Topological Design of Photofunctional Organic Framework

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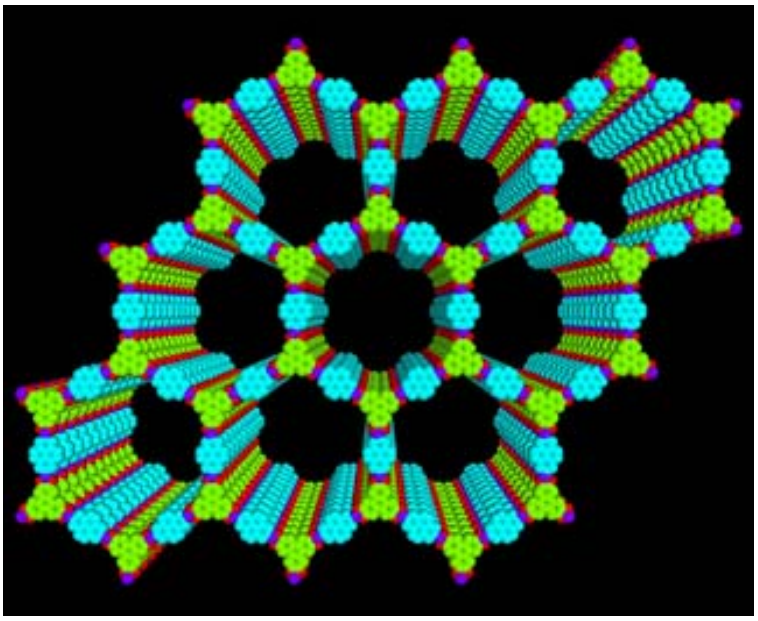
Covalent organic frameworks (COFs) are porous and crystalline polymer with a well defined and predictable network of building blocks. Compared with inorganic porous materials, COFs are unique in that they are made from lighter elements, are robust towards air and organic solvents, and have tunable skeletons. From a synthetic viewpoint, COFs are attracted motifs since they allow total control over structural parameters, including composition and porosity. Most studies up to date have only focused on the development of synthetic methodologies with the aim of optimizing pore size and surface area. In contrast, the functions of COFs, except for gas storage, have not yet been well explored. This motivated us to explore the possibility of constructing functional COFs with novel properties by utilizing highly ordered π-conjugation systems. Herein, we reported the first example of a luminescent and semiconducting COF (TP-COF), which adopts a belt shape and consists of pyrene and triphenylene functionalities alternately linked in a mesoporous hexagonal skeleton.

A new family of covalent organic framework (TP-COF) based on π electron system was synthesized by condensation polymerization with triphenylene and pyrene derivatives as monomers. TP-COF adoptes belt morphology with thickness of about 100 nm, width of about 300 nm, and length of micrometers. When triphenylene and pyrene unit were selectively excited by ultraviolet and visible light, TP-COF displays strong blue fluorescence at 474 nm, as a result of an efficient energy transfer between two units. This result suggests that TP-COF collects photons of a wide range covering from ultraviolet to the visible regions and converts them to blue emission efficiently. In addition, due to the ultimate π stacking of large π-conjugated components, TP-COF is electrically semiconducting. Upon doping with iodine, the electric current was increased remarkably, which suggests that TP-COF is *p*-type semiconductor.



References

(1) Shun Wan, Jia Guo, Jangbae Kim, Hyotcherl Ihee, Donglin Jiang, "A Belt-Shaped, Blue Luminescent and Semiconducting Covalent Organic Framework", *Angew. Chem. Int. Ed.*, **2008**, 47, 8826 (VIP). Selected as a frontispiece of *ACIE*.

(2) Highlighted by Chemical & Engineering News. Jyllian N. Kemsley, "Covalent Conducting Belts", *C & EN*, October 13, 2008 Volume 86, Number 41 P. 29.