

Design of Porous Polymer Frameworks

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Covalent organic frameworks (COFs) are a new class of porous architectures that allow the integration of organic units with atomic precision into long-range-ordered two and three-dimensional structures. From a synthetic point of view, COFs are intriguing since they allow a new degree of control of porosity, composition and component positions. However, the construction of COFs to date has been limited to certain monomers, and the lack of suitable protocols utilizing other units has impeded further advances in this emerging field. To advance this emerging field it is important to extend the limited number of synthetic protocols and monomer units available. In our group, we have developed various π -electronic 2D COFs with porphyrin and phthalocyanine.¹⁻³⁾

Conjugated microporous polymers (CMPs) are another class of porous frameworks consisting of extended π -conjugation and inherent nanopores. As high surface-area porous materials, CMPs emerge as a new medium for gas adsorption and have been developed as a new type of nanoreactors and heterogeneous catalysts upon the integration of catalytic sites into the skeletons.⁴⁾ From a synthetic point of view, CMPs are unique because they allow the elaborate control of both skeletons and pores. In this context, a promising way to the exploration of CMPs is to combine the structural advantages of being π -conjugation and possessing inherent pores. We have developed such a cooperative porous framework based on aza-fused CMPs for supercapacitive energy storage and electric power supply.⁵⁾

1. Two-Dimensional Phthalocyanine Polymer and Covalent Organic Framework

NiPc-COF was synthesized by the boronate esterification reaction of $(\text{OH})_8\text{NiPc}$ and 1,4-benzene diboronic acid (BDDBA) in dimethylacetamide (DMAc)/*o*-dichlorobenzene under solvothermal conditions (Figure 1a). PXRD patterns of NiPc-COF exhibited strong diffraction peaks at 3.78° , 7.72° , 11.56° and 26.62° assignable to 100, 200, 300 and 001 facets, respectively. Based on the PXRD pattern, the center-to-center

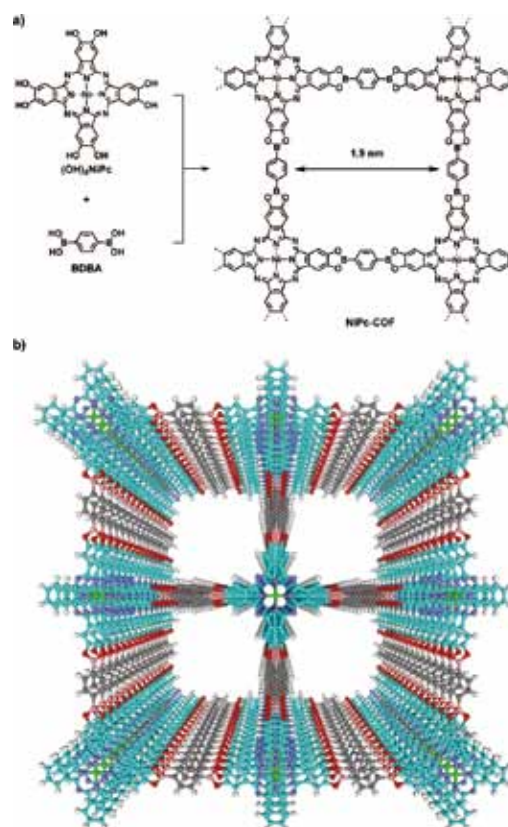


Figure 1. a) Schematic representation of the synthesis of NiPc-COF based on boronate esterification reaction. b) Eclipsed stack of phthalocyanine 2D sheets and microporous channels in NiPc-COF ($a \times 2$ grid). Colors used for identification are as follows: phthalocyanine unit (sky blue), Ni (green), N (violet), C (grey), O (red), B (orange) and H (white).

distance between neighboring pores was evaluated as 2.36 nm and the separation between the sheets as 3.32 Å. Simulations using the $P4/mmm$ space group with $a = b = 23.12247$ Å and $c = 3.36358$ Å gave a PXRD pattern in good agreement with the experimentally observed pattern. The phthalocyanine units are

located at nodes separated by 2.3 nm in the 2D plane and stack to form layers separated by a distance of 3.36 Å. In contrast, the staggered arrangement resulting from an *I4* space group did not reproduce the experimental pattern. In this stacking, the phthalocyanine units overlap on the pores of the neighboring planes.

