Angewandte Chemie

DOI: 10.1002/anie.200900881

Photoconductive Structures

A Photoconductive Covalent Organic Framework: Self-Condensed Arene Cubes Composed of Eclipsed 2D Polypyrene Sheets for Photocurrent Generation**

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Covalent organic frameworks (COFs) are porous crystalline materials with predesignable 2D and 3D polymer structures.[1–6] Owing to the covalent linkage of the components, as well as the elaborate control of structural parameters, including porosity and composition, COFs are promising for the design of tailor-made porous materials for gas storage.[1e,7,8] We recently reported the cocondensation of triphenylene and pyrene monomers to create a semiconducting π-conjugated COF (TP-COF).[4] The well-defined crystalline structure of COFs should have a high probability of forming a conduction path that transports charge carriers across the framework.

We are interested in the synthesis of photofunctional COFs, in particular a photoconductive COF, which would require 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 the lattice followed by charge separation at the molecule–electrode interface.[9] To fulfill this prerequisite, we investigated an arene-based COF, which should retain a crystal-lattice-like highly ordered arene arrangement, absorb photons in the visible region, and be robust under irradiation. Herein, we report the first example of a photoconductive COF, in which sheets composed of arene building blocks lie above one another in an eclipsed arrangement (Figure 1, PPy-COF).

We chose the self-condensation of pyrenediboronic acid (Figure 1 a, PDBA) as the polymerization reaction for structure formation, as we anticipated that this reaction would lead to the integration of pyrene units on edges and

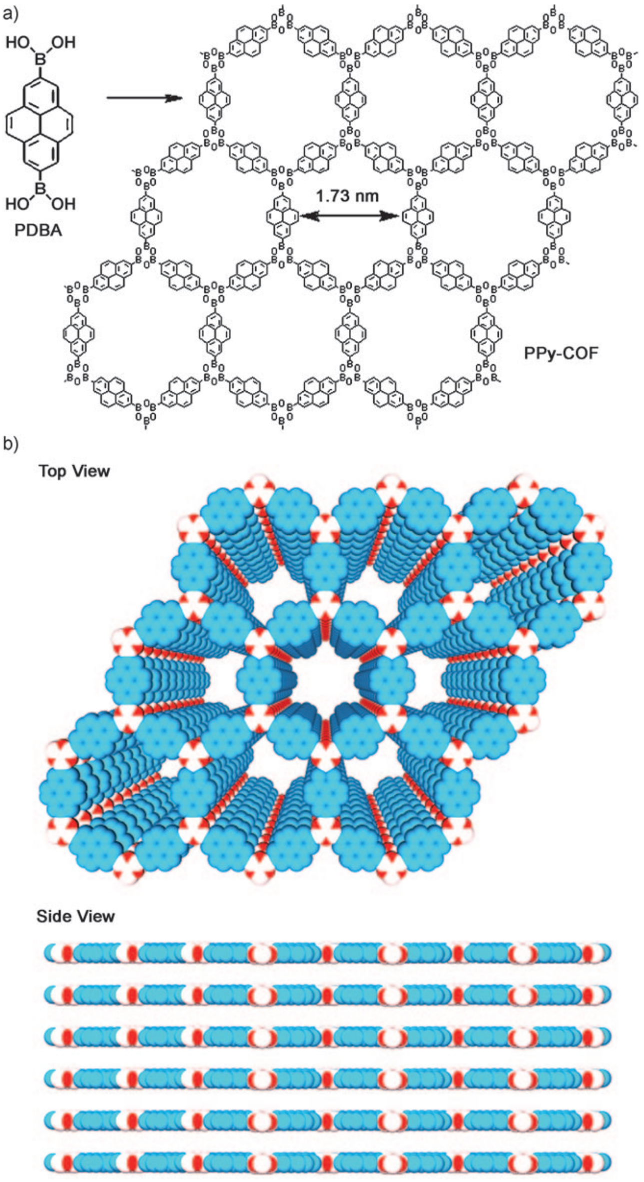

Figure 1. Schematic representation of a) the synthesis and b) the structure of PPy-COF. The structure is based on quantum-chemical calculations and crystal-lattice parameters (B white, O red, pyrene blue; H atoms are omitted for clarity).

