

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].

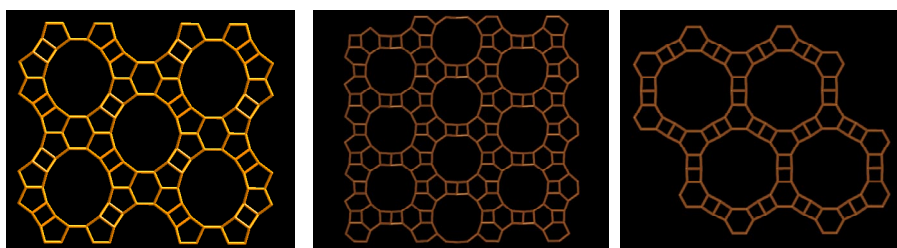


Figure 11. (left) The three-dimensional framework of UTD-1 (DON) with elliptical 14-ring windows; Reprinted with permission from <http://www.iza-structures.org/> and reference [30]. (middle) the three-dimensional framework of $\text{AlPO}_4\text{-8}$ (AET) showing 14-ring windows (right) the three-dimensional 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.

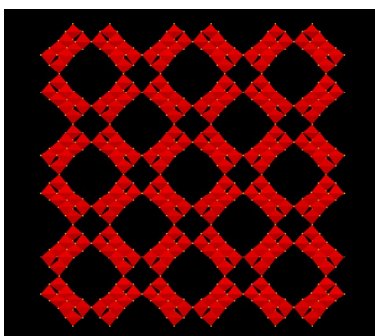


Figure 12. The three-dimensional framework of UCR-23 family of sulfides showing 16-ring channels.

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.

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