Conjugated Microporous Polymers—A New Class of Porous Frameworks for Function Design

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Conjugated microporous polymers (CMPs) are a new class of porous materials with amorphous three-dimensional organic framework. Unlike other porous materials, CMPs are unique in that they enable the elaborate integration of π-electronic components to the covalent framework while retaining a permanent porous structure. Most studies on CMPs to date have focused on the development of synthetic approaches for the control of pore size and surface area. However, the functions of CMPs, apart from gas storage, have not yet been well explored. We have focused on the development of functional CMPs via molecular design of the CMP skeletons.

1. Light-Harvesting Conjugated Microporous Polymers: Rapid and Highly Efficient Flow of Light Energy with a Porous Polyphenylene Framework as Antenna

The molecular design of light-harvesting antennae requires not only the segregation of a large number of chromophore units in a confined nanospace but also the cooperation of these units in achieving highly efficient energy transduction. We have focused on the development of photofunctional CMPs with the expectation that the energy-donating CMPs with dense π-electronic components could serve as antennae for the collection of photons, while inherent pores within the framework could spatially confine energy-accepting counterparts, thus leading to the creation of an unprecedented donor–acceptor system for energy transduction mediated by the three-dimensional porous framework.

Here we report the synthesis and functions of a polyphenylene-based conjugated microporous polymer (Figure 1, PP-CMP). PP-CMP was recently designed and synthesized by Suzuki polycondensation reaction and used as antenna for the noncovalent construction of light-harvesting system. In contrast to linear polyphenylene, PP-CMP consists of conjugated three-dimensional polyphenylene scaffolds and holds inherent porous structure with uniform pore size (1.56 nm) and large surface area (1083 $m^2\ g^{-1}$). It emits blue photoluminescence, is capable of excitation energy migration over the framework, and enables rapid transportation of charge carrier with intrinsic

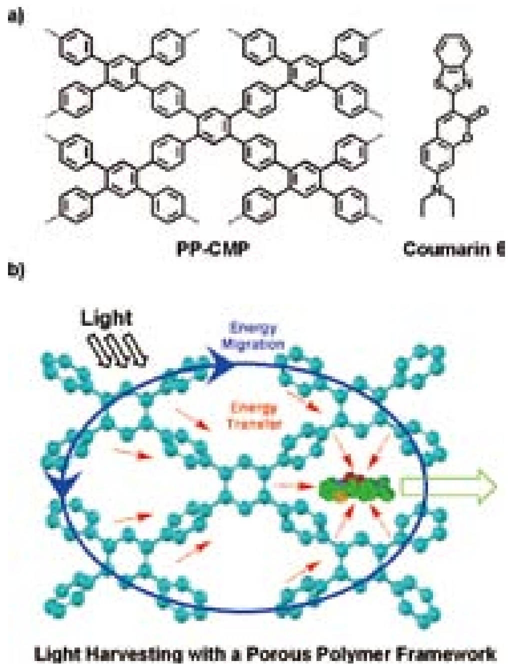

Figure 1. Schematic representations of (a) the synthesis and (b) the framework of PPy-COF (Structure is based on quantum calculation and crystal lattice parameters; Red: B, White: O, Blue: Pyrene; H atoms are omitted for clarity).

mobility as high as 0.04 $cm^2V^{-1}s^{-1}$. The microporous structure of PP-CMP allows for the spatial confinement of energy-accepting coumarin 6 molecules in the pores and makes the high throughput synthesis of light-harvesting systems with designable donor–acceptor compositions possible. Excitation of PP-CMP skeleton leads to brilliant green emission from coumarin 6, whose intensity is 21 fold as high as that upon direct excitation of coumarin 6 itself; while the fluorescence from PP-CMP itself is wholly quenched, as a result of energy transfer from the light-harvesting PP-CMP framework to coumarin 6. PP-CMP skeleton is highly cooperative with averagely 176 phenylene units working together to channel the excitation energy to one coumarin 6 molecule and features the energy transfer process with quick, efficient and vectorial character. These unique characteristics clearly originate from the conjugated porous structure and demonstrate the usefulness of CMPs in the exploration of π-electronic functions, in addition to their gas adsorption properties thus far reported. The light-harvesting antennae based on CMPs constitutes an important step for molecular optoelectronics based on porous polymeric materials.

