sole edge transitive nets with a hexagonal prism as a vertex figure (12-connected d6R). Accordingly, these two nets are ideal blueprints for the design of MOFs. Nevertheless, as clearly alluded to in your appreciated question, why the delay in having these already enumerated nets appear in the MOF repertoire? The simple answer is that in order to target MOFs based on augmented **shp** or **alb** nets, it is vital to have access to the requisite 12-connected molecular building blocks (MBB) with points of extensions matching the vertices of the d6R. Markedly, it is only recently that our research group has found the right reaction conditions to generate rare-earth based polynuclear clusters accommodating 8-, 12- or 18- coordinating carboxylate moieties and affording the readily available access to highly-connected building units (8-c, 12-c, 18-c). This discovery enabled isolation of the reaction conditions for the *in situ* formation of the requisite 12-c MMB resembling the d6R. Now that the requisite 12-c MBB is accessible, all that is needed is the judicious selection of the complementary organic MBB with the right attributes (shape and connectivity); namely: (i) the square-shaped tetracarboxylate ligand was elected to deliberately construct the targeted **shp**-MOF, and (ii) a hexacarboxylate ligand, allowing positioning of the carbon of the carboxylates in a trigonal prismatic fashion, was designed and synthesized to construct the first **alb**-MOF.

Frederik Haase asked: Have you considered exploring quasicrystalline and other aperiodic nets for MOFs and what kind of organic or inorganic nodes would lead to such structures?

Mohamed Eddaoudi answered: MOF chemistry and reticular Chemistry enabled the synthesis of various intricate structures with various degrees of complexity. In my mind, and in principle, I don't see any reasons or obstacles prohibiting the use of reticular chemistry principles for the construction of quasicrystalline materials. The plausible and foreseen challenges will be the need to develop new tools and approaches for the full characterization of the MOF quasicrytalline materials.

Wenbin Lin said: When you make complicated systems it is difficult to molecularly engineer organic functional components since these need to have symmetry. What are the consequences of determining the structures of the MOFs? Are there issues with symmetry-imposed disorder?

Mohamed Eddaoudi replied: The examples presented in this manuscript pertaining to **shp**-MOFs and **alb**-MOFs required the utilization of simple to intricate organic ligands with some encompassing 12-carboxylates with relative flexibility. All the presented structures were solved based on single-crystal structure data with relatively high accuracy but, as expected and alluded to in your question, some local disorder was observed for the flexible ligands.

It is worth noting that disorder always imposes a symmetry and not vice versa. That said, if the selected symmetry imposes a disorder then the proposed solution model for your crystal structure is incorrect.

Gareth Lloyd asked: You use symmetry to describe this process as a type of crystal structure prediction. Are we thinking about the problem through thermodynamic minima only? And are we taking into account kinetics? Are we targeting structures thermodynamically, and then trying crystal growth until we achieve it, *i.e.* we are not taking crystal growth mechanisms in a prediction/theory into account?

Mohamed Eddaoudi replied: Thanks for the to-the-point questions. As clearly illustrated in the presentation and noticeably articulated in the Faraday discussions manuscript, edge-transitive nets are ideal targets for the design and construction of MOFs. However, where there are various possibilities for the assembly of given building blocks, the shape and connectivity of a given building block might not be sufficient to direct the assembly of one net over another (thermodynamics and kinetics are in play). For example, there are two edge transitive nets based on the assembly of square and tetrahedral building units, namely **pts** and **pth**, but the **pts** is the most dominant underlying topology in MOF chemistry. Plausibly, in order to direct/promote the assembly of a **pth**-MOF, a structure directing agent, as employed in zeolite chemistry, could be a valuable addition. On the other hand, and most importantly as stated in the present Faraday discussions manuscript, nets with high connectivity offer the prospect of being unique for the assembly of the given highly-connected building blocks. The two examples presented in this manuscript attest to the uniqueness of highly-connected nets for the deliberate design and construction of MOFs; namely **shp** and **alb** nets are the sole edge transitive nets with the hexagonal prism as a vertex figure (12-connected d6R). In this study, we introduced the net-coded building unit concept in combination with minimal edge transitive nets (3 nodes, 2 edges) as a valued design tool for the design of a select MOF with a particular topology.

Mircea Dincă commented: Very nice work. Is there a way to computationally relate topology to shape selective separations or some other applications for topology in general? Then, in response to the original question, regarding separation, would you say that it's not just the entrance, it's also the diffusion of gases within the system?

