

Finally, the participants recommended that the guidelines on implementation of this Act should adequately be gender-sensitized with special consideration to female-headed households and women's role in community conservation. The important role of women farmers in conservation demands adequate inclusiveness in the recognition and reward, and other National Gene Fund-based conservation promotion activities.

1. Section 27.3(b) of Trade Related aspects of Intellectual Property Rights require Member countries to provide protection to plant varieties either by patents or by an effective system of *sui generis* or by a combination thereof.
2. Section 4(j) of the Second Patent (Amendment) Act, 2002 declaring plants and ani-

mals and parts thereof as non-patentable subject.

3. Section 28 of the Protection of Plant Variety and Farmers' Rights Act, 2001.
4. FAO Conference Resolution 9/83; <http://www.fao.org/ag/cgrfa/default.htm>
5. The International Treaty on Plant Genetic Resources for Food and Agriculture, adopted by the 31st Session of the Conference of the Food and Agricultural Organization, UN, Rome, 3 November 2001, p. 45.
6. Govindaswamy, S. and Krishnamurthy, A., *Rice Newsl.*, 1958, **6**, 22–24.
7. Bala Ravi, S., *Manual on Farmers' Rights*, M.S. Swaminathan Research Foundation, Chennai, 2004, p. 80.
8. Section 39(1)(iii) of the Protection of Plant Variety and Farmers' Rights Act, 2001.
9. Section 45(1) of the Protection of Plant Variety and Farmers' Rights Act, 2001.

10. Sections 14(c) and 39(1)(i) of the Protection of Plant Variety and Farmers' Rights Act, 2001.
11. Sections 2(j)(ii) and 15(2) of the Protection of Plant Variety and Farmers' Rights Act, 2001.
12. Rule number 24(1) of the Protection of Plant Variety and Farmers' Rights Act, 2001.
13. Section 39(2) of the Protection of Plant Variety and Farmers' Rights Act, 2001.
14. Rule number 66 of the Protection of Plant Variety and Farmers' Rights Act, 2001.

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RESEARCH NEWS

Are 'secondary building units' the true building blocks in crystal engineering of coordination polymers?

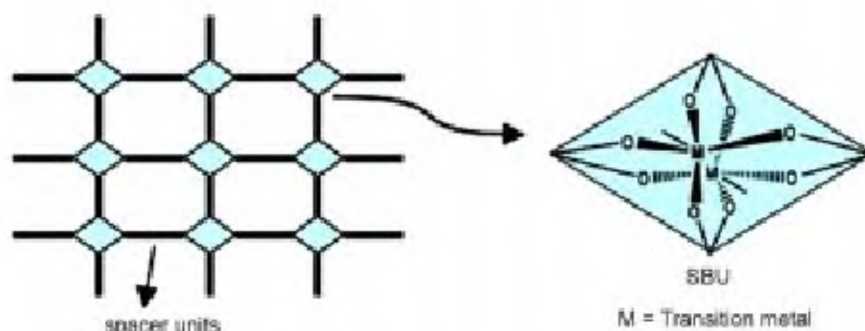
Kumar Biradha

Crystal engineering of coordination polymers/metal organic frameworks (MOFs) is a burgeoning field of research due to the interesting applications of these compounds in areas as diverse as gas adsorption, separation, host-guest chemistry, optics, magnetism, catalysis and photoluminescence¹⁻⁴. Among all these, porosity is the most explored and targeted property of these materials in view of the possible importance of hydrogen gas-based economy in future decades. In fact, MOFs are considered as rival candidates to zeolites due to their excellent porous properties (Scheme 1). The structural characteristics of MOFs offer unprecedented advantages in the fine-tuning of shapes and sizes of the channels and also the network connectivity. Further, they offer control over the chemistry of the channels due to ease in the introduction of various functional groups which can act as active sites for catalysis and sorption. The term 'hybrid materials' is also in regular usage to describe those MOFs which range from organic polymers bear-

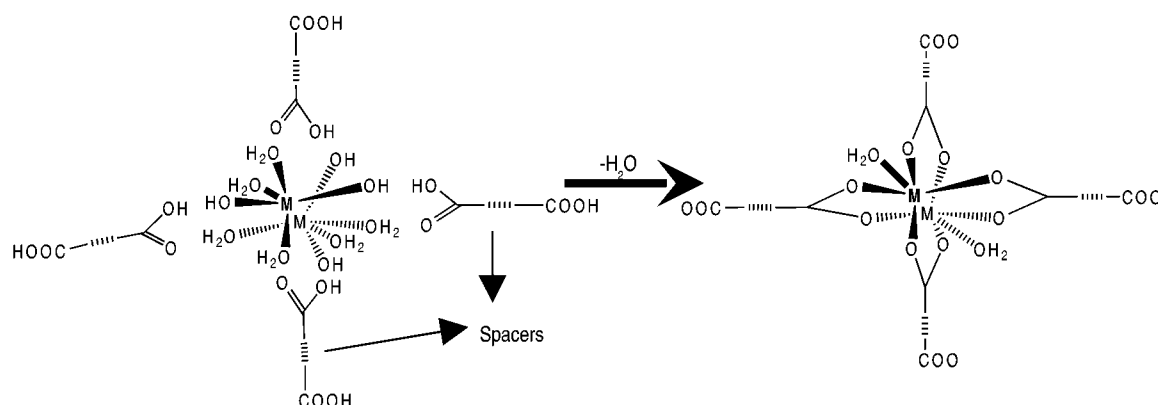
ing inorganic bridges to organically grafted inorganic materials^{1,5}.

