

clusters by in-situ generated tetradentate dye molecules [119]. The structure consists of three-dimensional inorganic-organic open framework with large uni-dimensional channels. The combination of dye molecules and the inorganic cluster unit in the same material creates a synergistic effect that greatly enhances the emission of the inorganic cluster at 580nm. Such an emission can be excited by an unusually broad spectral range down to the UV, which is believed to result from the absorption of dye molecules and the subsequent energy transfer.

6 Extra-large Pore Crystalline Molecular Sieves

Thus far, an extra-large pore material is conveniently understood as those having a ring size of over 12 tetrahedral atoms [120]. In zeolites, the maximum pore size of a 12-ring pore is about 8\AA . The recent progress in metal-organic frameworks has made it possible to obtain porous materials with pore size larger than 8\AA by using larger organic linkers rather than by forming pores with more than 12 metal cations.

Among silicates, the extra-large pore has only been found in two high silica zeolites and one beryllosilicate. The first extra-large pore zeolite (UTD-1) was reported in 1996 (Fig. 11) [121,122]. UTD-1 (DON) was synthesized using bis(pentamethylcyclopentadienyl) cobalticinium cations and has a ring size of 14 tetrahedral atoms. It has a one-dimensional channel system with the approximate free diameter of $7.5 \times 10\text{\AA}$ for the 14-ring pore. Another extra-large pore zeolite (CIT-5) was reported in 1997 [123,124]. Like UTD-1, CIT-5 (CFI) also has a ring size of 14 tetrahedral atoms with a one-dimensional channel system. The effective pore size (6.4\AA measured using the Horvath-Kawazoe method) of CIT-5 is similar to that of one-dimensional 12-ring channel in SSZ-24 (AFI) [125]. Very recently, a hydrated potassium beryllosilicate called OSB-1 (OSO) was found to have an extra-large pore size of 14 tetrahedral atoms [30].

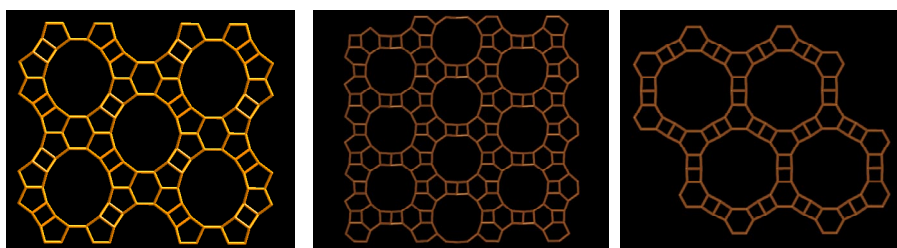


Figure 11. (left) The three-dimensional framework of UTD-1 (DON) with elliptical 14-ring windows; Reprinted with permission from <http://www.iza-structures.org/> and reference [30]. (middle) the three-dimensional framework of AlPO₄-8 (AET) showing 14-ring windows (right) the three-dimensional framework of VPI-5 (VFI) with 18-ring windows.

Most extra-large pore materials such as cacoxenite, VPI-5, cloverite, and JDF-20 are found in phosphates [15,126,127,128]. While the ring size of only 14 tetrahedral atoms is known in silicates, extra-large pore phosphates come with various ring sizes including 14, 16, 18, 20, and 24. Structures of these phosphates sometimes deviate from those of typical zeolites in several aspects including framework interruptions by terminal OH, F, or H₂O groups and non-tetrahedral coordination. These deviations tend to lower the thermal stability of extra-large pore phosphates. On the other hand, it is often because of these deviations that extra-large pores are formed.

The first synthetic extra-large pore phosphate is VPI-5 with one-dimensional channel defined by 18 oxygen atoms (Fig. 11) [15]. Unlike most aluminophosphate molecular sieves, VPI-5 is a hydrated aluminophosphate and does not contain any organic structure-directing agent. Under suitable heating conditions, VPI-5 can be recrystallized into another extra-large pore phosphate called AlPO₄-8 (AET) with a 14-ring pore size (Fig. 11) [129].

Among the most recent development in the area of microporous phosphates is the synthesis of two extra-large pore nickel phosphates denoted as VSB-1 and VSB-5 [130,131]. Similar to VPI-5, both VSB-1 and VSB-5 are hydrates and organic amines used in the syntheses were not occluded into the final structures. VSB-1 and VSB-5 have one-dimensional 24-ring channels and both of them have good thermal stability. The nitrogen adsorption shows the type I isotherms typical of a microporous material.

The synthesis of VPI-5, VSB-1, and VSB-5 demonstrates that neither large nor small organic structure-directing agents are essential for the preparation of extra-large pore sizes. The formation of different pore sizes likely depends on types of small structural units that eventually come together to create the framework and the pore. The structural and synthetic factors that affect the formation of these small structural units may have a substantial effect on the creation of extra-large pore materials.

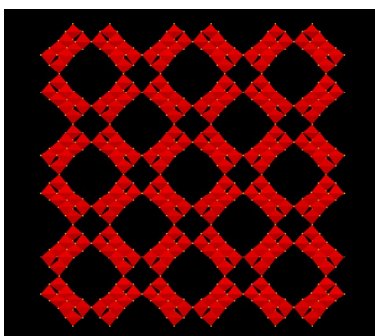


Figure 12. The three-dimensional framework of UCR-23 family of sulfides showing 16-ring channels.