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[**] This research was supported by Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST) (D.J.). D.J. thanks the JSPS Asian core program. J.G. thanks the JSPS for a Young Scientist Fellowship. H.I. thanks Creative Research Initiatives (Center for Time-Resolved Diffraction) of MEST/KOSEF for a grant.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200900881.

boronic ester rings at vertices (Figure 1) and thus ensure the uniform arrangement of the single aromatic component in the framework. We found that the reaction led to the desired eclipsed alignment of 2D polypyrene sheets in micrometer-scale cubes under solvothermal conditions (Figure 1 b). This arrangement of superimposed sheets of uniform structure facilitates exciton migration and carrier transportation significantly. PPy-COF harvests visible light and triggers photocurrent generation with a quick response to irradiation with visible light, enables repetitive switching of the photocurrent without deterioration, and displays a large on–off ratio of more than 8.0×10^4.

In a typical procedure for the synthesis of PPy-COF, a mixture of PDBA (25.0 mg) in 1,4-dioxane/mesitylene (1:1 v/v, 5 mL) in a 10 mL pyrex tube was degassed through three freeze–pump–thaw cycles. The tube was sealed, placed in an autoclave, and heated at 120 °C for 2 days. The resulting precipitate was collected by centrifugation, washed with anhydrous acetone, and dried at 150 °C under vacuum to give PPy-COF (22 mg) in 88 % yield as a pale-yellow solid. PPy-COF was characterized unambiguously through various spectroscopic measurements. Field-emission scanning electron microscopy (FESEM) showed that PPy-COF adopts a cubic shape, and that no other morphologies, such as belt, fiber, sphere, or rod shapes, are present (Figure 2 a–d). Careful checking at high magnification confirmed that the cubes are of micrometer scale with similar dimensions. High-resolution transmission electron microscopy (HRTEM) along the (110) facet revealed aligned 2D polymer sheets with a face-to-face distance of about 3.4 Å (Figure 2 e,f), which is reasonable for a π–π stack. These observations indicate that the self-condensation of PDBA leads to the formation of a quite uniform cube-shaped COF with well-aligned polypyrene sheets.

To fully understand the structure of PPy-COF, we carried out powder X-ray diffraction (PXRD) analysis, quantum simulation, and gas sorption experiments. The PXRD pattern of PPy-COF displayed a main peak at 4.6° due to the 100 diffraction, together with minor peaks at 9.3, 12.2 and 26.2° due to the 200, 210, and 001 diffraction, respectively (Figure 3 a, black curve). To elucidate the lattice packing, we first carried out quantum-chemical calculations with the program Gaussian 03 Rev. C01 at the PM3 level to optimize the geometry of the pore unit structure. We then performed molecular modeling and Pawley refinement by using Reflex (implemented in Materials Studio version 4.2), a software package for crystal-structure determination from the PXRD pattern. Simulation with the *P*6/*mmm* space group and $a = b = 22.16295$ Å, $c = 3.42066$ Å resulted in a PXRD pattern

