

Design of Porous Polymer Frameworks

Department of Materials Molecular Science
Division of Molecular Functions



JIANG, Donglin
NAGAI, Atsushi
LIU, Xiaoming
GUO, Zhaoqi
LIN, Jianbin
XU, Yanhong
DING, Xuesong
JIN, Shangbin
CHEN, Xiong
FENG, Xiao
CHEN, Long
XU, Hong
WU, Yang
SUZUKI, Hiroko

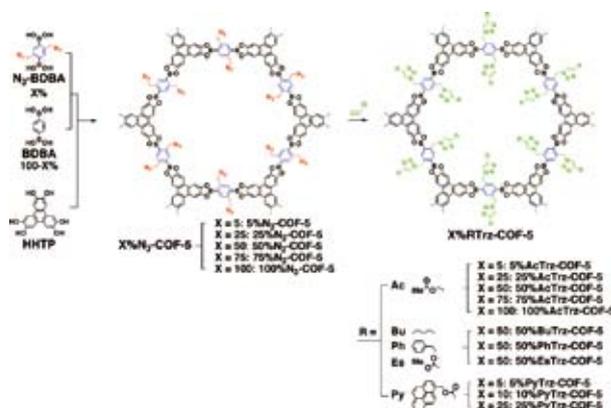
Associate Professor
Assistant Professor
Post-Doctoral Fellow
Post-Doctoral Fellow
Post-Doctoral Fellow
Graduate Student
Secretary

Covalent organic frameworks (COFs) are crystalline porous polymers that allow organization of organic units into long-range-ordered two and three-dimensional periodicities.¹⁾ COFs are intriguing frameworks because they allow a new degree of control of porosity, composition and component positions. In our group, we have pioneered the synthesis of π -electronic 2D COFs with various π -units.¹⁻⁶⁾

Conjugated microporous polymers (CMPs) are a class of porous organic frameworks consisting of extended π -conjugation and inherent nanopores. The π -conjugation skeletons together with the well-defined nanopores enable the development of novel materials that are completely different from traditional linear conjugated polymers and conventional porous polymeric materials lacking of strong π correlations among the building blocks. We have developed CMPs as a new platform to achieve light-emitting, light-harvesting, catalysis, energy storage, and sensing functions.^{7,8)}

1. Pore Surface Engineering of COFs

COFs are a class of important porous materials that enable pre-designable pore size and geometry; however, pore surface engineering in COFs remains challenging. COFs, which offers precise control over the composition, density, and functionalities of organic groups anchored onto the pore walls.²⁾ For this purpose, an azide-appended phenylene block was synthesized and utilized as the wall component in a two-component condensation system for the construction of COFs with azide-integrated walls. The two-component system was further developed to a three-component system that consists of azide-appended phenylene and 'naked' phenylene walls, and corner blocks, thereby enabling the synthesis of COFs bearing a tunable content of azide units on the walls. The azide units on the COF walls were found to undergo quantitative click reaction with alkynes to form triazole-linked groups on the wall surfaces. Consequently, the combination of a three-component condensation system with click reaction led to the establishment of a protocol that allowed control of both the composi-



tion and density of organic groups in the pores (Figure 1). This methodology was widely useful for the creation of various specific surfaces in COF pores.²⁾

COF-5 is a typical mesoporous COF that consists of triphenylene at the corners and phenylene on the walls of a boronate ester-linked 2D hexagonal skeleton.¹ We introduced azide groups to the 2 and 5 positions of the phenylene unit of 1,4-benzenediboronic acid and utilized the azide-appended benzenediboronic acid (N_3 -BDBA) as wall blocks for the condensation reaction with hexahydroxytriphenylene (HHTP) (Figure 1). The resulting hexagonal skeleton is identical to that of COF-5, with triphenylene corners but azide-appended phenylene walls. Such a strategy allows the growth of various specific groups on the surface because the azide units in the

skeletons are reactive groups that can click with various alkynes for pre-designable functionalization. The content of azide units on the pore walls can be tuned using a three-component condensation system using HHTP as the corners and a mixture of N_3 -BDAB and BDBA as the walls, because the azide units in N_3 -BDAB did not affect the reactivity of BDBA in the condensation.

Azide units are well established for click reactions with alkynes to introduce functional groups via 1,2,3-triazole rings (Trz). Reaction of azide units on the walls of $X\%N_3$ -COF-5 ($X = 5, 25, 50, 75,$ and 100) in a typical click reaction with 2-propynyl acetate in anhydrous N,N -dimethylacetamide (DMAc) at $50\text{ }^\circ\text{C}$ with CuI present as a catalyst gives the corresponding $X\%AcTrz$ -COF-5 in quantitative yields. The present strategy can be further extended to the introduction of various specific groups onto the walls of COFs. We selected a paraffinic unit, aromatic hydrocarbon, and ester groups as typical examples to react with $50\%N_3$ -COF-5. The click reactions of $50\%N_3$ -COF-5 with 1-hexyne, 3-phenyl-1-propyne, and methyl propiolate were quantitatively achieved and led to the integration of *n*-butyl, benzyl, and methyl ester units to the walls of COF-5.