One strategy for the preparation of the extra-large pore size is to generate a large number of small rings, particularly 3-rings. Because the average ring size in a three-dimensional four-connected net is approximately 6, the presence of small rings will be accompanied by large or extra-large rings so that the average ring size will be about 6 [132]. This strategy can be illustrated with the recent discovery of a large family of extra-large pore sulfides.

Because of the large T-S distances and small T-S-T angles, 3-rings often occur in open framework metal sulfides. Correspondingly, large pore and extra-large pore sizes are typically structural features in sulfides. For example, UCR-20, UCR-21, and UCR-22, and UCR-23 consist of adamantane-shaped clusters (T_4S_{10}) with 3-rings. While both UCR-20 and UCR-21 are large-pore sulfides, UCR-23 has three-dimensional intersecting 16-, 12-, and 12-ring channels (Fig. 12) and UCR-22 consists of interpenetrating three-dimensional framework with 24-ring window size.

Other strategies for increasing the pore size include the use of large structural building units such as clusters and the use of long linker molecules between two structural building units. For example, the use of chalcogenide supertetrahedral clusters as large artificial tetrahedral atoms has resulted in a number of three-dimensional frameworks with extra-large pore sizes. Equally successful is the use of dicarboxylates as molecular linkers to join together metal cations or their clusters to generate a series of metal-organic frameworks with pore sizes $> 10\text{\AA}$. By using different supertetrahedral clusters and carboxylates, the pore size of the resulting open framework materials can be tuned.

Acknowledgement

We thank Dr. Qisheng Huo for critical evaluation of this manuscript and Nanfeng Zheng for assistance with figures.

References

1. Rouquerol J., Avnir D., Fairbridge C. W., Everett D. H., Haynes J. H., Pernicone N., Ramsay J. D. F., Sing K. S. W. and Unger, K. K. Recommendations for the characterization of porous solids, *Pure Appl. Chem.* **66** (1994) pp. 1739-58.
2. McCusker L. B., Liebau F. and Engelhardt G., Nomenclature of structural and compositional characteristics of ordered microporous and mesoporous materials with inorganic hosts (IUPAC recommendations 2001), *Pure Applied Chem.* **73** (2001) pp. 381-394.
3. Barton T. J., Bull L. M., Klemperer W. G., Loy D. A. McEnaney B., Misono M., Monson P. A., Pez G., Scherer B., Vartuli J. C. and Yaghi O. M., Tailored Porous Materials, *Chem. Mater.* **11** (1999) pp. 2633-2656.
4. Weitkamp J., Zeolites and catalysis, *Solid State Ionics* 131 (2000) pp. 175-188.

5. Smith J. V., Definition of a Zeolite, *Zeolites* **4** (1984) pp. 309-310.
6. Foley, H. C., Carbogenic molecular sieves: synthesis, properties and applications, *Micro. Mater.* **4** (1995) 407-433.
7. Barrer R. M., Synthesis of a zeolitic mineral with chabazitelike sorptive properties, *J. Chem. Soc.* (1948) pp. 127-132.
8. Milton R. M., Molecular sieve science and technology. A historical perspective, *ACS Symposium Series* (1989), **398** (Zeolite Synth.), pp. 1-10.
9. Argauer R. J. and Landolt G. R. Crystalline Zeolite ZSM-5 and Method of Preparing the Same, US Patent 3,702,886, 1972.
10. Flanigen E. M., Bennett J. M., Grose R. W., Cohen J. P., Patton R. L., Kirchner R. M. and Smith, J. V. Silicalite, a new hydrophobic crystalline silica molecular sieve, *Nature* **271** (1978) pp. 512-516.
11. Wilson S. T., Lok B. M., Messina C. A., Cannan T. R. and Flanigen E. M., Aluminophosphate Molecular Sieves: A New Class of Microporous Crystalline Inorganic Solids, *J. Am. Chem. Soc.* **104** (1982) pp. 1146-1147.
12. Wilson S. T., Lok B. M., Messina C. A., Cannan T. R. and Flanigen, E. M., Aluminophosphate molecular sieves: a new class of microporous crystalline inorganic solids, *ACS Symposium Series* (1983), **218** (Intrazeolite Chem.), pp. 79-106.
13. Cheetham A. K., Ferey G. and Loiseau T., Open-Framework Inorganic Materials, *Angew. Chem. Int. Ed.* **38** (1999) pp. 3268-3292.
14. Bowes C. L. and Ozin G. A., Self-Assembling Frameworks: Beyond Microporous Oxides, *Adv. Mater.* **6** (1996) pp. 13-28.
15. Davis M. E., Saldarriaga C., Montes C., Garces J. and Crwoder C., A molecular sieve with eighteen-membered rings, *Nature* **331** (1988) pp. 698-699.
16. Davis M. E. Ordered porous materials for emerging applications, *Nature* **147** (2002) pp. 813-821.
17. Evans O. R., Lin W., Crystal Engineering of NLO Materials Based on Metal-Organic Coordination Networks, *Acc. Chem. Res.* **35** (2002) pp. 511-522.
18. Davis M. E. and Lobo R. F., Zeolite and Molecular Sieve Synthesis, *Chem. Mater.* **4** (1992) pp. 756-768.
19. Davis M. E., New Vistas in Zeolite and Molecular Sieve Catalysis, *Acc. Chem. Res.* **26** (1993) pp. 111-115.
20. Breck D. W., *Zeolite Molecular Sieves*, Wiley, New York, 1974.
21. Barrer R. M., *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, Academic Press, 1978.
22. Dyer A., *An Introduction to Zeolite Molecular Sieves*, John Wley & Sons, 1988.
23. van Bekkum H., Flanigen E. M. and Jansen J. C., *Studies in Surface Science and Catalysis*, Vol. **58** (*Introduction to Zeolite Science and Practice*) Elsevier, New York, 1991.

