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Open channels in porous molecular crystals: host-guest structures and interactions

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Porous organic materials have attracted much attention in the material science field due to their functions such as gas sorption, catalytic abilities, and others. One of the interesting families of the materials is Porous Molecular Crystal (PMC). It is constructed by discrete organic molecules forming a framework structure in the crystal. When intrinsic porous molecule such as cage or ring molecules stack columnar in crystal, a porous channel should be formed as open pores in the PMC.

Diboronic acid and racemic tetrol are found to form a self-assembled macrocyclic boronic ester in the presence of appropriate guest molecules [1]. In the crystal, stacking of macrocyclic ring is observed to form infinite "cuboid" open channel. This structure accommodates various small guest molecules such as toluene, chloroform, p-dicyanobenzene, and THF. The stabilization energy of the toluene molecule in the channel was calculated in which dispersion force dominated. The guest molecules were easily released by heating to leave a PMC with guest-free open channel which was analyzed by the powder structure determination technique [2].

An interesting function of this crystal is the carbon dioxide absorption. This macrocyclic boronic ester molecule found to take carbon dioxide molecules as the guest molecules during the recrystallisation from gassed solvent . The crystal structure was analyzed to show two symmetry related dioxide molecules in the host cage. From the energy calculations, it is noteworthy that electrostatic force contributed to the attractive force of carbon dioxide molecule. The total stabilization energy of the host-guest molecule was smaller than toluene case, and similar to the weak hydrogen bonding energy.

Another example of PMC is Cycloparaphenylene (CPP) case. C_3-symmetrical [12]CPP-hexacarboxylate molecule was synthesised, and the molecules were stacked as a column to form the open channel structure with benzene rings as wall [3]. In the crystal, the channels accommodated solvent molecules (chloroform and n-hexane) that may play an important role to realize the columnar stacking. Interestingly, when the compound was deposited on a defined Au surface, a tube structure with 1.64nm in diameter was recorded by STM technique. It means a self-assembled columnar nanostructure (200nm long) is possible without guest molecules, and thus this compound is promising as PMC materials.

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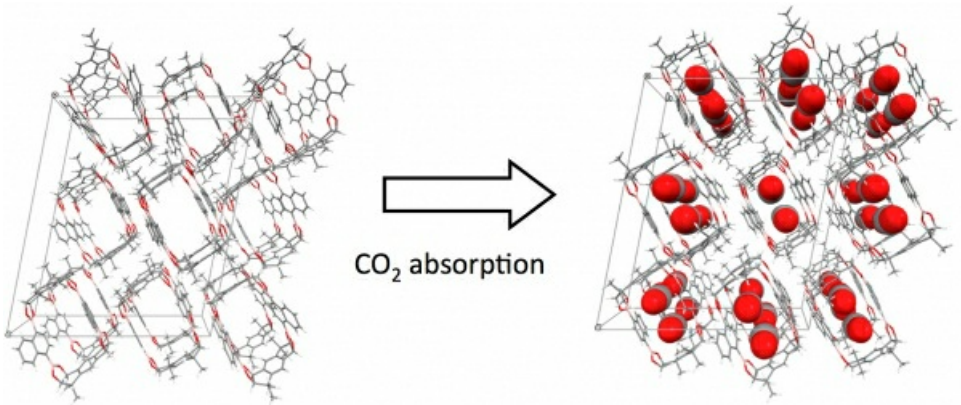

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