

# Topological Design of Sheet-Shaped Macromolecules and Organic Frameworks

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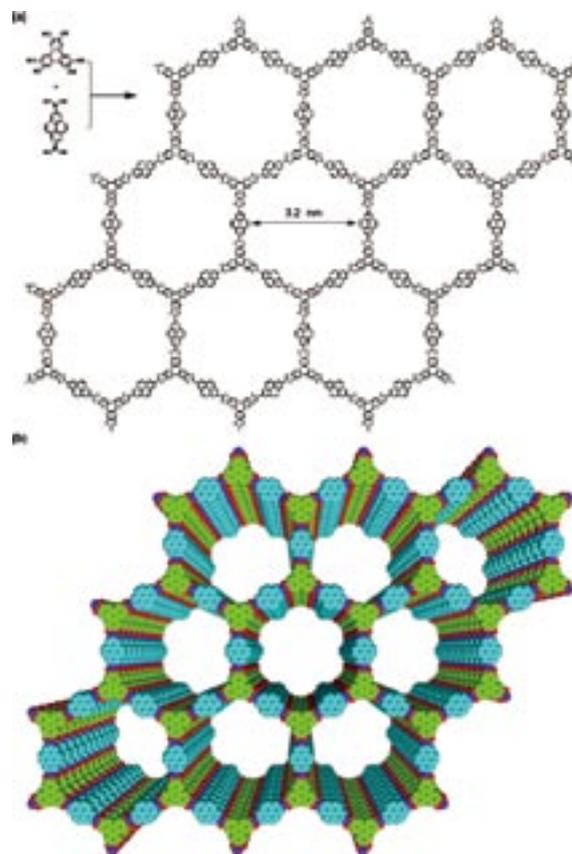
Covalent organic frameworks (COFs) are porous and crystalline macromolecules with a well-defined and predictable network of building blocks. Compared with inorganic porous materials, COFs are unique in that they are made from light elements, tunable in skeleton and robust against air and organic solvents. From synthetic point of view, COFs are attractive motifs since they allow, upon topological design, a total control over structure parameters including composition and porosity. Most studies up to date have focused on the development of synthetic methodologies with an aim to optimize pore size and surface area. By contrast, the functions of COFs except for gas storage have not yet been well explored. This motivated us to explore the possibility for constructing functional COFs with novel properties by utilizing highly ordered  $\pi$ -conjugation systems. We succeeded in the molecular design and synthesis of a series of novel COFs with unique semi-conductive and photoconductive functionalities.

## 1. A Belt-Shaped, Blue Luminescent and Semiconductive Covalent Organic Framework

Herein, we report the first example of a luminescent and semiconductive COF, which adopts belt shape and consists of pyrene and triphenylene functionalities linked alternatively in a mesoporous hexagonal skeleton (Figure 1, TP-COF).

TP-COF was topologically designed by employing a  $D_{3h}$  symmetric monomer as corner and a  $D_{2h}$  symmetric monomer as edge for pore hexagons and synthesized by a condensation reaction of 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) and pyrene-2,7-diboronic acid (PDBA). FE SEM images of TP-COF reveal that the condensation polymerization of PDBA and HHTP afford belts with length extended to micrometers and width of about 300 nm and thickness of 100 nm. The belt morphology is quite uniform with a similar width and thickness to one another, and no other morphologies are observable. In high resolution TEM, clear aligned patterns were observed along the (110) facet. From the aligned layer structure, the distance between sheets is estimated to be 3.40 Å, which is

reasonable for  $\pi$ - $\pi$  stacking. Such a belt texture with a uniform morphology and the direct visualization of a stacked sheet structure are unprecedented for COFs. To our surprise, along the (001) facet, hexagonal mesostructure can be observed and enables the estimation of center-to-center distance between the neighboring pores to be about 3.3 nm. Powder x-ray diffraction (PXRD) exhibits a main diffraction peak due to 100 at 2.70°, along with diffractions owing to 110, 200, 210, 300, 310, and

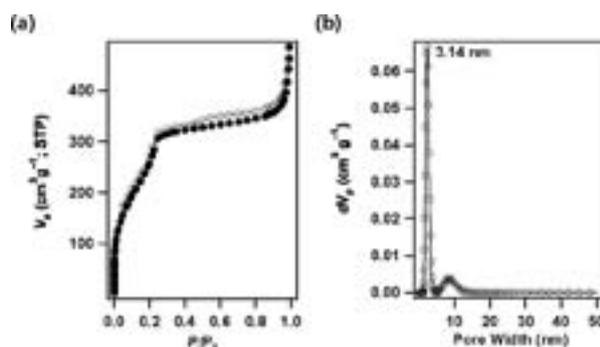


**Figure 1.** (a) Synthesis of TP-COF. (b) Schematic representation of TP-COF (Structure is based on quantum calculation and crystal lattice parameters; Purple: B, Red: O, Green: Triphenylene, Blue: Pyrene; H atoms are omitted for clarity).