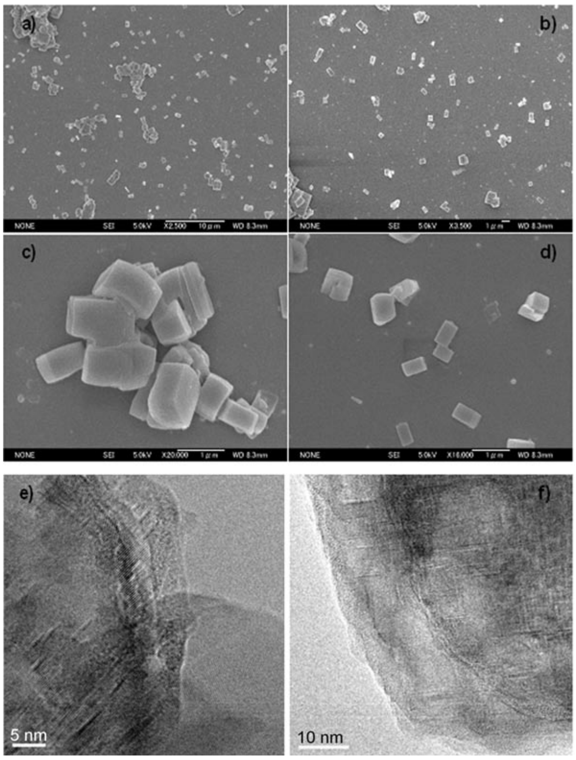

Figure 2. a–d) FESEM and e,f) HRTEM images of PPy-COF. Scale bar in (a): 10 μm; scales bars in (b–d): 1 μm.

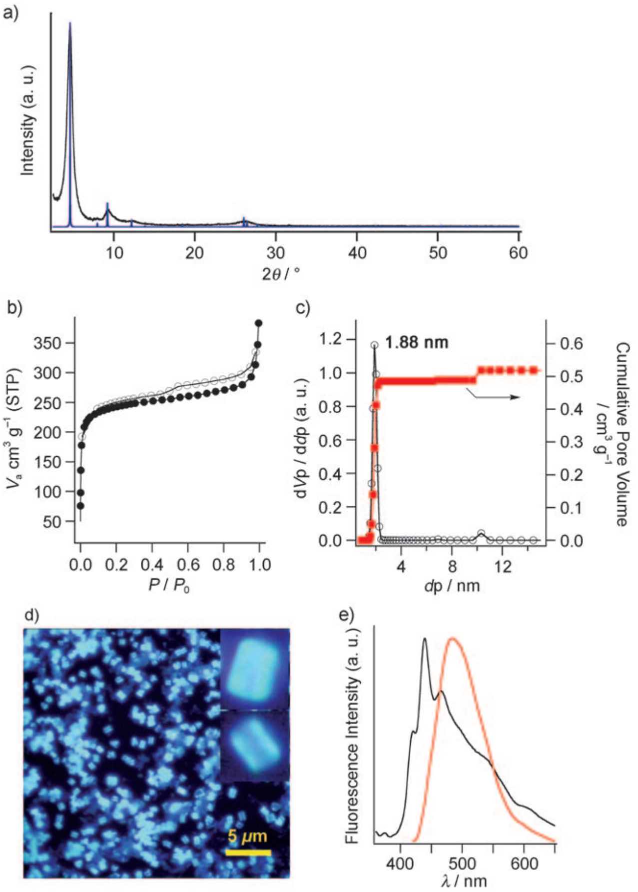

Figure 3. a) Experimentally observed PXRD pattern (black curve) and PXRD pattern simulated with the *P*6/*mmm* space group (blue curve). b) Nitrogen adsorption (●) and desorption (○) isotherm profiles of PPy-COF at 77 K. STP = standard temperature and pressure. c) Pore-size distribution (black curve) and cumulative pore volume (red curve) of PPy-COF, as determined by NLDFT modeling on the nitrogen-adsorption isotherms. *dp* = pore diameter, *Vp* = pore volume. d) Fluorescence microscopic image of PPy-COF (inset: enlargement of individual cubes). e) Normalized fluorescence spectra of PPy-COF (red curve) and PDBA (black curve) upon excitation at 414 nm at 25 °C.

(blue curve, Figure 3a) that is in good agreement with the experimentally observed pattern (see Figure S3 in the Supporting Information). On the other hand, simulation with the *P*63/*mmc* space group gave a staggered alignment of 2D polymer sheets; in this case, the calculated PXRD did not reproduce the experimental pattern (see Figure S4 in the Supporting Information). We therefore concluded that the 2D polypyrene sheets stack along the *c* axis in a perfectly eclipsed fashion, with all vertices and edges superimposed on those of neighboring sheets. Aligned tubular channels result, with a pore diameter of 1.73 nm (Figure 1 < xfigr1). Gas sorption measurements with N_2 at 77 K showed a typical type-I sorption profile, which suggests a microporous character (Figure 3b).[10] The BET (Brunauer–Emmett–Teller) surface area was evaluated to be 923 $m^2 g^{-1}$, and the pore width was calculated by the NLDFT method (nonlocal density functional theory) to be 1.88 nm (Figure 3c). These results indicate that PPy-COF is a supermicroporous crystalline macromolecule with an eclipsed alignment of polypyrene sheets.