24. Jansen J. C., Stocker M., Karge H. G. and Weitkamp, *Studies in Surface Science and Catalysis*, Vol. **85** (*Advanced Zeolite Science and Applications*), Elsevier, 1994.
25. Atwood J. L., Davies J. E. D., MacNicol D. D. and Vogtle F., *Comprehensive Supramolecular Chemistry*, Vol. **7** (*Solid-State Supramolecular Chemistry: Two- and Three-Dimensional Inorganic Networks*, eds. Altermann G. and Bein T.), Elsevier, 1996.
26. Fricke R., Kosslick H., Lischke G. and Richter M., Incorporation of Gallium into Zeolites: Syntheses, Properties and Catalytic Application. *Chem. Rev.* **100** (2000) pp. 2303-2405.
27. Saxton R. J., Crystalline microporous titanium silicates, *Topics in Catalysis* **9** (1999) pp. 43-57.
28. Rocha J. and Anderson M. W. Microporous Titanosilicates and other Novel Mixed Octahedral-Tetrahedral Framework Oxides, *Eur. J. Inorg. Chem.* (2000) pp. 801-818.
29. Loewenstein W., The distribution of aluminum in the tetrahedra of silicates and aluminates, *Am. Mineralogist* **39**, (1954), pp. 92-96.
30. Baerlocher Ch., Meier W. M., Olson D. H. *Atlas of Zeolite Framework Types*, 2001, Elsevier.
31. Smith J. V., Topochemistry of zeolites and related materials. 1. Topology and geometry, *Chem. Rev.* **88** (1988), pp. 149-82.
32. Gier T. E., Bu X., Feng P. and Stucky G. D., Synthesis and organization of zeolite-like materials with three-dimensional helical pores, *Nature* **395** (1998), pp. 154-157.
33. Zones S. I., Davis M. E., Zeolite materials: Recent discoveries and future prospects. *Curr. Opin. Solid State Mater. Sci.* **1** (1996) pp. 107-117.
34. Kessler H., Patarin J., Schott-Daric C., in The opportunities of the fluoride route in the synthesis of microporous materials, *Studies in Surface Science and Catalysis* (1994), **85**(*Advanced Zeolite Science and Applications*), pp. 75-113.
35. Kuperman A., Nadimi S., Oliver S., Ozin G. A., Garces J. M., Olken M. M., Non-aqueous synthesis of giant crystals of zeolites and molecular sieves, *Nature* **365** (1993) pp. 239-242.
36. Cambor M. A., Villaescusa L. A., Diaz-Cabanias M. J., Synthesis of all-silica and high-silica molecular sieves on fluoride media, *Topics in Catalysis* **9** (1999) pp. 59-76.
37. Cambor M. A., Corma A., Lightfoot P., Villaescusa L. A., Wright P. A., Synthesis and structure of ITQ-3, the first pure silica polymorph with a two-dimensional system of straight eight-ring channels, *Angew. Chem. Int. Ed.* **36** (1997) pp. 2659-2661.

