

Two-Dimensional Polymers and Covalent Organic Frameworks

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Education

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Professional Employment

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2000 Group Leader, JST ERATO Aida Nanospace Project
2005 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies
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Awards

2006 The Young Scientists' Prize, The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology, Japan
2006 Wiley Award, The Society of Polymer Science, Japan

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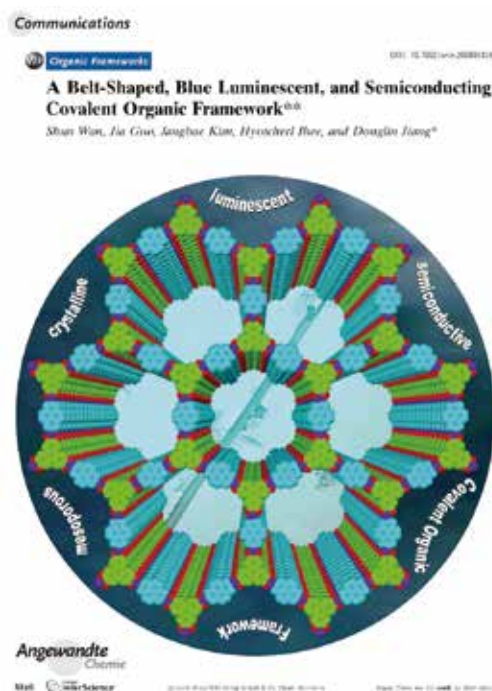
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Keywords

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Two-dimensional (2D) polymers and their layered frameworks (covalent organic frameworks: COFs) are a class of crystalline porous materials that enable precise integration of organic components into periodicities. Different from conventional polymers and typical porous zeolite materials in the aspects structure, synthesis, and functions, COF materials have emerged as a new platform for designing advanced multiple functional materials, including gas adsorption, catalysts, semiconductors, light-emitters, and active materials for batteries and solar cells. We have pioneered the field of COFs by exploring molecular design principle, synthetic reactions, functions and applications.

Figure 1. The first semiconducting 2D COF.



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).
- S. Wan, J. Guo, J. Kim, H. Ihee and D. Jiang*, "A Photoconductive Covalent Organic Framework: Self-Condensed Arene Cubes with Eclipsed 2D Polypyrene Sheets for Photocurrent Generation," *Angew. Chem., Int. Ed.* **48**, 5439–5442 (2009).
- 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. Radical Covalent Organic Frameworks for Capacitive Energy Storage

Organic radicals have received considerable attentions because their unpaired electrons endow the materials with unusual electronic, magnetic, optical, and redox properties. In this study, we developed a facile and general strategy that converts a conventional COF to an outstanding redox-active platform for energy storage *via* post-synthetic channel-wall functionalization with organic radicals. With this achievement, we show a new platform based on radical COFs for energy storage. We demonstrated this strategy using a conventional imine-linked NiP-COF (Figure 2) as a scaffold with nickel porphyrin at the vertices and TEMPO radicals on the walls.

The radical frameworks with open-accessible polyradicals immobilized on the pore walls undergo rapid and reversible redox reactions, leading to capacitive energy storage with high

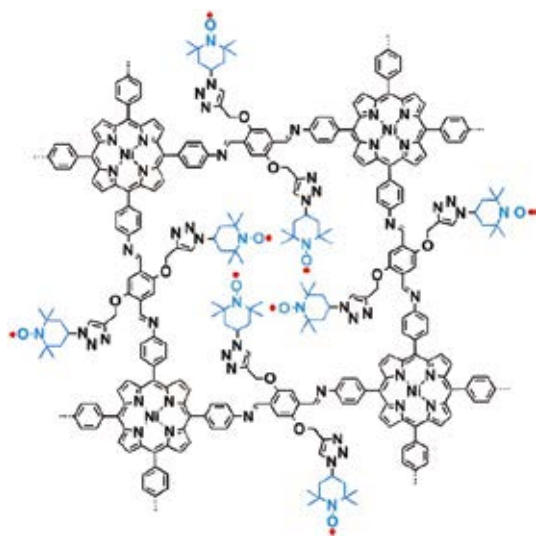


Figure 2. A NiP-COF with TEMPO radicals immobilized on the walls.

capacitance, high-rate kinetics, and robust cycle stability. The results suggest that channel-wall functional engineering with redox-active species will be a facile and versatile strategy to explore COFs for energy storage. Our results reveal the enormous potential of COFs as an appealing platform for construction of electrode materials for energy storage. We anticipate that the present post-synthetic channel-wall engineering strategy will be critical to exploring COF materials for high-performance energy storage and power supply.

