

XXL Cages: Organometallic lattice with unusually large pores can house gases and ferrocene molecules

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It's full of holes and yet it holds together: Whether as a place to store gas molecules; for the separation of substances; as sensors, catalysts, and nanoreactors; or materials for optoelectronics, porous crystalline solids with a regular array of defined pores have become indispensable in science and technology.

Organometallic compounds can also form porous structures and have greatly broadened the palette of porous materials, though until now these have been limited to species with very small pores. In the journal *Angewandte Chemie*, Korean researchers led by Jaheon Kim now report the synthesis and characterization of a mesoporous organometallic lattice with cagelike pores that are 3.9 to 4.7 nm in diameter.

Previously, only a few stable structures made of metal atoms or ions and organic ligands have been made that have larger pores, called mesopores (>3 nm in diameter). Among the reasons for this is the special type of bonding that takes place between a metal and a ligand, known as complex coordination. Large cavities can easily destabilize this type of lattice. Just as difficult as the synthesis of such structures is their characterization at the atomic level.

The Korean researchers have overcome both challenges. Their lattice structures are made of ions of the rare-earth metal terbium and an organic ligand. By using X-ray crystallographic methods, the scientists

were also able to precisely determine the structures of both the crystal and the pores.

The use of nitrogen adsorption measurements also allowed them to confirm that there are two types of pore in the structure, some a little bigger, some smaller. When the samples are activated at 160 °C, the specific surface area of the porous crystals increases further, but its sorption ratio does not change. This behavior is also confirmed in adsorption experiments with carbon dioxide.

When irradiated with light, the crystals fluoresce green. They are very thermally stable and hold out well enough in a vacuum to be loaded up by means of a sublimation process with guest molecules that are catalytically active or useful for optoelectronics. The researchers tested this with ferrocene, a molecular “sandwich” with two aromatic five-membered rings acting as the “bread” and an iron atom as the “filling”. With ferrocene guests in its pores, the crystal no longer fluoresces green. Instead, emission from the ferrocene is observed.

The researchers believe that the crystal lattice absorbs the photons like an antenna and passes them on to the ferrocene unit in the form of “energy bundles”. The ferrocene molecule in turn gives off this energy in the form of light. However, its emission is stronger than that given off in the irradiation of ferrocene alone. Systems using this construction principle could be useful for future optoelectronic components such as novel light-emitting diodes.

Citation: Jaheon Kim, Crystal Structure and Guest Uptake of a Mesoporous Metal-Organic Framework Containing Cages of 3.9 and 4.7nm in Diameter, *Angewandte Chemie International Edition*, doi: 10.1002/anie.200702324

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