38. Barrett A., Cambor M. A., Corma A., Jones H. and Villaescusa, Structure of ITQ-4, a New Pure Silica Polymorph Containing Large Pores and a Large Void Volume, *Chem. Mater.* **9** (1997) pp. 1713-1715.
39. Villaescusa L., Barrett P. and Cambor M. A., ITQ-7: A new Pure Silica Polymorph with a Three-Dimensional System of Large Pore Channels, *Angew. Chem. Int. Ed.* **38** (1999) pp. 1997-2000.
40. Corma A., Diaz-Cabanas M. J., Martinez-Triguero J., Rey F. and Rius J., A large-cavity zeolite with wide pore windows and potential as an oil refining catalyst, *Nature* **418** (2002) pp. 514-517.
41. Blasco T., Corma A., Diaz-Cabanas M. J., Rey F., Vidal-Moya J. A. and Zicovich-Wilson C. M., Preferential Location of Ge in the Double Four-Membered Ring Units of ITQ-7 Zeolite, *J. Phys. Chem. B* **106** (2002) pp. 2634-2642.
42. Corma A., Navarro M. T., Rey F. and Valencia S., Synthesis of pure polymorph C of Beta Zeolite in a fluoride-free system, *Chem. Commun.* (2001) pp. 1486-1487.
43. Bu X., Feng P. and Stucky G. D. Novel Germanate Zeolite Structures with 3-Rings. *J. Am. Chem. Soc.* **120** (1998) pp. 11204-11205.
44. O'Keeffe M., Yaghi O. M., Germanate zeolites: contrasting the behavior of germanate and silicate structures built from cubic T8O20 units (T = Ge or Si). *Chem. Eur. J.* **5** (1999) pp. 2796-2801.
45. Martin J. D. and Greenwood K. B., Halozeotypes: A New Generation of Zeolite-Type Materials, *Angew. Chem.* **36** (1997) pp. 2072-2075.
46. Zheng N., Bu X., Wang B., Feng P., Microporous and Photoluminescent Chalcogenide Zeolite Analogs, *Science* **298** (2002) pp. 2366-2369.
47. Breck D. W., Eversole W. G., Milton R. M., New synthetic crystalline zeolites, *J. Am. Chem. Soc.* **78** (1956) pp. 2338-9.
48. Effenberger H., Giester G., Krause W. and Bernhardt H.-J. Tschortnerite, a copper-bearing zeolite from the Bellberg volcano, Eifel, Germany, *Am. Mineralogist* **83** (1998) pp. 607-617.
49. Bu X., Feng P., Stucky G. D. Large-cage zeolite structures with multidimensional 12-ring channels, *Science* **278** (1997) pp. 2080-2085.
50. Feng P., Bu X. and Stucky G. D. Hydrothermal syntheses and structural characterization of zeolite analog compounds based on cobalt phosphate, *Nature* **388** (1997) pp. 735-741.
51. Bennett J. M., Cohen J. P., Flanigen E. M., Pluth J. J., Smith J. V., Crystal structure of tetrapropylammonium hydroxide-aluminum phosphate Number 5, *ACS Symposium Series* **218** (1983) (*Intrazeolite Chem.*), pp. 109-118.
52. Lok B. M., Messina C. A., Patton R. L., Gajek R. T., Cannan T. R. and Flanigen E. M., Silicoaluminophosphate Molecular Sieves: Another New Class of Microporous Crystalline Inorganic Solids, *J. Am. Chem. Soc.* **106** (1984) pp. 6092-6093.

53. Wilson S. T. and Flanigen E. M., Synthesis and Characterization of Metal Aluminophosphate Molecular Sieves, in *Zeolite Synthesis, ACS Symposium Series* **398** (1989), pp. 329-345, Eds. Occelli M. L. and Robson H. E., American Chemical Society, Washington DC.
54. Chen J., Jones R., Natarajan S., Hursthouse M. B. and Thomas J. M., A Novel Open-Framework Cobalt Phosphate Containing a tetrahedral Coordinated Cobalt(II) Center: $\text{CoPO}_4 \cdot 0.5\text{C}_2\text{H}_{10}\text{N}_2$, *Angew. Chem. Int. Ed. Engl.* **33** (1994) pp. 639-640.
55. Xiao F., Qiu S., Pang W., Xu R. New Development in Microporous Materials, *Adv. Mater.* **11** (1999) 1091-1099.
56. Bibby D. M. and Dale M. P., Synthesis of silica-sodalite from nonaqueous systems, *Nature* **317** (1985) pp. 157-8.
57. Soghomonian V., Chen Q., Haushalter R. C., Zubieta J. and O'Connor C. J., An Inorganic Double Helix: Hydrothermal Synthesis, Structure, and Magnetism of Chiral $[(\text{CH}_3)_2\text{NH}_2]\text{K}_4[\text{V}_{10}\text{O}_{10}(\text{H}_2\text{O})_2(\text{OH})_4(\text{PO}_4)_7] \cdot 4\text{H}_2\text{O}$, *Science* **259** (1993) pp. 1596-1599.
58. Chippindale A. M., Walton, R. I. Synthesis and characterization of the first three-dimensional framework cobalt-gallium phosphate $[\text{C}_5\text{H}_5\text{NH}]^+[\text{CoGa}_2\text{P}_3\text{O}_{12}]$, *J. Chem. Soc., Chem. Commun.* (1994) pp. 2453-2454.
59. Cowley A. R., Chippindale A. M., Synthesis and characterization of $[\text{C}_4\text{NH}_{10}]^+[\text{CoGaP}_2\text{O}_8]^-$, a CoGaPO analog of the zeolite gismondine, *Chem. Commun.* (1996) pp. 673-674.
60. Chippindale A. M., Cowley A. R., CoGaPO-5: Synthesis and crystal structure of $(\text{C}_6\text{N}_2\text{H}_{14})_2[\text{Co}_4\text{Ga}_5\text{P}_9\text{O}_{36}]$, a microporous cobalt-gallium phosphate with a novel framework topology, *Zeolites* **18** (1997) pp. 176-181.
61. Bedard R. L., Wilson S. T., Vail L. D., Bennett J. M. and Flanigen, E. M. The next generation: synthesis, characterization, and structure of metal sulfide-based microporous solids in *Zeolites: Facts, Figures, Future. Proceedings of the 8th International Zeolite Conference*, (1989) pp. 375-387. eds. Jacobs P. A. and van Santen, R. A. Elsevier, Amsterdam.
62. Feng P., Zhang T., Bu X., Arsenate Zeolite Analogues with 11 Topological Types, *J. Am. Chem. Soc.* **123** (2001) pp. 8608-8609.
63. Bu X., Feng P., Gier T. E., Zhao D. and Stucky G. D., Hydrothermal Synthesis and Structural Characterization of Zeolite-like Structures Based on Gallium and Aluminum Germanates, *J. Am. Chem. Soc.* **120** (1998) pp. 13389-13397.
64. Li H. and Yaghi O. M., Transformation of Germanium Dioxide to Microporous Germanate 4-Connected Nets, *J. Am. Chem. Soc.* **120** (1998) pp. 10569-10570.
65. Li H., Laine A., O'Keeffe M., Yaghi O. M., Supertetrahedral Sulfide Crystals with Giant Cavities and Channels, *Science* **283** (1999) pp. 1145-1147.

