

Two-Dimensional Polymers and Covalent Organic Frameworks

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Keywords Two-Dimensional Covalent Polymer, Porous Organic Polymers

Two-dimensional (2D) polymers and their layered frameworks (covalent organic frameworks: COFs) are a class of crystalline porous materials that allow an atomically precise integration of organic components into a 2D or 3D periodicity. The COF materials are different from conventional polymers and typical porous meta-organic framework in the aspects structure, synthesis, and functions and have emerged as a new platform for designing advanced materials, including gas adsorption, catalysts, semiconductors, light-emitters, and active materials for batteries and polymer solar cells. We have pioneered the field of COFs by exploring molecular topologies, building blocks, linkages, and functions and applications.

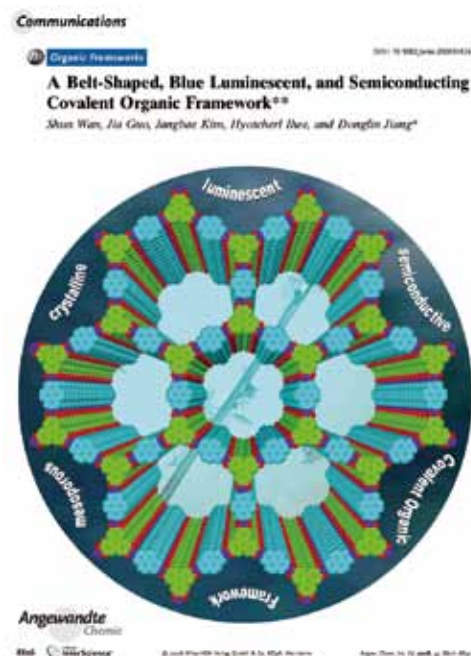


Figure 1. The first semiconducting 2D COF.

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. Azine-Linked 2D Polymers and COFs

To discover new covalent bonds for the construction of crystalline and permanent porous organic frameworks remains challenging in the field of reticular chemistry. Successful attempts to achieve COFs have been limited to few covalent bonds, including boronate, boroxine, borosilicate, imine, triazine, hydrazone, and squaraine linkages. Among them, only few examples of COFs have been reported to show enough high thermal and chemical stabilities, which however, are crucial for applications. In this context, to explore a robust linkage for the synthesis of COFs that meet the requirement in crystallinity, porosity, and stability is of critical importance for the further advancement of the field from the viewpoints of both basic research and technological application.

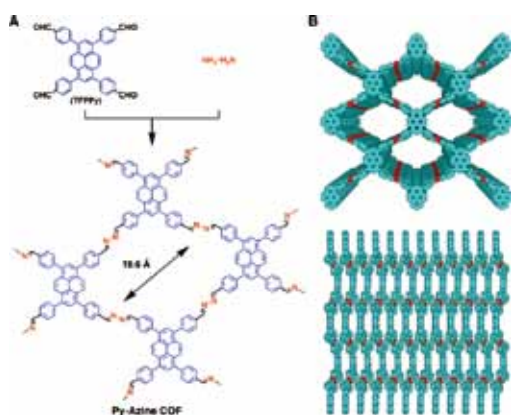


Figure 2. (A) Schematic representation of the Synthesis of the azine-linked COF (Py-Azine COF). (B) Top and side views of the AA stacking structure of the Py-Azine COF (sky blue: tetraphenylpyrene unit, red: nitrogen, H atoms are omitted).

