

Topological Design of Sheet-Shaped Macromolecules and Organic Frameworks

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Covalent organic frameworks (COFs) are porous and crystalline materials with pre-designable 2D and 3D polymer structures. Due to covalent linkage between components together with an elaborate control on structure parameters including porosity and composition, COFs are promising for the design of tailor-made porous materials for gas storages. Recently, co-condensation of triphenylene and pyrene monomers has been reported, to create a π -electronic COF that is semiconducting (TP-COF). The well-defined crystalline structure of COFs would have a high probability of forming conduction path that transports charge carriers across the framework. Inspired by this finding, we are interested in the synthesis of photofunctional COFs, especially photoconductive COF that requires photoinduced carrier generation and carrier transportation in the framework. Crystal engineering has demonstrated that high quality single crystals of certain π -conjugated arenes are photoconductive as the result of exciton migration over lattice followed by charge separation at molecule-electrode interface. To fulfill this prerequisite, we turned to the exploration of arene-based COF, which should retain crystal-lattice-like highly ordered arene arrangement, can absorb photons of visible region, and is robust under irradiation. Herein, we report the first example of photoconductive COF, bearing eclipsed molecular order of arene building blocks in the framework (Figure 1, PPy-COF).

1. Toward Photoconductive Sheet-Shaped Macromolecules and COFs

We employed self-condensation of pyrene diboric acid (Figure 1a, PDBA) for polymerization that would topologically integrate pyrene unit on edges and boronic ester ring at vertices (Figure 1), to assume uniform and single aromatic component of the framework. We found that under solvothermal condition it successfully leads to the desirable eclipsed alignment of 2D

polypyrene sheets in the micrometer-scale cubes (Figure 1b). Such an ultimately superimposed stack together with uniform composition in sheet structure significantly facilitates exciton migration and carrier transportation. We highlight that PPy-COF harvests visible light and triggers photocurrent generation with a quick response to visible light irradiation, allows

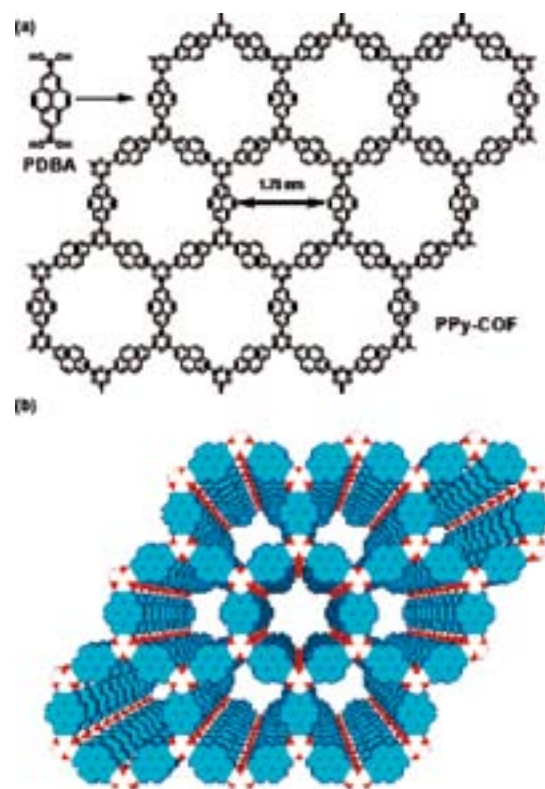


Figure 1. Schematic representations of (a) the synthesis and (b) the framework of PPy-COF (Structure is based on quantum calculation and crystal lattice parameters; Red: B, White: O, Blue: Pyrene; H atoms are omitted for clarity).

repetitive switching of photocurrent without deterioration, and displays a large on-off ratio over 8.0×10^4 .

FE SEM shows that PPy-COF adopts cubic shape, while no any other morphologies such as belt, fiber, sphere, or rod are present. Close checks at high magnification confirm that the cubes are in micrometer scale with similar dimension. HR TEM reveals the aligned 2D polymer sheets with face-to-face distance of about 3.4 Å, which is reasonable for π - π stack. These observations indicate that self-condensation of PDBA leads to the formation of quite uniform cube-shaped COF with well-aligned polypyrene sheets.