66. Cahill C. L., Parise J. B., On the formation of framework indium sulfides, *J. Chem. Soc. Dalton Trans.* (2000) pp. 1475-1482.
67. Bu X., Zheng N., Li Y., Feng P., Pushing Up the Size Limit of Chalcogenide Supertetrahedral Clusters: Two- and Three-Dimensional Photoluminescent Open Frameworks from $(\text{Cu}_5\text{In}_{30}\text{S}_{54})^{13-}$ Clusters, *J. Am. Chem. Soc.* **124** (2002) pp. 12646-12647.
68. Dance I. G., Choy A., Scudder M. L., Syntheses, Properties, and Molecular and Crystal Structures of $(\text{Me}_4\text{N})_4[\text{E}_4\text{M}_{10}(\text{SPh})_{16}]$ (E =S, Se; M = Zn, Cd): Molecular Supertetrahedral Fragments of the Cubic Metal Chalcogenide Lattice, *J. Am. Chem. Soc.* **106** (1984) pp. 6285-6295.
69. Dance I. And Fisher K., Metal Chalcogenide Cluster Chemistry, in *Prog. Inorg. Chem.* (1994) pp. 637-803, Ed. Karlin K. D., John Wiley & Sons, Inc.
70. Conradson T., Dadachov M. S. and Zou X. D., "Synthesis and structure of $(\text{Me}_3\text{N})_6[\text{Ge}_{32}\text{O}_{64}] \cdot (\text{H}_2\text{O})_{4.5}$, a thermally stable novel zeolotype with 3D interconnected 12-ring channels, *Micro. Meso. Mater.* **41** (2000) pp. 183-191.
71. Krebs B., Thio- and Seleno-Compounds of Main Group Elements- Novel Inorganic Oligomers and Polymers, *Angew. Chem. Int. Ed. Engl.* **22** (1983) pp. 113-134.
72. Pivan J. Y., Achak O. A., Louer M. and Louer D., The Novel Thiogermanate $[(\text{CH}_3)_4\text{N}]_4\text{Ge}_4\text{S}_{10}$ with a High Cubic Cell Volume. Ab Initio Structure Determination from Conventional X-ray Powder Diffraction, *Chem. Mater.* **6** (1994) pp. 827-830.
73. Yaghi O. M., Sun Z., Richardson D. A. and Loy T. L. Directed Transformation of Molecules to Solids: Synthesis of a Microporous Sulfide from Molecular Germanium Sulfide Cages, *J. Am. Chem. Soc.* **116** (1994) pp. 807-808.
74. Nellis D. M., Ko Y., Tan K., Koch S. and Parise J. B., A One-dimensional Germanium Sulfide Polymer Akin to the Ionosilicates: Synthesis and Structural Characterization of DPA-GS-8, $\text{Ge}_4\text{S}_9(\text{C}_3\text{H}_7)_2\text{NH}_2(\text{C}_3\text{H}_7)\text{NH}_2(\text{C}_2\text{H}_5)$, *J. Chem. Soc., Chem. Commun.* (1995) pp. 541-542.
75. MacLachlan M. J., Petrov S., Bedard R. L., Manners I. And Ozin G. A., Synthesis and Crystal Structure of $\delta\text{-GeS}_2$, the First Germanium Sulfide with an Expanded Framework Structure, *Angew. Chem. Int. Ed.* **37** (1998) pp. 2076-2079.
76. Jiang T. and Ozin G. O., New directions in tin sulfide chemistry, *J. Mater. Chem.* **8** (1998) pp. 1099-1108.
77. Parise J. B. and Ko Y., Material Consisting of two Interwoven 4-Connected Networks: Hydrothermal Synthesis and Structure of $[\text{Sn}_5\text{S}_9\text{O}_2][\text{NH}(\text{CH}_3)_3]_2$, *Chem. Mater.* **6** (1994) pp. 718-720.
78. Schiwy W., Krebs B. $\text{Sn}_{10}\text{O}_4\text{S}_{20}^{8-}$: A New Type of Polyanion, *Angew. Chem. Int. Ed.* **14** (1975) p. 436.