2. A Photoresponsive Smart Covalent Organic Framework

Materials with structures that are transformable in response to external stimuli, such as light, heat and pressure, are attracting increasing attention because of their broad applications in various fields. In particular, when the structural transformations are accompanied by changes in physiochemical properties, these materials are considered “smart” and “dynamic” and can function as stimuli-responsive materials.

Two-dimensional covalent organic polymers (2D COPs) and their layered covalent organic frameworks (COFs) are a class of crystalline porous polymers that allow atomically precise integration of organic units into periodic columnar π -arrays and ordered one-dimensional (1D) open channels. The integration of stimuli-responsive π -units into COFs is likely to yield structurally-dynamic frameworks in which the structure can be transformed upon external stimulation. However, a “smart” COF is unprecedented and the possibility of structural transformation is to be exemplified.

The anthracene units stacked in the π -columns of Ph-An-COF are responsive to irradiation, which induces interlayer $[4\pi + 4\pi]$ cycloaddition reactions, causes conformational

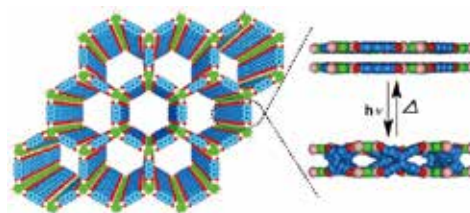


Figure 3. Anthracene-based photoresponsive COF.

changes of the π -columns, and triggers a structural transformation of the layers. These photoinduced hierarchical transformations are reversible by virtue of the thermally allowed reversibility of the cycloaddition reaction. Notably, the structural transformations are accompanied by profound changes in properties and functions, including gas adsorption, π -electronic adsorption and luminescence. Our results demonstrate the first example of photoresponsive structurally-dynamic COFs and suggest that COFs could be designed as “smart” materials whose gas-adsorption, molecular storage, sensing, and semiconducting properties are controllable by external stimuli.

References

- 1) S. Dalapati, M. Addicoat, S. Jin, T. Sakurai, J. Gao, H. Xu, S. Irle, S. Seki and D. Jiang, *Nat. Commun.* **6**:7786 (2015).
- 2) N. Huang, R. Krishna and D. Jiang, *J. Am. Chem. Soc.* **137**, 7079–7082 (2015).
- 3) S. Jin, M. Supur, M. Addicoat, K. Furukawa, L. Chen, T. Nakamura, S. Fukuzumi, S. Irle and D. Jiang, *J. Am. Chem. Soc.* **137**, 7817–7827 (2015).
- 4) N. Huang, X. Ding, J. Kim, H. Ihee and D. Jiang, *Angew. Chem., Int. Ed.* **54**, 8704–8707 (2015). (VIP)
- 5) F. Xu, H. Xu, X. Chen, D. Wu, Y. Wu, H. Liu, C. Gu, R. Fu and D. Jiang, *Angew. Chem., Int. Ed.* **54**, 6814–6818 (2015).
- 6) X. Chen, M. Addicoat, E. Jin, L. Zhai, H. Xu, N. Huang, Z. Guo, L. Liu, S. Irle and D. Jiang, *J. Am. Chem. Soc.* **137**, 3241–3247 (2015).
- 7) C. Gu, N. Huang, F. Xu, J. Gao, and D. Jiang, *Sci. Rep.* **5**, 8867 (2015).
- 8) F. Xu, S. Jin, H. Zhong, D. Wu, X. Yang, X. Chen, H. Wei, R. Fu and D. Jiang, *Sci. Rep.* **5**, 8225 (2015).
- 9) N. Huang, X. Chen, R. Krishna and D. Jiang, *Angew. Chem., Int. Ed.* **54**, 2986–2990 (2015).