The present method for the pore surface engineering of COFs is simple and universal. This approach is high throughput due to the high efficiency condensation reaction and the quantitative click reaction. The most significant feature is that the combination of condensation and click reactions enables the molecular design of pore surface with controlled composition, component, and density. Therefore, this approach provides a new aspect in the chemistry of these well-defined porous materials, and provides a means to tailor pores for specific purposes and applications.

2. Highly Luminescent CMPs with Facilitated Exciton Migration and Improved Light-Emitting Activity

Conjugated polymers play a vital role in lasing, light-emitting diodes, flexible transistors, and solar cells. Owing to their rigid conformation, they have a high tendency to aggregate in solution and the solid state. Such aggregation leads to the dissipation of excitation energy and ultimately limits their utility as light-emitting motifs.

Herein we report a new strategy for the construction of light-emitting conjugated polymers based on conjugated microporous architectures.⁷⁾ We have developed a highly luminescent CMP with tetrakisphenylethene (TPE) as building block (Figure 2, TPE-CMP). Owing to the crosslinking nature of CMP, TPE-CMP can suppress the rotation of TPE units, thus allowing the high luminescence in both solution and solid states. As a result, a positive ‘‘CMP effect’’ was observed, *i.e.* the interweaving CMP architecture can promote π conjugation, facilitates excitation migration, and improves luminescence activity. Changing the reaction time allows for the synthesis of a series of CMPs with different size and absorption band. As the reaction time increased, the TPE-CMP

particles become larger to give an increased surface area and display red-shifted electronic absorption band accordingly.

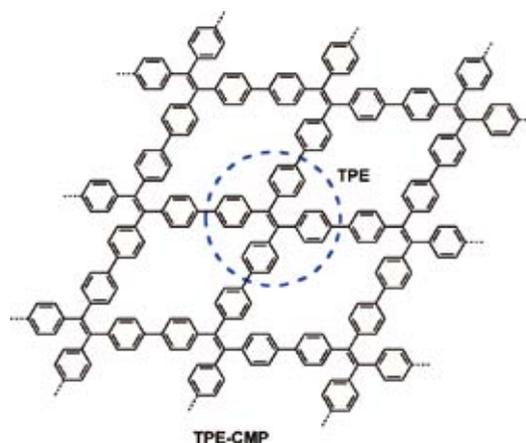


Figure 2. Structure of TPE-CMP.

These results the propagation of network structure takes place with the reaction time. The fluorescence quantum yield could reach 40%. In contrast, linear TPE polymer showed a low quantum yield of only 0.65% at otherwise identical condition. Interesting, owing to the crosslinking nature of the network, TPE-CMP is highly luminescent in various solvents such as methanol, dioxane, tetrahydrofuran, dichloromethane, chloroform, hexane, dimethylformamide, benzene, and water while the linear polymer analogue is almost nonemissive in solvents such as dichloromethane, chloroform, and tetrahydrofuran. Furthermore, TPE-CMP emits strong luminescence at solid state with a similar emission band as that in solutions. Fluorescence anisotropy measurements suggest that the exciton can migrate over the three-dimensional CMP skeletons. These positive CMP effects suggest that the CMP architecture provides a new platform for the design of highly luminescent materials

References

- 1) X. Feng, X. Ding and D. Jiang, *Chem. Soc. Rev.* **41**, 6102 (2012).
- 2) A. Nagai, Z. Guo, X. Feng, S. Jin, X. Chen, X. Ding and D. Jiang, *Nat. Commun.* **2**:536 doi: 10.1038/ncomms1542 (2011).
- 3) X. Ding, X. Feng, A. Saeki, S. Seki, A. Nagai and D. Jiang, *Chem. Commun.* **48**, 8952–8954 (2012).
- 4) X. Feng, L. Chen, Y. Honsho, O. Saengsawang, L. Liu, L. Wang, A. Saeki, S. Irle, S. Seki, Y. Dong and D. Jiang, *Adv. Mater.* **24**, 3026–3031 (2012).
- 5) X. Feng, L. Liu, Y. Honsho, A. Saeki, S. Seki, S. Irle, Y. Dong, A. Nagai and D. Jiang, *Angew. Chem., Int. Ed.* **51**, 2618–2622 (2012).
- 6) X. Ding, L. Chen, Y. Honsho, X. Feng, O. Saengsawang, J. Guo, A. Saeki, S. Seki, S. Irle, S. Nagase, P. Vudhichai and D. Jiang, *J. Am. Chem. Soc.* **133**, 14510–14513 (2011).
- 7) Y. Xu, L. Chen, Z. Guo, A. Nagai and D. Jiang, *J. Am. Chem. Soc.* **133**, 17622–17625 (2011).
- 8) X. Liu, Y. Xu and D. Jiang, *J. Am. Chem. Soc.* **134**, 8738–8742 (2012).