79. Achak O., Pivan J. Y., Maunaye M., Louer M. and Louer D. The *ab initio* structure determination of $[(\text{CH}_3)_4\text{N}]_2\text{Ge}_4\text{MnS}_{10}$ from X-ray powder diffraction data, *J. Alloys Compounds* **219** (1995) pp. 111-115.
80. Achak, O., Pivan J. Y., Maunaye M., Louer M., Louer D., Structure Refinement by the Rietveld Methods of the Thiogermanates $[(\text{CH}_3)_4\text{N}]_2\text{MGe}_4\text{S}_{10}$ (M=Fe, Cd), *J. Solid State Chem.* **121** (1996) pp. 473-478.
81. Tan K., Darovsky A. and Parise J. B., Synthesis of a Novel Open-Framework Sulfide, $\text{CuGe}_2\text{S}_5 \cdot (\text{C}_2\text{H}_5)_4\text{N}$, and Its Structure Solution Using Synchrotron Imaging Plate Data, *J. Am. Chem. Soc.* **117** (1995) pp. 7039-7040.
82. Cahill C. L. and Parise J. B. Synthesis and Structure of $\text{MnGe}_4\text{S}_{10} \cdot (\text{C}_6\text{H}_{14}\text{N}_2) \cdot 3\text{H}_2\text{O}$: A Novel Sulfide Framework Analogous to Zeolite Li-A(BW), *Chem. Mater.* **9** (1997) pp. 807-811.
83. Cahill C. L., Ko Y. and Parise J. B., A Novel 3-Dimensional Open Framework Sulfide Based upon the $[\text{In}_{10}\text{S}_{20}]^{10-}$ Supertetrahedron: DMA-InS-SB1, *Chem. Mater.* **10** (1998) pp. 19-21.
84. Li H., Eddaoudi M., Laine A., O'Keeffe M. and Yaghi O. M., Noninterpenetrating Indium Sulfide Supertetrahedral Cristobalite Framework, *J. Am. Chem. Soc.* **121** (1999) pp. 6096-6097.
85. Zheng N., Bu X., Feng P., Nonaqueous Synthesis and Selective Crystallization of Gallium Sulfide Clusters into Three-Dimensional Photoluminescent Superlattices, *J. Am. Chem. Soc.* **125** (2003) pp. 1138-1139.
86. Krebs B., Voelker D., Stiller K., Novel Adamantane-like Thio- and Selenoanions from Aqueous Solution: $\text{Ga}_4\text{S}_{10}^{8-}$, $\text{In}_4\text{S}_{10}^{8-}$, $\text{In}_4\text{Se}_{10}^{8-}$, *Inorg. Chim. Acta* **65** (1982) pp. L101-L102.
87. Wang C., Li Y., Bu X., Zheng N., Zivkovic O., Yang C., Feng P. Three-Dimensional Superlattices Built from $(\text{M}_4\text{In}_{16}\text{S}_{33})^{10-}$ (M = Mn, Co, Zn, Cd) Supertetrahedral Clusters, *J. Am. Chem. Soc.* **123** (2002) pp. 11506-11507.
88. Wang C., Bu X., Zheng N., Feng P., Nanocluster with One Missing Core Atom: A Three-Dimensional Hybrid Superlattice Built from Dual-Sized Supertetrahedral Clusters, *J. Am. Chem. Soc.* **124** (2002) pp. 10268-10269.
89. Su W., Huang X., Li J. and Fu H., Crystal of Semiconducting Quantum Dots Built on Covalently Bonded T5 $[\text{In}_{28}\text{Cd}_6\text{S}_{54}]^{12-}$: The Largest Supertetrahedral Clusters in Solid State, *J. Am. Chem. Soc.* **124** (2002) pp. 12944-12945.
90. Ferey, G., Microporous Solids: From Organically Templated Inorganic Skeletons to Hybrid Frameworks...Ecumenism in Chemistry, *Chem. Mater.* **13** (2001) pp. 3084-3098.
91. Batten S. R., Coordination polymers, *Cur. Opin. Solid State Mater. Sci.* **5** (2001) pp. 107-114.
92. Hoskins B. F. and Robson R., Design and Construction of a New Class of Scaffolding-like Materials Comprising Infinite Polymeric Frameworks of 3D-Linked Molecular Rods. A Reappraisal of the $\text{Zn}(\text{CN})_2$ and $\text{Cd}(\text{CN})_2$ structures and the Synthesis and Structures of the Diamond-Related Frameworks