Owing to ordered stacking of the phthalocyanine units, NiPc-COF becomes photoconductive, generating a prominent photocurrent. Irradiation from a Xenon light source (> 400 nm) with a UV cut-off module resulted in a significant increase in current from 20 nA (dark current) to 3 μA (photocurrent). Further, on-off switching experiments showed that NiPc-COF quickly responded to light irradiation and that the photocurrent can be switched on and off many times without deterioration. In contrast, (MeO)₈NiPc did not show any photoresponse under the same conditions. To investigate the wavelength dependence of the photosensitivity, we irradiated with light passed through band-pass filters (± 5 nm). NiPc-COF was panchromatically responsive to different wavelengths and was extremely sensitive to deep-red and near-infrared photons. The increased light-harvesting capability and enhanced carrier mobility accounts for the high photoconductivity and sensitivity. Therefore, owing to well-ordered stacking of the phthalocyanine unit, NiPc-COF shows enhanced light-harvesting capability in the visible and near-infrared regions, is semi-conducting and facilitates charge carrier transport. NiPc-COF is highly photoconductive, exhibiting a panchromatic light response and exceptional sensitivity to visible and near-infrared photons. These properties are unique and highly correlated with the structure of NiPc-COF. The remarkable results demonstrate the enormous potential of two-dimensional polymers in novel optoelectronics applications.

2. Aza-Fused Conjugated Microporous Polymers for Supercapacitive Energy Storage and Electric Power Supply

Supercapacitors are energy storage and power supply devices that are in increasing demand with the broadening of applications such as vehicles and electric devices. Supercapacitive energy storage operates on the electric double layer by accumulation of charges at the electrode/electrolyte interface, where the stored energy is proportional to the capacitance of the electrode. Therefore, a breakthrough in the electrode materials holds the key to fundamental advances in supercapacitors. Despite the extensive efforts in synthesis, the rational design of supercapacitive electrodes that meet large capacitance, high energy density, and outstanding stability remains a substantial challenge.

Aza-CMPs were synthesized by the condensation reaction of 1,2,4,5-benzenetetramine with triquinoyl hydrate (Figure 2, Aza-CMPs). Aza-CMPs comprise four features: (1) fused CMP frameworks that are conductive, (2) aza units in the skeletons that enable dipolar interaction with electrolyte

cations and accumulate protons on the walls of pores, (3) inherent micropores with optimized size that allows quick ion motion during charge-discharge processes, and (4) high surface area provide large interface for the formation of electrostatic charge-separation layers in the pores. Ultimately, these structural features work cooperatively, leading to exceptional energy storage and power supply capacities.

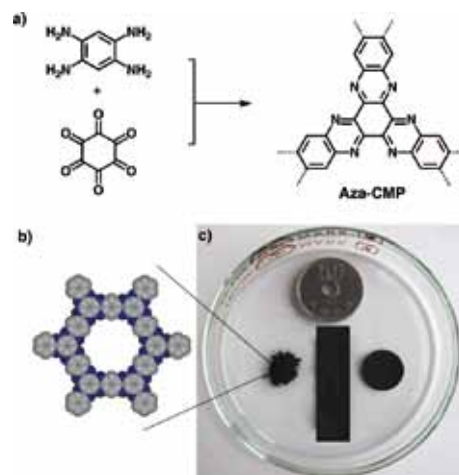


Figure 2. a) Schematic representation of the synthesis of Aza-CMP. b) The elementary pore structure of Aza-CMPs (grey is carbon network and blue is nitrogen). c) Photographic image of the powder and flexible thin films with different shapes of Aza-CMPs.

We have explored CMPs for supercapacitive energy storage, through the construction of an aza-fused porous framework with built-in aza units and high surface-area micropores. The fused skeleton, dense aza units, and well-defined micropores work cooperatively and facilitate electrostatic charge-separation layer formation. Consequently, Aza-CMPs exhibit large capacitance, high energy and power densities, and enable repetitive energy storage and power supply with excellent cycling life. These remarkable results demonstrate the enormous potential of conjugated microporous polymers in the exploration of energy materials.

References

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