Mohamed Eddaoudi replied: Thank you for your comments. Very much appreciated. Indeed, there is a possibility of correlating certain topological features (openings, channel geometry, chirality, *etc.*) to separations; for example, the **fcu** net exclusively offers one kind of triangular window as a sole opening/access to plausible 3-periodic MOF structures with this underlying **fcu** topology. Accordingly, we constructed various isoreticular **fcu**-MOFs where shortening the bridging linker allowed for the exclusion of related molecules based on their relative size and shape. The **fcu**-MOF based on the hexanuclear yttrium cluster and fumarate ligand allows, for example, the separation of butane and isobutane; in fact only butane was adsorbed and isobutane was excluded due to the constrained triangular window in the fumarate based **fcu**-MOF.[1]

[1] A. H. Assen, Y. Belmabkhout, K. Adil, P. M. Bhatt, D.-X. Xue, H. Jiang, M. Eddaoudi, Ultra-tuning of the rare-earth fcu-MOF aperture size for selective molecular exclusion of branched paraffins, *Angew. Chem., Int. Ed.*, 2015, **54**, 14353–14358.

Ivo Stassen stated: I have a question regarding the chiral D6R dodecacarboxylate (HBCPD) linker. The dihedral angle between the core and the arms of the molecule is critical to the 'internal geometry' of the building block: an angle of approximately 45° is shown in the article, though an opposite angle of −45° yields a second conformational isomer. The ligand geometry of these two cases is different. Are both forms embedded in the framework or do you perhaps have any experimental indications to the contrary (it is mentioned that the net is not chiral, but is this also the case for the MOF)?

Mohamed Eddaoudi answered: Indeed, the D6R dodecacarboxylate ligand is chiral but the whole framework in In-**alb**-MOF-1 is not due to the symmetry operations (center of inversion and reflection in a mirror plane) which relate the opposite enantiomers. This is clearly confirmed by single-crystal X-ray diffraction analysis: |E*E-1| equals 0.994 and in the case of solution in the space group P6 the Flack parameter is 0.5.

Jing Li opened a general discussion of the paper by Karen Leus: The results from elemental analysis gave an average thiol loading of 3.45 mmol –SH g^{-1}. Can you convert this data to the number of –SH per ligand, which can easily be done? This will confirm that the functional groups remain intact during the synthesis.

Karen Leus answered: Unfortunately, we did not do elemental analysis (CHN) or TGA for the sample. The thiol loading was calculated from the sulfur content measured by ICP-OES. Hence, we cannot present any quantitative data on the amount of –SH per ligand as the thiol groups can also oxidize to form disulfide bonds (S–S) in the UiO-66–$(SH)_2$ material.

Jet-Sing Lee remarked: Upon functionalising UiO-66 with para-di-thiol groups, the surface area is more than halved from 1100 to 499 $m^2\ g^{-1}$, and you note than there is an average binding of 0.34 Hg^{2+} ions per thiol group.

Rather than using a para-di-thiol linker, have you considered using one with a single thiol group so that you can balance the surface area with thiol content and may yield a higher average Hg^{2+} binding per thiol group and better sorption kinetics?

Karen Leus replied: Indeed, we have considered using single thiol group-containing H_2BDC. We agree that UiO-66–SH would have a higher surface area which may result in better accessibility of the thiol groups in the framework. However, we showed in our intra-particle diffusion kinetic plot (Fig. 4) that the high thiol loading in the pores of UiO-66–$(SH)_2$ did not affect the initial adsorption of Hg onto the adsorbent's surface.

Omar Farha asked: In the paper you call the MOF a perfect crystalline material. Are there any defects in this material?

Karen Leus replied: It is known from previous studies[1,2] that the pristine UiO-66 exhibits structural defects. Hence, it is likely that there are structural defects in UiO-66–$(SH)_2$. We did not see any defects from our TEM images but the existence of such defects cannot be completely ruled out.

1 G. C. Shearer, S. Chavan, S. Bordiga, S. Svelle, U. Olsbye and K. P. Lillerud, *Chem. Mater.*, 2016, **28**, 3749–3761.
2 G. C. Shearer, S. Chavan, J. Ethiraj, J. G. Vitillo, S. Svelle, U. Olsbye, C. Lamberti, S. Bordiga and K. P. Lillerud, *Chem. Mater.*, 2014, **26**, 4068–4071.

Carlo Lamberti commented: What is the stoichiometry of sulfur to mercury? Do you have some experimental or theoretical evidence for tilting of the dithiol-functionalized ligands before and after mercury absorption? The presence of such tilting may be a way to explain the loss of surface area of the dithiol-functionalized UiO-66 MOF.

