

Preparations and Functions of Conjugated Covalent Organic Frameworks

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Covalent organic frameworks (COFs) are a class of porous crystalline polymers with two- or three-dimensional periodicity [1]. From structure point of view, COFs are unique in that they are built from blocks of light elements (C, B, O, N, and Si) and connected by strong covalent bonds. COFs emerge as a new media for gas adsorption and are promising to offer a novel platform for molecular optoelectronics [2]. Up to date, the successful synthesis of COFs has been limited to certain reactions that explore C-B, B-O, C-C, C-Si, and C=N bonds for the connection of building blocks. The development of new linkages is highly desired, with a high probability of finding new porous materials.

Here we report the development of a new linkage for the construction of COFs, which consisted of squaraine and azine linkages.

In the case of Squaraine-Linked COF, We have developed a new reaction for COF synthesis based on squaraine chemistry. A high-throughput protocol was established for the condensation reaction SA with porphyrin. The SQ-linked COF features high crystallinity, inherent porosity, and robust solvent stability. The SQ linkage is unique because it extends the π -conjugation over the 2D skeleton and provides new molecular motif for π -cloud communications. Their improved light-harvesting capacity, lowered band gap, layered π -stacking porphyrin arrays, and open mesoporous are useful properties for developing functional molecular systems, *e.g.*, photocatalytic systems. [3]

In the case of Azine-Linked COF, Condensation of hydrazine with 1,3,6,8-tetrakis(4-formylphenyl)pyrene under solvothermal conditions yields highly crystalline two-dimensional covalent organic frameworks. The pyrene units occupy the vertices and the diazabutadiene (-C=NN=C-) linkers locate the edges of rhombic-shaped polygon sheets, which further stack in an AA-stacking mode to constitute periodically ordered pyrene columns and one-dimensional microporous channels. The azinelinked 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. [4]

References

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Figures

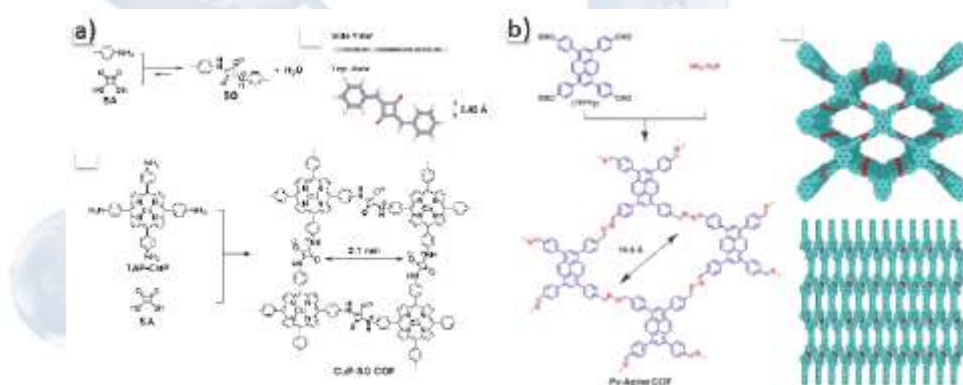


Figure 1. a) Squaraine-Linked COF and b) Azine-Linked COF