2. CMPs as Scaffolds for Constructing Porous Catalytic Frameworks: A Built-In Heterogeneous Catalyst with High Activity and Selectivity Based on Nanoporous Metalloporphyrin Polymers

Recently, CMPs have been developed to load metal nanoclusters for the synthesis of heterogeneous catalysts. Because the polymer skeleton does not incorporate any catalytic sites, post treatment of CMPs via noncovalent interactions is a prerequisite for loading catalysts in the pores. In contrast to this approach, we are interested in the exploration of covalently built-in catalysis systems based on CMPs. If catalytic functionalities could be integrated into the skeleton of CMPs, one would have a chance to create a novel porous polymer in which the skeleton itself serves as the catalysts and the pores provide spaces for the transformation. Here we report a strategy for the synthesis of a new type CMP-based heterogeneous catalyst that consists of an inherent porous framework with built-in catalytic sites in the skeleton (Figure 2, FeP-CMP).

FeP-CMP was newly synthesized *via* a Suzuki polycondensation reaction and was developed as a heterogeneous catalyst for the activation of molecular oxygen to convert sulfide to sulfoxide under ambient temperature and pressure. FeP-CMP is intriguing because the polymer skeleton itself is built from catalytic moieties and serves as built-in catalysts, bears inherent open nanometer-scale pores that are accessible for substrates, and possesses high surface areas (1270 m^2 g^{-1}) that facilitate the transformation reaction. It is highly efficient with high conversion (up to 99%) and large turnover number (TON = 97,320), is widely applicable to various sulfides covering from aromatic to alkyl and cyclic substrates, displays high selectivity (up to 99%) to form corresponding sulfoxides, and is highly chemoselective for the oxidation of sulfide group even in the co-existence of other oxidative functionalities. Owing to the covalent linkages between catalytic sites in the frameworks, FeP-CMP can be recycled with good retention of its porous structure and allows for large-scale transformation. These unique characteristics clearly originate from the covalent porous catalytic framework structure and demonstrate the usefulness of CMPs in the exploration of built-in heterogeneous catalysts, a new potential of these materials that have thus far been reported to exhibit noteworthy gas adsorption functions.

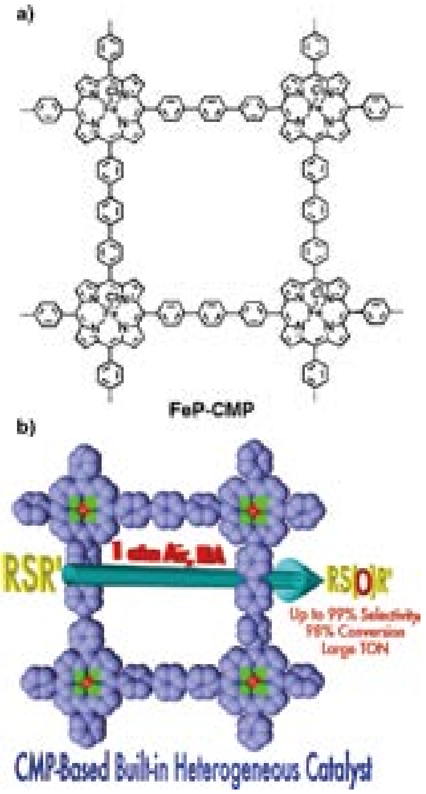

Figure 2. a) Schematic representation of the nanoporous polymer with metalloporphyrin built-in skeleton (FeP-CMP). b) Schematic representation of the transformation of sulfides to sulfoxides catalyzed by FeP-CMP.

Exploration of conjugated microporous polymers has a high probability of leading to the development of new functional materials. In summary, we developed a novel strategy for the construction of built-in catalysts based on CMPs architecture and demonstrated the utility of a newly synthesized FeP-CMP as a heterogeneous catalyst. A clear future potential for CMPs is to develop photocatalyst in which multiple functions including light-harvesting, energy transfer and catalytic processes can be seamlessly merged in one polymer skeleton. Therefore, the CMPs-based built-in catalyst constitutes a new step for the molecular design of heterogeneous catalyst systems.

References

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