Karen Leus responded: The calculated Hg : S ratio is 0.34. At the moment, we do not have any experimental or theoretical evidence for tilting of the dithiol-functionalized ligands in the MOF structure.

Jing Li said: The two –SH sites are equivalent based on symmetry considerations, therefore they have the same accessibility to mercury. However, the Hg loading is very low, 0.34 per thiol site. This discrepancy was attributed to possible channel blocking, especially at pore constricted regions. To prove that this is indeed the case, you may vary the particle sizes of the adsorbent samples.

Reducing particle size will greatly decrease the extent of pore blocking, reduce the travel pathway and enhance the diffusion rate of the adsorbate.

Karen Leus replied: Thank you for the suggestions. We will take them into account in future work.

Miguel Jorge asked: Upon thiol functionalisation, there is a decrease in surface area of about 60%, and a significant decrease in the pore volume. Additionally, the mercury coverage is only 34%, again suggesting that about 65% of the thiol groups are not accessible (assuming the 1 : 1 adsorption mechanism proposed in the paper is correct). As the thiol groups and Hg are uniformly distributed, at least for the samples shown in Fig. 1 and 2, and the adsorption kinetics are unaffected by functionalisation, this suggests that the low Hg coverage is not caused by pore blocking. Instead, I propose that there is some collapse of the pore structure upon functionalisation, such that a percentage of the material becomes non-porous (*i.e.* amorphous), while the remaining material behaves like a crystalline functional MOF. This could potentially explain the reductions in surface area, pore volume and Hg coverage, reconciling these results with the kinetic data. Perhaps this could be checked in a relatively easy way? One option could be modelling.

Karen Leus responded: Indeed, modelling could be a powerful tool in elucidating the reduction in surface area after thiol functionalization of UiO-66 and the low Hg:S ratio. Thank you for the suggestion.

Omar Farha remarked: Have you compared the volumetric uptake of your materials against what is published?

Karen Leus responded: The maximum adsorption capacity (mg g^{-1}) of our material in comparison to other nanoporous materials is presented in Table 2.

Shengqian Ma said: We have set a new benchmark for both mercury ion and mercury vapor capture in our 2017 JACS paper.[1] Did you measure the K_d value? How low can you reduce mercury concentration level to in the solution?

1 Q. Sun, B. Aguila, J. Perman, L. D Earl, C. W. Abney, Y. Cheng, H. Wei, N. Nguyen, L. Wojtas and S. Ma, *J. Am. Chem. Soc.*, 2017, **139**, 2786–2793.

Karen Leus responded: Thank you for the update on the benchmark adsorbent on Hg removal. The calculated K_d value is 2.26×10^{-5} mL g^{-1}. The equilibrium concentration of mercury in the solution after the adsorption process is below the ICP-MS detection limit which is 0.05 g L^{-1}.

Jeffrey Paulo H. Perez addressed Shengqian Ma and Karen Leus: Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the concentration of mercury in the solution after adsorption. The quantification of mercury was done using gallium (10 g L^{-1}) as an internal standard and a linearity criteria of $R^2 > 0.9990$. The limit of detection (LoD) for mercury was determined to be 0.05 g L^{-1} using eqn (1), where s_{blank} is the standard deviation of the intensity of seven blanks and a is the sensitivity.

(1) $\text{LoD} = 3\times(s_{\text{blank}}/a)$

Shengqian Ma asked: What is the residual concentration after you removed the mercury?

Karen Leus replied: The equilibrium concentration of mercury in the solution after the adsorption process is below the ICP-MS detection limit which is 0.05 g L^{-1}.

Shengqian Ma asked: Did you use any methods to understand the coordination environment of mercury after it was absorbed to the thiol groups?

Karen Leus answered: No additional analytical/characterization techniques were used to explain the coordination environment of Hg to the thiol groups. However, we proposed a possible binding mechanism (eqn 3 and 4) for Hg onto the thiol groups in the MOF.

Omar Farha asked: Can you have one mercury interacting with two thiols?

Karen Leus replied: At the pH range used for the adsorption experiments, Hg(II) is expected to exist as Hg^{2+} and $Hg(OH)^{+}$ species. It might be possible for Hg^{2+} species to bind with two thiol groups to form –SHgS–. However, we have not performed any analysis that can support this hypothesis.

Shengqian Ma commented: Did UiO-66–SH show uptake for other metals, *e.g.* copper and iron?