To fully understand the structure of PPy-COF, we carried out PXRD analysis, quantum simulation and gas sorption experiments. PXRD measurement of PPy-COF displays a main peak at 4.6° due to 100 diffraction together with minor peaks at 9.3 , 12.2 and 26.2° due to 200, 210, 001 diffractions, respectively. To elucidate the lattice packing, we first carried out quantum chemical calculation with Gaussian 03. Rev. C01 at PM3 level to optimize the geometry of pore unit structure and then performed molecular modeling and Pawley refinement by using Reflex, a software package for crystal structure determination from the PXRD pattern, implemented in Materials Studio modeling version 4.2. Simulation using *P6/mmm* space group with $a = b = 22.16295$ Å and $c = 3.42066$ Å results in a PXRD pattern that is in good agreement with the experimentally observed one. Therefore, the 2D polypyrene sheets stack along *c* axis in a perfectly eclipsed fashion, with all vertices and edges superimposed on those from neighbouring sheet, thus leaving aligned tubular channels with a pore diameter of 1.73 nm. Gas sorption measurement with N_2 at 77 K displays typical type-I sorption profile, suggesting a microporous character. The BET surface area was evaluated to be $923 \text{ m}^2\text{g}^{-1}$ and the pore width was 1.88 nm calculated by NLDFT method. These results indicate that PPy-COF is supermicroporous crystalline macromolecule with eclipsed alignment of polypyrene sheets.

Upon excitation at 414 nm, PPy-COF emits at 484 nm. In contrast, the simple solid of PDBA gives an emission at 421 nm. Therefore, the fluorescence of PPy-COF most likely originates from excimer, as a result of close packing of pyrene building blocks. Along this line, we further investigated the fluorescence anisotropy upon excitation with a polarized light. When a chromophore with a restricted Brownian motion is excited by a polarized light, it emits a polarized fluorescence. However, the fluorescence should be depolarized when the excitation energy migrates within the lifetime of the excited state. PDBA shows an anisotropy (*p*) value of 0.020. In contrast, PPy-COF under identical conditions exhibited a significantly depolarized fluorescence with an extremely low *p* value of 0.001. This value is much smaller than that of previously reported TP-COF (0.017). Unlike TP-COF that contains two alternatively linked components with difference in energy gaps, the exciton migration in the single component PPy-COF is facilitated, since it can flow “borderlessly” not only over the

sheet plane but across the stacked layers as well.

The well-defined sheet structure together with superimposed layer alignment of PPy-COF would also benefit the flow of carriers. To verify this, we measured the electrical conductivity by using a two-probe method across a 10- μm -width Pt gap. PPy-COF displays an almost linear *I*-*V* profile in air at 25°C , while the gap itself is silent, irrespective of voltage bias. In contrast, PDBA shows a low current under otherwise identical conditions. The electric current of PPy-COF can be on-off switched for many times. The relatively high electrical conductivity is clearly resulted from the highly aligned molecular order. Upon doping with iodine to induce hole generation, the electric current increased, suggesting that PPy-COF is a hole transporting material.

We investigated the photoconductivity of PPy-COF by casting a thin film of PPy-COF on Al electrode and vapor depositing 30-nm thick Au on the top of the film to fabricate sandwich-type electrodes. Indeed, on irradiation from Au side with visible light ($> 400 \text{ nm}$) of a xenon lamp, PPy-COF is highly responsive and shows sharp rise in photocurrent generation to give a linear *I*-*V* profile. Moreover, the photocurrent can be repetitively switched for many times without deterioration at an on-off ratio over 8.0×10^4 . Such a quick response together with a large on-off ratio is most likely related to the facilitated exciton migration and carrier transportation in PPy-COF. In sharp contrast, PDBA hardly shows response to light irradiation under otherwise identical conditions. On the other hand, TP-COF consisting of co-condensed triphenylene and pyrene network shows a low photocurrent with significantly decreased on-off ratio, which is only one-fourth that of PPy-COF. Although 1,4-benzene diboronic acid forms a crystalline COF, which, however, eventually adopts staggered structure and hardly absorbs any photons in the visible region.

In summary, we demonstrate the first example of photoconductive COF, newly synthesized by self-condensation of pyrene diboronic acid under solvothermal condition. The ultimate alignment of 2D polypyrene sheets in perfectly eclipsed fashion leads to the formation of micrometer-scale cubes that favor exciton migration and carrier flow over the framework. PPy-COF harvests visible photons and triggers prominent photocurrent generation, displays quick response to light irradiation, and is capable of repetitive on-off photocurrent switching with large on-off ratio. These unique properties are unprecedented and thus constitute an important step to the utility of COFs in optoelectronics and photovoltaics.

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