New covalent organic framework using boron and phosphorus allows for better connectivity

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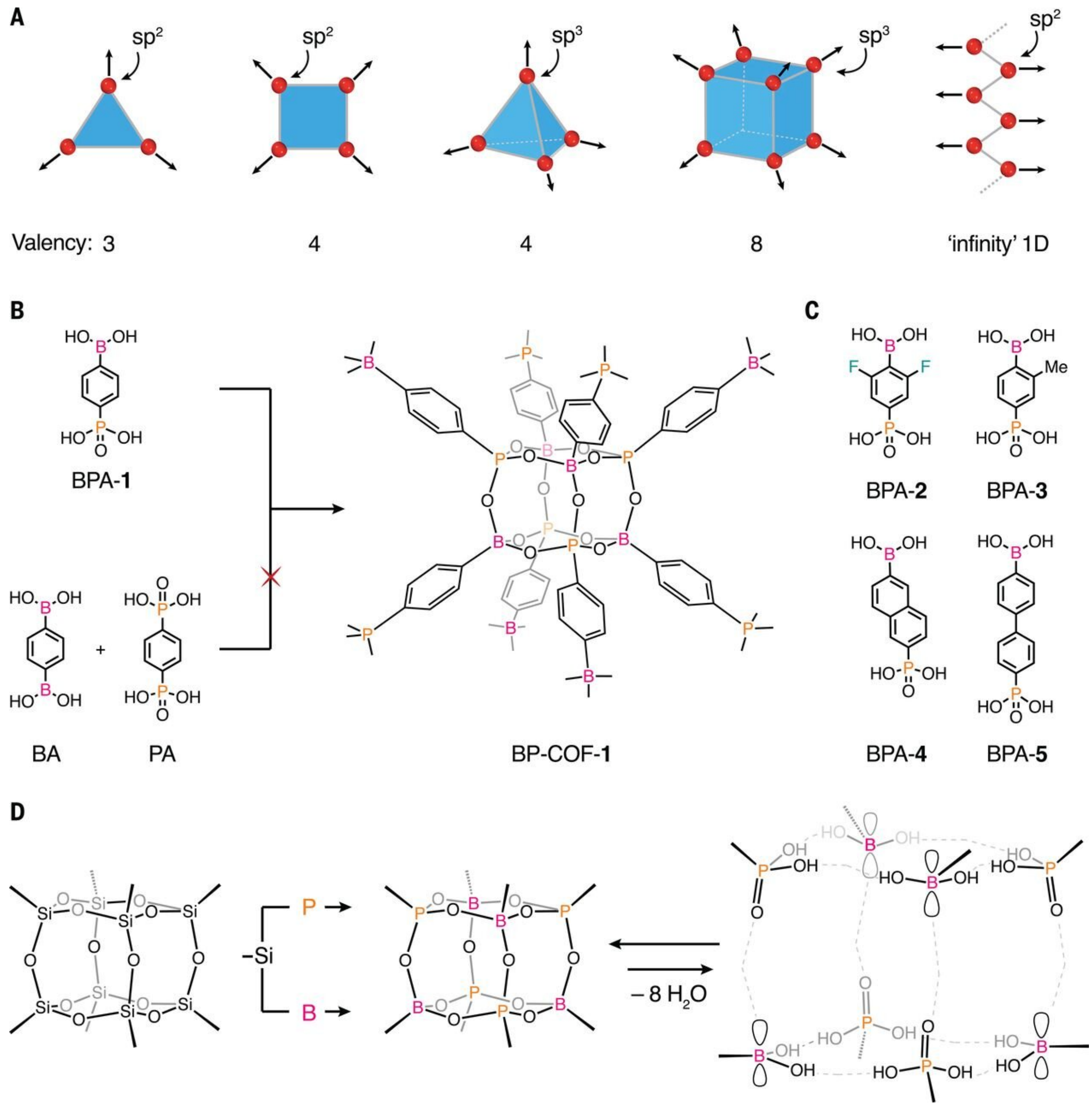

Higher valency in COFs and synthetic strategy for polycubanes. (A) Building units of valency 3 and 4 are currently used in the design and synthesis of 3D COFs; cubes with valency of 8 and infinite 1D rods have not been reported. (B) Reticulation of a linker designed to hold two functionalities (BPA-1) affords BP-COF-1 with valency of 8; the alternative strategy involving BA and PA gives instead COFs of lower valency. (C) Linkers with different functionalities (BPA-2 and 3) and lengths (BPA-4 and 5) were prepared and used to make the corresponding COFs. (D) Isoelectronic replacement as a conceptual basis for creating reversible in situ formation of the cubic units. Credit: *Science* (2020). DOI: 10.1126/science.abd6406

A team of researchers affiliated with both the University of California–Berkeley and the Kavli Energy Nanoscience Institute at UC, has developed a new covalent organic framework (COF) using boron and phosphorus—one that allows for higher connectivity than those now in use. In their paper published in the journal *Science*, the group describes their work in overcoming the limitations of the geometry of carbon bonds in COF architectures and how it led to the development of a whole new class of COFs.

COFs are organic solids with unique structures that allow them to be used as building blocks for making structures useful for certain applications, such as hydrogen or methane storage. But as the researchers note, research and development efforts involving COFs have lagged behind those for metal organic frameworks due mainly to the geometry of carbon bonds in COF architectures. In this new effort, the researchers have found a way to use boron and phosphorus to overcome some of those limitations.

The work involved developing a borophosphonic acid linker with a boron group that could be added to one end of a phenyl ring—on the other end of the ring, they added different members of a phosphorus group. They then dunked the results in a solution that allowed for a controlled reaction rate as it was heated. The result was the creation of a COF made from repeating self-assembling borophosphate cubes—each made from eight linkers. The cubes could then be used as building blocks to create complex assemblages. The researchers note that each cube can be used as the basis for adding an additional eight cubes. And they also note that because of the nature of the bonds, the cubes can be used to create repeating structures of cubes by manipulating the amount of water that is released during the reaction. Testing showed the cubes to be thermally stable, as well, up to 500 degrees C.

The researchers claim the new kind of COFs expand the scope of what can be done with COFs in general, suggesting that they will lead to the development of new types of structures for use in a wide variety of applications.

More information: Cornelius Gropp et al. Design of higher valency in covalent organic frameworks, *Science* (2020). DOI: 10.1126/science.abd6406