Karen Leus answered: UiO-66–$(SH)_2$ also showed uptake for Fe and Cu. However, the Hg concentration (10 g L^{-1}) used in the experiments for competing ions is 100-fold lower compared to that of Fe or Cu (1 mg L^{-1}). We assume that the Hg binds with the thiol groups while Fe or Cu is adsorbed on the pore walls of UiO-66–$(SH)_2$.

Pascal Van Der Voort said: I'd like to make a general comment on the mercury sorption, which is more complex but well studied. Thiol groups that are close to each other will form disulfide bonds, that also adsorb mercury. This can be studied with Raman spectroscopy. We also made thiol-functionalized PMOs as mercury sorbents. We mixed inert linkers with thiol linkers and even with 100% thiol linkers. At high loading we got crystals, cinnabar, or HgS. We still do not understand how you form these in mesopores. Secondly, I assume it's right that there's amorphous structure in this MOF in part, whilst the porous part we have is recyclable for 4–5 cycles at least.

Jet-Sing Lee remarked: In order to tune the surface area with thiol amount, you could consider synthesising UiO-66 using a mixture of H_2BDC and H_2BDC-2,5SH linkers. This way, you would not need to synthesise any new organic linkers and can vary the ratios between them.

One issue is that the crystallinity of the MOF may be affected, but I not sure if this would play a role for Hg^{2+} sorption.

Karen Leus replied: Thank you for your good suggestion. We will take this into consideration.

Amir Hajiahmadi Farmahini asked: According to the data presented in your paper, Hg(II) adsorption has a faster uptake rate for UiO-66–$(SH)_2$ compared to the pristine MOF. It is also shown that the gradual adsorption of Hg(II) onto the micropores of the adsorbents (intra-particle diffusion) is the governing mechanism and the rate-limiting step in the adsorption process. Having this information, I am interested to know how the desorption kinetic differs between the two materials under investigation? Considering you have shown full recovery of Hg^{2+} in Fig. 7, I was wondering if you have observed any hysteresis or energy barrier in the system? How does desorption kinetic affect regeneration of Hg^{2+} during recurring cycles?

Pascal Van Der Voort replied: We did not examine the desorption of Hg on the pristine UiO-66 material so we could not make a comparison on their desorption kinetics. In the case of UiO-66–$(SH)_2$, higher desorption can be achieved at longer contact times between the eluent and the Hg-loaded MOF under ambient conditions. However, the desorption efficiencies did not show observable changes at varying time intervals at higher temperatures (70 °C).

Ivo Stassen said: I have a minor comment regarding Table 2 in the article. It has been suggested in the literature that the Langmuir theory is subject to a relatively high degree of inconsistency when applied to Type I physisorption isotherms.[1] Unless there is a particular reason to report the Langmuir specific surface area in the case of your material, could you add the BET specific surface area to the table?

1 P. Llewellyn, F. Rodriguez-Reinoso, J. Rouquerol, N. Seaton, *Studies in Surface Science and Catalysis*, 2007,**160**, 49–56.

Karen Leus answered: We used the Langmuir model because it is typically used for microporous materials and because much literature on metal-organic frameworks presents the surface area as the Langmuir surface. We agree, and know, that the Langmuir surface area overestimates largely the "actual" surface area, as the filling of the micropores is also considered to be surface. All areas were determined by a linear regression of the linearized Langmuir equation.

The BET surface area of the UiO-66–$(SH)_2$ is: 414 $m^2\ g^{-1}$.

Aron Walsh opened a general discussion of the paper by Nathaniel L. Rosi: For mixed components in a crystal, it is common to consider the thermodynamics of solid solutions. At low temperature ordered structures may be favoured, while at high temperatures you can approach a homogeneous distribution. For your process, do you believe it is kinetically controlled or may temperature be used to tune ligand distributions?

Nathaniel Rosi replied: We think it is kinetically controlled.

Carlo Lamberti asked: How is the gradient in ligand composition present in your MOFs reflected in the single crystal diffraction data? Do you see a splitting of the Bragg peaks or just a peak broadening?

Nathaniel Rosi responded: We do not see splitting of the peaks nor significant broadening. More sophisticated X-ray diffraction studies will be pursued to more completely understand the nature of the gradient structure.

Carlo Lamberti asked: In relation of your answer to question 228, I suggest you to perform μ-diffraction experiment on a synchrotron radiation beamline able to provide a μm, or sub-μm X-ray beam. This would allow you to appreciate the structural gradient of your complex and interesting materials.