- [N(CH₃)₄][Cu^IZn^{II}(CN)₄ and Cu^I[4,4',4'',4'''-tetracyanotetraphenylmethane] BF₄ · xC₆H₅NO₂, *J. Am. Chem. Soc.* **112** (1990) pp. 1546-1554.
93. Gardner G. B., Venkataraman D., Moore J. S., Lee S., Spontaneous assembly of a hinged coordination network, *Nature* **374** (1995) pp. 792-795.
 94. Gravereau P. P. and Hardy E. G. A., Les Hexacyanoferrates Zeolithiques: Structure Cristalline de K₂Zn₃[Fe(CN)₆]₂ · xH₂O, *Acta Cryst.* **B35** (1979) pp. 2843-2848.
 95. Yaghi O. M. Li G. and Li H., Selective binding and removal of guests in a microporous metal-organic framework, *Nature* **378** (1995) pp. 703-706.
 96. Li H., Eddaoudi M., Groy T. L. and Yaghi O. M., Establishing Microporosity in Open Metal-Organic Frameworks: Gas Sorption Isotherm for Zn(BDC) (BDC = 1,4-Benzenedicarboxylate), *J. Am. Chem. Soc.* **120** (1998) pp. 8571-8572.
 97. Chui, S. S. -Y, Lo S. M. -F, Charmant J. P. H., Orpen A. G. and Williams I. D. A Chemically Functionalizable Nanoporous Material [Cu₃(TMA)₂(H₂O)₃]_n, *Science* **283** (1999) pp. 1148-1150.
 98. Li H., Eddaoudi M., O'Keeffe M., Yaghi O. M., Design and synthesis of an exceptionally stable and highly porous metal-organic framework, *Nature* **402** (1999) pp. 276-279.
 99. Chen B., Eddaoudi M., Hyde S. T., O'Keeffe M. and Yaghi O. M., Interwoven Metal-Organic Framework on a Periodic Minimal Surface with Extra-Large Pores, *Science* **291** (2001) pp. 1021-1023.
 100. Eddaoudi M., Li H., Yaghi O. M., Highly Porous and Stable Metal-Organic Frameworks: Structure Design and Sorption Properties, *J. Am. Chem. Soc.* **122** (2000) pp. 1391-1397.
 101. Eddaoudi M., Kim J., Rosi N., Vodak D., Wachter J., O'Keeffe M. and Yaghi O. M., Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application In Methane Storage, *Science* **295** (2002) pp. 469-472.
 102. Chen B., Eddaoudi M., Reineke, T. M., Kampf, J. W., O'Keeffe M. and Yaghi O. M., Cu₂(ATC) · 6H₂O: Design of Open Metal Sites in Porous Metal-Organic Crystals (ATC: 1,3,5,7-Admantane Tetracarboxylate), *J. Am. Chem. Soc.* **122** (2000) pp. 11559-11560.
 103. Reineke T. M., Eddaoudi M., Fehr M., Kelley D. and Yaghi O. M., From Condensed Lanthanide Coordination Solids to Microporous Frameworks Having Accessible Metal Sites, *J. Am. Chem. Soc.* **121** (1999) pp. 1651-1657.
 104. Seo J. S., Whang D., Lee H., Jun S. I., Oh J., Jeon Y. J. and Kim K. A homochiral metal-organic porous material for enantioselective separation and catalysis, *Nature* **404** (2000) pp. 982-986.
 105. Seki K., Design of an adsorbent with an ideal pore structure for methane adsorption using metal complexes., *Chem. Commun.* (2001) pp. 1496-1497.

106. Noro S., Kitagawa S., Kondo M. and Seki K. A New Methane Adsorbent, Porous Coordination Polymer $[\{\text{CuSiF}_6(4,4'\text{-bipyridine})_2\}_n]$, *Angew. Chem. Int. Ed.* **39** (2000) pp. 2082-2084.
107. Yaghi O. M. and Li H., T-Shaped Molecular Building Units in the Porous Structure of $\text{Ag}(4,4'\text{-bpy})\cdot\text{NO}_3$, *J. Am. Chem. Soc.* **118** (1996) pp. 295-296.
108. Yaghi O. M., Li H., Davis C., Richardson D. and Groy T., Synthetic Strategies, Structure Patterns, and Emerging Properties in the Chemistry of Modular Porous Solids, *Acc. Chem. Res.* **31**, pp. 474-484.
109. Eddaoudi M., Moler D. B., Li, H., Chen B., Reineke T. M., O'Keeffe, M. and Yaghi O. M., Modular Chemistry: Secondary Building Units as a Basis for the Design of Highly Porous and Robust Metal-Organic Carboxylate Frameworks. *Acc. Chem. Res.* **34** (2001) pp. 319-330.
110. Wang Q. M., Shen D., Bulow M., Lau M. L., Deng S. Fitch F. R., Lemcoff N. O. and Semanscin J., Metallo-organic molecular sieve for gas separation and purification, *Microporous Mesoporous Mater.* **55** (2002) pp. 217-230.
111. Tao J., Tong M., Shi J., Chen X., Ng S. W., Blue photoluminescent zinc coordination polymers with supertetranuclear cores, *Chem. Commun.* (2000) pp. 2043-2044.
112. Lin C. Z-J., Chui S. S-Y, Lo S. M-F., Shek F. L-Y, Wu M., Suwinska K., Lipkowski J. and Williams I. D., Physical stability vs. chemical stability in microporous metal coordination polymers: a comparison of $[\text{Cu}(\text{OH})(\text{INA})]_n$ and $[\text{Cu}(\text{INA})_2]_n$: INA = 1,4-(NC₅H₄CO₂), *Chem. Commun.* (2002) pp. 1642-1643.
113. Abrahams B. F., Hoskins B. F., Michail D. M. and Robson R., Assembly of porphyrin building blocks into network structures with large channels, *Nature* **369** (1994) pp. 727-729.
114. Kosal M., Chou J., Wilson S. R., and Suslick K. S., A functional zeolite analogue assembled from metalloporphyrins, *Nature Mater.* **1** (2002) pp. 118-121.
115. Lin K-J, SMTP-1: The First Functionalized Metalloporphyrin Molecular Sieves with Large Channels, *Angew. Chem. Int. Ed.* **38** (1999) pp. 2730-2732.
116. Yang S. Y., Long L. S., Jiang Y. B., Huang R. B., Zheng L. S., An Exceptionally Stable Metal-Organic Framework Constructed from the Zn₈(SiO₄) Core, *Chem. Mater.* **14** (2002) pp. 3229-3231.
117. Kim J., Chen B., Reineke T. M., Li H., Eddaoudi M., Moler D. B., O'Keeffe M. and Yaghi O. M., Assembly of Metal-Organic Frameworks from Large Organic and Inorganic Secondary Building Units: New Examples and Simplifying Principles for Complex Structures, *J. Am. Chem. Soc.* **123** (2001) pp. 8239-8247.
118. Hagrman D., Hagrman P., and Zubieta J., Solid-State Coordination Chemistry: The Self-Assembly of Microporous Organic-Inorganic Hybrid Frameworks