Despite plethora of recent literature on MOFs, prediction of framework geometries for a given ligand and transition metal still remains elusive⁶. Further, almost no attention has been paid towards the mechanism of formation of MOFs as crystalline materials. Crystallization of

these materials from solution raises some fascinating but so far unanswered questions: What is the true building block of the framework? Is there a limit to the size of a building block in solution? Is it possible to predict chemical building blocks which, through an iterative self-assembling process, will lead to higher-dimensional frameworks with complete



Scheme 1. Part of the two-dimensional coordination polymer built with 1,4-benzene dicarboxylate spacer and the SBU (paddlewheel cluster).



Scheme 2. Conversion of supramolecular assembly of PZCs and dicarboxylic acid into MOFs by dehydrative condensation.

control of network topologies? What is the contribution of template effects by solvents, guest molecules and anions?

The recent contribution by Ramanan and Whittingham⁷ is a significant one, which tries to address some of these points. Their paper is critical of the secondary building unit (SBU) approach and proposes point zero charge (PZC) molecules as true building units. In the MOF literature, the term SBU is in regular usage whenever polynuclear clusters are involved in the networks (Scheme 1)^{2,8}. Indeed, the term 'SBU' was first used for zeolites to simplify and understand their complicated three-dimensional structures⁹. Subsequently, they were considered as prefabricated units which may exist in solution to provide a nucleating point and offer a mode for growth by their sequential addition. However, there is no chemical basis or experimental evidence for the existence of such building blocks in the solution prior to crystallization of zeolites. In other words, there is no experimental or computational evidence that they are synthetic intermediates during the growth of a crystalline phase. Due to such limitations, the role of SBUs should be limited to the understanding of the topology of a given architecture rather than be extended to their use in the synthetic design strategy. The SBU approach gained major footage in MOF chemistry because it helps in the categorization of MOFs in terms of nodes and spacers. While SBUs are the structural units from which multidimensional frameworks may be derived by applying retrosynthesis

concepts¹⁰, they do not have the advantage that supramolecular synthons seem to possess in molecular crystal engineering in terms of having been detected in the pre-crystallization stages^{11,12}.

The currently proposed PZC theory by Ramanan and Whittingham is based on chemical intuition in that as soon as the metal salt is dissolved in solution, a soluble metal complex is formed, which later undergoes hydrolysis/condensation/ligand (H₂O or solvent) exchange to give the resultant networks (Scheme 2). The authors propose that the geometry of the MOF formed depends upon on how those soluble species (PZCs) interact with organic functional groups in the given solvent. Therefore, the essential requirement for prediction/rationalization of the geometry of a particular MOF is the understanding of hydrogen-bonding assemblies of PZCs with organic functional molecules in a given solvent. In addition to these factors, one has to consider the fact that the transition metals rapidly exchange their ligands at quite a considerable rate along their coordination sphere, which implies that the existence of SBUs or PZCs is quite dependent on the ligand exchange dynamics. The slower the dynamics, the higher the probability for the existence of preformed building units that can be manipulated chemically. At this point, we can state with candour that both the SBU and PZC approaches are merely speculative without actual proofs. Of course, it is interesting to note that a recent report by Walton and co-workers¹³ provides EXAFS evidence for the existence of SBUs in the synthesis of {Fe₃O

(CH₃OH)₃[O₂C(CH₂)₄-CO₂]₃Cl·6(MeOH)_n, (MIL-89).

- Hagrman, P. J., Hagrman, D. and Zubieta, J., *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 2639–2684.
- O'Keeffe, M. and Yaghi, O. M., *Acc. Chem. Res.*, 2001, **34**, 319–330.
- Moulton, B. and Zaworotko, M. J., *Chem. Rev.*, 2001, **101**, 1629–1658.
- Kitagawa, S., Kitaura, R. and Noro, S. I., *Angew. Chem., Int. Ed. Engl.*, 2004, **43**, 2334–2375.
- Sanchez, C. and Ribot, F., *New J. Chem.*, 1994, **18**.
- Biradha, K., Sarkar, M. and Rajput, L., *Chem. Commun.*, 2006, 4169–4179.
- Ramanan, A. and Whittingham, M. S., *Cryst. Growth Des.*, 2006, **6**, 2419–2421.
- Ockwig, N. W., Delgado-Friedrichs, O., O'Keeffe, M. and Yaghi, O. M., *Acc. Chem. Res.*, 2005, **38**, 176.
- Knight, C. T. G., *Zeolites*, 1990, **10**, 140–144.
- Desiraju, G. R., *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311–2327.
- Parveen, S., Davey, R. J., Dent, G. and Pritchard, R. G., *Chem. Commun.*, 2005, 1531–1533.
- Banerjee, R., Bhatt, P. M., Kirchner, M. T. and Desiraju, G. R., *Angew. Chem., Int. Ed. Engl.*, 2005, **44**, 2515–2520.
- Surblé, S., Millange, F., Serre, C., Férey, G. and Walton, R. I., *Chem. Commun.*, 2006, 1518–1520.

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