001 at 4.74°, 5.46°, 7.26°, 8.24°, 9.54° and 26.32°, respectively. Simulation using the space group of  $P6/mmm$  (No. 191) with  $a = b = 37.5412 \text{ \AA}$  and  $c = 3.3784 \text{ \AA}$  gives a PXRD pattern in good agreement with the experimentally observed one. All the diffraction peaks can be reasonably assigned. Therefore, the 2-D sheets crystallize in an eclipsed fashion to give a perfect superimposition of the triphenylene and pyrene units on themselves. Such a crystalline structure would provide open and aligned mesopores of 3.26 nm in diameter. In fact, TP-COF exhibits a typical type IV nitrogen sorption curve, indicative of a mesoporous character (Figure 2). BET calculation gives specific surface area and pore volume of  $868 \text{ m}^2 \text{ g}^{-1}$  and  $0.7907 \text{ cm}^3 \text{ g}^{-1}$ , respectively. Estimation of pore size with the DFT model shows a diameter of 3.14 nm, which is close to the theoretical one. Pore distribution profile shows that the specific surface area in TP-COF originates predominately from the persistent mesopores, whereas contributions of other pores formed between belts or from defects are small. All the above results indicate that TP-COF is a crystalline material with a uniformly sized mesopore formed via the eclipsed packing of the polymeric sheets.

Fluorescence microscopy exhibits that the belts of TP-COF are highly blue luminescent. Fluorescence spectroscopy shows that TP-COF emitted a luminescence at 474 nm, upon excitation of the pyrene units at 376 or 417 nm. Excitation of the triphenylene units in TP-COF at 340 nm resulted in negligibly weak emission at 402 nm from the triphenylene units but a strong emission from the pyrene moieties at 474 nm, where the fluorescence intensity ratio  $I_{474 \text{ nm}}/I_{402 \text{ nm}}$  was as high as 16. In sharp contrast, when a 2:3 mixture of HHTP and PDDBA was excited at 340 nm, it emitted predominately at 402 nm to furnish a low  $I_{474 \text{ nm}}/I_{402 \text{ nm}}$  ratio (0.6). Therefore, the strong pyrene fluorescence, observed for TP-COF upon 340 nm excitation, is obviously due to an intramolecular singlet energy from the triphenylene units to pyrene units. Comparison of the excitation spectrum with diffuse reflectance UV-Vis spectrum, the quantum yield of energy transfer was estimated to be 60%. Therefore, by virtue of the triphenylene units, TP-COF can harvest photons of a wide wavelength range covering from ultraviolet to visible regions and converts them to blue emission. We further investigated the fluorescence anisotropy of TP-COF upon excitation with a polarized light. The 2:3 mixture of HHTP and PDDBA shows a  $p$  value of 0.058. In sharp contrast, TP-COF under identical conditions exhibited a significantly depolarized fluorescence with an extremely low  $p$  value of 0.017. This observation reveals that TP-COF not only mediates energy transfer between components but facilitates energy migration over the crystalline belt as well.

Single crystals of pyrene and triphenylene have been reported to function as semiconductors. Due to the ultimate  $\pi$ -stacking of these large  $\pi$ -conjugated components, TP-COF



**Figure 2.** (a) Nitrogen adsorption (●) and desorption (○) isotherm profiles of TP-COF at 77 K. (b) Pore size distribution of TP-COF by DFT modeling on the  $\text{N}_2$  adsorption isotherms.

may have a high probability of becoming electrically semi-conductive. We investigated this possibility by measuring the electric conductivity with a 10- $\mu\text{m}$  width Pt gap using a two-probe method. TP-COF in air at 25 °C shows an almost linear I-V profile, while the gap itself is silent irrespective of voltage bias. For example, at 2-V bias voltage, the electric current is 4.3 nA. In contrast, a 2:3 mixture of HHTP and PDDBA shows a low current (79 pA) under otherwise identical conditions. Moreover, the electric current can be on/off switched repeatedly for many times without significant deterioration. The relatively high electric current observed for TP-COF is likely related to the highly ordered structure that enables the formation of a conductive path. Upon doping with iodine, the electric current was increased, suggesting a  $p$ -type semiconductor character of TP-COF.

Exploration of functional COFs is a subject with a high probability to the development of new materials. We have succeeded in the synthesis of a new COF based on the condensation reaction of triphenylene and pyrene monomers. TP-COF is highly luminescent, harvests a wide wavelength range of photons and allows energy transfer and migration. Furthermore, TP-COF is electrically conductive and capable of repetitive on-off current switching at room temperature. These characters are unique and clearly originate from the highly ordered structure of TP-COF. By filling the mesopores with photoactive molecules such as electron acceptor, we expect the fabrication of COF-based optoelectronic device, which is one of the targets under investigation.

## Reference

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## Award

CHEN, Long; Student Lecture Award of Chemical Society of Japan (2008).