Herein, we report the development of a new covalent bond based on the azine linkage for the synthesis of COFs that exhibit high crystallinity, high porosity, and robust chemical stability (Figure 2, Py-Azine COF). Condensation of hydrazine with 1,3,6,8-tetrakis(4-formylphenyl)pyrene under solvothermal conditions affords highly crystalline two-dimensional covalent organic frameworks. The pyrene units occupy the vertices and the diazabutadiene ($-\text{C}=\text{N}-\text{N}=\text{C}-$) linkers locate the edges of rhombic-shaped polygon sheets, which further stack in an AA-stacking mode to afford periodically ordered pyrene columns and one-dimensional microporous channels. The azine-linked frameworks feature permanent porosity with high surface area and exhibit outstanding chemical stability. By virtue of the pyrene columnar ordering, the azine-linked frameworks are highly luminescence, whereas the azine units serve as open docking sites for hydrogen-bonding interactions. These synergistic functions of the vertices and edges units endow the azine-linked pyrene frameworks with extremely high sensitivity and selectivity in chemosensing, for example, the selective detection of 2,4,6-trinitrophenol explosive. We anticipate that the extension of the present azine-linked strategy would not only increase the structural diversity but also expand the scope of functions based on this highly stable class of covalent organic frameworks.

2. Pore Surface Engineering for Constructing Donor–Acceptor COFs

Two strategies have been established for the synthesis of donor–acceptor COFs. By using electron donor and acceptor as monomers, we have developed a covalent methodology for the synthesis of donor–acceptor COFs, whereas the skeletons are built from alternately linked donor and acceptor π -arrays and leave open channels unused. As an alternative way, we and other groups have explored a supramolecular approach by spatially confining electron acceptors within the open channels of electron-donating frameworks. Clearly, the former approach requires a planar conformation of the monomer units and is not applicable to the zero-dimensional molecules, such as buckyballs, a class of widely utilized electron acceptors. The second approach based on physical filling can load buckyballs; however, it encounters a problem on the fullerene elution from the channels.

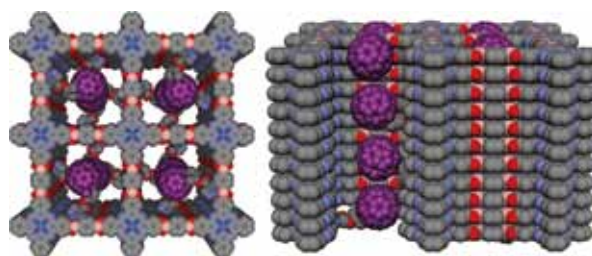


Figure 3. Surface engineering of pore walls for covalent linking of fullerenes to constitute donor–acceptor systems.

In this work, we developed a method for converting the open lattice of COFs into photoelectric structures in which electron-accepting buckyballs were spatially confined within the nanochannels via covalent anchoring on the channel walls (Figure 3). The donor–acceptor heterojunctions trigger photo-induced electron transfer and allow charge separation with radical species delocalized in the π -arrays, whereas the charge separation efficiency was dependent on the buckyball content. This new donor–acceptor strategy explores both skeletons and pores of COFs for charge separation and photoenergy conversions.

References

- 1) S. Dalapati, S. Jin, J. Gao, Y. Xu, A. Nagai and D. Jiang, *J. Am. Chem. Soc.* **135**, 17310–17313 (2013).
- 2) S. Jin, K. Furukawa, M. Addicoat, L. Chen, S. Takahashi, S. Irle, T. Nakamura and D. Jiang, *Chem. Sci.* **4**, 4505–4512 (2013).
- 3) J. Guo, Y. Xu, S. Jin, L. Chen, T. Kaji, Y. Honsho, M. A. Addicoat, J. Kim, A. Saeki, H. Ihee, S. Seki, S. Irle, M. Hiramoto, J. Gao and D. Jiang, *Nat. Commun.* **4**: 2736 doi: 10.1038/ncomms3736 (2013).
- 4) C. Gu, N. Huang, Y. Xu and D. Jiang, *Angew. Chem., Int. Ed.* **53**, 4850–4844 (2014).
- 5) L. Chen, K. Furukawa, J. Gao, A. Nagai, T. Nakamura, Y. Dong and D. Jiang, *J. Am. Chem. Soc.* **136**, 9806–9809 (2014).
- 6) H. Xu and D. Jiang, *Nat. Chem.* **6**, 564–566 (2014).