Omar Farha asked: Have you seen a difference in the pore size distribution?

Nathaniel Rosi answered: We are currently examining this.

Wenbin Lin said: You are trying to solve a very challenging problem. I am concerned that the technique you use to detect what is going on might not be sensitive enough. You assume a solid solution gradient between the two domains based on distribution but it is very difficult to use any techniques to figure this out. Are there any other strategies beside confocal microscopy techniques to detect this?

Nathaniel Rosi replied: Wenbin, you are right that this is a challenging problem, which makes it particularly interesting. We are currently considering and trying several methods. One, in particular, is microtome slicing the crystals and then using Raman microscopy to analyze functional group distribution from the core to the shell.

Omar M. Yaghi remarked: Have you tried to assemble crystals from the 3 different linkers? Can you compare proportionation of these in crystals compared with diffusing them in? Is diffusion for postsynthetic modification of linkers controlled by defects or defect sites in crystals, or pore structure? What is the mechanism? Do you know what is controlling the diffusion? for example, linker hopping or similar?

Nathaniel Rosi answered: We have not tried doing *de novo* syntheses with the 3 linkers simultaneously. We don't know the precise mechanism, but we think it is probably associative.

Omar M. Yaghi said: The fact you can make long and short chains means you must be making defects. Must there be defect sites present?

Nathaniel Rosi replied: We are likely making transient defects during the process. Defects may be necessary for the process to occur, but we haven't identified defect sites.

Monique van der Veen remarked: I like your approach of gradually changing the linkers within one metal-organic framework crystal. You are aiming towards a gradient in the diffusion properties of the pores. My suggestion is that FRAP – Fluorescence Recovery After Photobleaching – could be an interesting microscopy technique for you as it can image the local self-diffusion coefficient of diffusing fluorescent molecule.

Susumu Kitagawa asked: In this case, the dimensionality is very important. Regarding the transport of molecules and ions in a crystal, it is difficult to demonstrate directional transport from the core side to the outside or vice versa in a MOF crystal? Here, Utilizing a 1D channel system is very interesting, so what kind of technique do you expect for realizing this system? For example, do you use coordination modulation, which can control crystal size and shape, and core shell and sandwich form of crystals? What kind of properties do you expect about the concentric gradient crystals you're describing?

Nathaniel Rosi responded: We expect, initially, to be able to focus or concentrate specific target analytes on one region of the MOF crystal by creating analyte affinity gradients for selective molecular transport. In the long term, we envision building MOF crystals with multiple functionally distinct compartments that would be connected *via* directed functionality gradients through which matter would flow between compartments in a directional fashion. A provocative analogy would be thinking about the MOF as a biological cell, where the different compartments constitute organelles and the 'gradients' represent pathways (channels) connecting the different compartments.

Xiaowei Liu asked: What will happen if you use the three different ligands at the same time - do they compete with each other? Which MOF is most stable?

Nathaniel Rosi replied: We have not performed that experiment.

Omar Farha commented: Is the pK_a more important than linker length for exchange?

Nathaniel Rosi replied: pK_a certainly has an effect, but we haven't yet teased out all the details to say definitively that one is more important than the other.

Omar M. Yaghi commented: Susumu and Wenbin say that this problem is challenging. From their tone of voice it is clear that they think you shouldn't be doing it, but it is a fascinating problem. Why can't we attack real challenging problems? We can see real applications - compartments open but that function differently. Can we not see this as having the potential to uncover something that does prompt you to use a certain technique or develop a new characterisation technique?

Omar M. Yaghi returned to the discussion of the paper by Nathaniel L. Rosi: The issue with correlating diffusion with specific design defects means that we move molecules along a certain pathway in the crystal. We call these solid solutions, which don't have specific points where you bind as here, so it is not proper to call them solid solutions?

Karena Chapman said: It is interesting that you see a single well-defined diffraction peak from a crystal containing a compositional gradient with a large difference in lattice dimensions for the compositional end members. It seems that their are two possible explanations for this:

(1) The lattice dimension within the single crystal changes directly with the ligand composition but these changes occur over a short length-scale such that the coherent domain size is too small to have well defined diffraction peaks. In this case, you would only be seeing the diffraction peak from the crystal core which has a uniform composition.

(2) There is only a single lattice dimension within the crystallite, in spite of the compositional gradient. The outer layer of the crystal is subjected to a high degree of compressive strain constrained by the lattice dimensions of the underlying crystal. (In this case, dissecting the crystal to look at part of the crystal changes the strain scenario, so is not diagnostic).