

Two-Dimensional Covalent Polymers and Organic Frameworks

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Keywords

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Covalent organic frameworks (COFs) are a class of porous polymers that enable the atomically precise incorporation of organic units into periodic structures, creating highly ordered π -columnar arrays and one-dimensional open channels. One significant structural feature is that they can be pre-designed at both primary and high-order structure levels. COFs have emerged as a platform for materials design and functional explorations and exhibit great potential for applications in gas storage, manufacture of semiconductive and photoconductive devices, energy conversion and storage, and heterogeneous catalysis. The key to the design of COFs is their topology diagram, which defines the polygon size and shape and determines the crystal lattice. Hexagonal and tetragonal topologies have been exploited for the design of COFs with discrete pores and ordered skeletons. The introduction of new topologies is highly desired to broaden the structural diversity and application of COF materials.

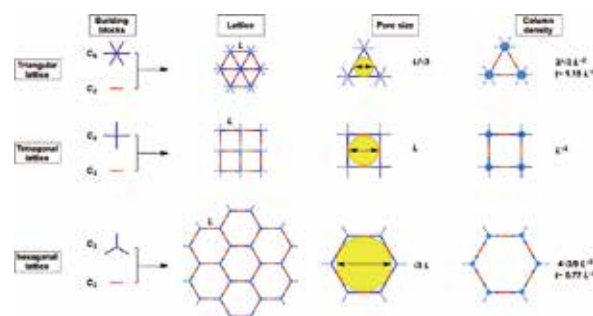


Figure 1. Comparison of topological diagrams for the synthesis of 2D COFs. The different diagrams required different building blocks and result in different lattices, π -densities, and pore sizes. The trigonal topology leads to the highest π -density and smallest pore size among the topologies thus far developed.

Selected Publications

- X. Feng, X. Ding and D. Jiang*, "Covalent Organic Frameworks," *Chem. Soc. Rev.* **41**, 6010–6022 (2012).
- S. Wan, J. Guo, J. Kim, H. Ihee and D. Jiang*, "A Belt-Shaped, Blue Luminescent and Semiconducting Covalent Organic Framework," *Angew. Chem., Int. Ed.* **47**, 8826–8830 (2008) (VIP).
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- J. Guo, Y. Honsho, M. A. Addicoat, J. Kim, A. Saeki, H. Ihee, S. Seki, S. Irle, M. Hiramoto, J. Gao and D. Jiang*, "Conjugated Organic Framework with Three-Dimensionally Ordered Stable Polymer with Delocalized π Clouds," *Nat. Commun.* **4**: 2736 doi: 10.1038/ncomms3736 (2013).

1. Design of COFs with Trigonal Topology

In this study, we developed a strategy for the rational design and synthesis of a new class of COFs based on the triangular topology (Figure 1). The triangular topology consists of C_6 -geometric vertices, which is the highest symmetry of a benzene system and has a potential to efficiently exploit space for tiling organic units into a crystal lattice. With this geometry, a triangular COF would feature the smallest pore size and most dense π -columns among all of the COF materials. However, the triangular topology has not been reported for the practical synthesis of COFs. We demonstrate the synthesis of two triangular COFs (defined as HPB-COF and HBC-COF) by using two different C_6 -symmetric vertices—one is hexaphenylbenzene (HPB), which is a typical propeller-shaped π -unit, and the other is hexabenzocoronene (HBC), which is a large graphitic π -unit—for Schiff-base polymerization with C_2 -symmetric benzene linkers. These triangular COFs form supermicropores with pore sizes of as low as 12 Å, which is among the lowest reported for COFs, whereas the density of π -columns can reach 0.25 nm⁻², which exceeds those of the COFs and supramolecular π -arrays reported to date. These crystalline COFs exhibit excellent thermal and solvent stabilities. We demonstrate that the triangular COFs enable both intra- and inter-layer π -cloud delocalization and exhibit a prominent photoconductivity, with carrier mobilities as high as 0.7 cm² V⁻¹ s⁻¹, which is among the highest reported for COFs and polygraphitic ensembles. These results suggest that the triangular topology is useful for designing COFs with unique structures to be used in a wide variety of applications, such as gas storage, catalysis, and the manufacture of sensing and semiconducting devices.

2. Light-Harvesting Porous π -Network Films: Cascade Exciton-Pumping Engines with Manipulated Speed and Efficiency

Light-harvesting antennae are the machinery for exciton pumping in natural photosynthesis, whereas cascade energy transfer through chlorophyll is key to long-distance, efficient energy transduction. Numerous artificial antennae have been developed. However, they are limited in their cascade energy-transfer abilities because of a lack of control over complex chromophore aggregation processes, which has impeded their advancement.

Here we report a viable approach for addressing this issue by using a light-harvesting porous polymer film in which a three-dimensional π -network serves as the antenna and micropores segregate multiple dyes to prevent aggregation. The porous organic polymer (POP) films are synthesized with a controlled thickness via the previously reported electrochemical method and emit bright blue luminescence. The three-dimensional π -network drastically enhances the interface of energy transfer to relay and acceptor dyes, whereas the nanopores within the film permit segregated molecular docking of multiple laser dyes with desired properties and in specific proportions.

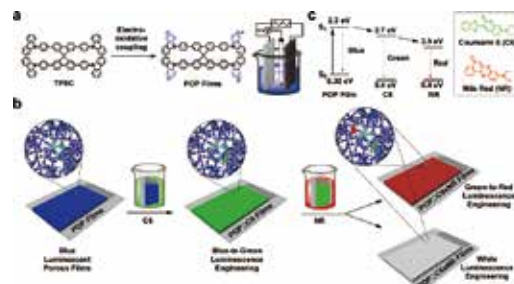


Figure 2. a, Schematic representation of the synthesis of POP films by the electro-oxidative coupling reaction. Inset: cell setup for electro-oxidative coupling for the preparation of POP thin films on ITO working electrode. b, Graphical protocol for the preparation of exciton-pumping films by dipping the films into the corresponding laser dye solutions of coumarin 6 and Nile red followed by rinsing. Inset: Enlarged circles show porous structures of the frameworks (blue: POP framework; sky blue: highlight of one TSPC unit; green: coumarin 6; red: Nile red). c, Diagram of cascade energy transfer from the POP film to coumarin 6 and to Nile red. Inset: Chemical structures of coumarin 6 and Nile red.

Mechanistic studies reveal that the light-harvesting films allow the integration of a cascade energy-transfer engine that functions in a vectorial and highly efficient manner and enables total control over the speed and efficiency of the energy transfer through tuning of the distribution and types of dye introduced. This film system allows for accurate and versatile luminescence engineering in producing thirty different luminescence hues, including blue, green, red and white (Figure 2). By virtue of the antenna effect, the films exhibit considerably amplified luminescence and gain exceptional quantum efficiencies. We envisage that replacement of the dyes with redox-active components may lead to application of the present technology for highly efficient photosynthesis and photoenergy conversion.

References

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Award

GU, Cheng; MOF2014 Kobe Best Poster Award.