- Constructed from Tetrapyrrolylporphyrin and Bimetallic Oxide Chains or Oxide Clusters, *Angew. Chem. Int. Ed.* **38** (1999) pp. 3165-3168.
119. Zheng N., Bu X., Feng P., Self-Assembly of Novel Dye Molecules and $[\text{Cd}_8(\text{SPh})_{12}]^{4+}$ Cubic Clusters into Three-Dimensional Photoluminescent Superlattices, *J. Am. Chem. Soc.* **124** (2002) pp. 9688-9689.
 120. Davis M. E., The Quest for Extra-Large Pore, Crystalline Molecular Sieves, *Chem. Eur. J.* **3** (1997) pp. 1745-1750.
 121. Freyhardt C. C., Tsapatsis M., Lobo R. F., Balkus K. J. Jr. and Davis M. E., A high-silica zeolite with a 14-tetrahedral-atom pore opening, *Nature* **381** (1996) pp. 295-298.
 122. Lobo R. F., Tsapatsis M., Freyhardt C. C., Khodabandeh S., Wagner P., Chen C., Balkus K. J. Jr., Zones S. I. and Davis M. E., Characterization of the Extra-Large Pore Zeolite UTD-1, *J. Am. Chem. Soc.* **119** (1997) pp. 8474-8484.
 123. Wagner P., Yoshikawa M., Lovallo M., Tsuji K., Taspatsis M. and Davis M., CIT-5: a high-silica zeolite with 14-ring pores, *Chem. Commun.* (1997) pp. 2179-2180.
 124. Yoshikawa M., Wagner P., Lovallo M., Tsuji K., Takewaki T., Chen C., Beck L. W., Jones C., Tsapatsis M., Zones S. I. and Davis M. E., Synthesis, Characterization, and Structure Solution of CIT-5. A new, High-Silica, Extra-Large-Pore Molecular Sieve, *J. Phys. Chem. B* **102** (1998) pp. 7139-7147.
 125. Barrett P. A., Diaz-Cabanas M. J., Cambor M. A. and Jones R. H., Synthesis in fluoride and hydroxide media and structure of the extra-large pore pure silica zeolite CIT-5, *J. Chem. Soc., Faraday Trans.* **94** (1998) pp. 2475-2481.
 126. Moore P. B. and Shen J., An X-ray structural study of cacoxenite, a mineral phosphate, *Nature* **306** (1983) pp. 356-358.
 127. Estermann M., McCusker L. B., Baerlocher C., Merrouche A., Kessler H., A Synthetic Gallophosphate molecular sieve with a 20-tetrahedral-atom pore opening, *Nature* **352** (1991) pp. 320-323.
 128. Jones R. H., Thomas J. M., Chen J. Xu R., Huo Q., Li S., Ma Z. c Chippindale A. M., Structure of an Unusual Aluminum Phosphate $[\text{Al}_5\text{P}_6\text{O}_{24}\text{H}]^{2-} 2[\text{N}(\text{C}_2\text{H}_5)_3\text{H}]^+ \cdot 2\text{H}_2\text{O}$ JDF-20 with large elliptical Apertures, *J. Solid State Chem.* **102** (1993) pp. 204-208.
 129. Richardson J. W. Jr. and Vogt E. T. C., Structural determination and Rietveld refinement of aluminophosphate molecular sieve $\text{AlPO}_4\text{-8}$, *Zeolites* **12** (1992) pp. 13-19.
 130. Guillou N., Gao Q., Forster P. M., Chang J., Nogues M., Park S., Ferey G. and Cheetham A. K., Nickle(II) Phosphate VSB-5: A Magnetic Nanoporous Hydrogenation Catalyst with 24-ring Tunnels, *Angew. Chem. Int. Ed.* **40** (2001) pp. 2831-2834.

131. Guillou N., Gao Q., Nogues M., Morris R. E., Hervieu M., Ferey G. and Cheetham A. K., Zeolitic and magnetic properties of a 24-membered ring porous nickel(II) phosphate, VSB-1, *C. R. Acad. Sci. Paris, t. 2, Serie II c* (1999) pp. 387-392.
132. Brunner G. O., "Quantitative zeolite topology" can help to recognize erroneous structures and to plan syntheses, *Zeolites* **13** (1993) pp. 88-91.