Conjugated microporous polymers have been reported to emit fluorescence.[11] PPy-COF is highly blue-luminescent when exposed to visible light, as shown by fluorescence microscopic images (Figure 3d). Upon excitation at 414 nm, PPy-COF emits at 484 nm (Figure 3e, red curve). In contrast, the simple solid PDBA emits at 421 nm (black curve). Therefore, the fluorescence of PPy-COF most likely originates from excimers, as a result of the close packing of pyrene building blocks.

Along this line, we investigated fluorescence anisotropy upon excitation with polarized light. When a chromophore with a restricted Brownian motion is excited by polarized light, it emits polarized fluorescence. However, the fluorescence should be depolarized when the excitation energy migrates within the lifetime of the excited state. Herein, fluorescence anisotropy (p) is defined by $(I_{\parallel}-GI_{\perp})/(I_{\parallel}+GI_{\perp})$, in which $I_{\parallel}$ and $I_{\perp}$ are the fluorescence intensities of parallel and perpendicular components relative to the polarity of the excitation light, respectively, and G is an instrumental correction factor. PDBA showed a p value of 0.020. In contrast, under identical conditions, PPy-COF exhibited 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).[4] Unlike in TP-COF, which contains two alternately linked components with different energy gaps, exciton migration in single-component PPy-COF is facilitated: Excitons can flow unhindered not only over the sheet plane, but across the stacked layers as well.

The well-defined sheet structure together with the layer alignment of PPy-COF would also benefit the flow of carriers. To verify this hypothesis, we measured the electrical conductivity of PPy-COF across a gap of 10 μm between two Pt electrodes. PPy-COF displayed an almost linear *I*–*V* profile in air at 25 °C (Figure 4a, blue curve), whereas the gap itself is silent, irrespective of voltage bias (black curve). In contrast, a low current was observed with PDBA under otherwise identical conditions (see Figure S6a in the Supporting Information). The electric current of PPy-COF can be switched on and off many times (Figure 4b). The relatively high electrical conductivity clearly results from the high molecular order of the structure. Upon doping with iodine to induce hole generation, the electric current increased (Figure 4a, red curve), which suggests that PPy-COF is a hole-transporting material.

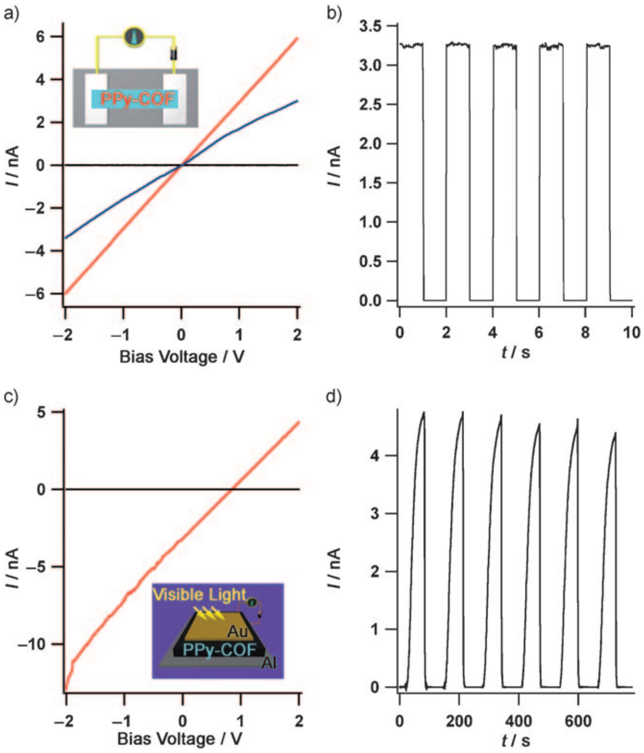

Figure 4. a) *I*–*V* profile of PPy-COF between two Pt electrodes 10 μm apart (black curve: without PPy-COF; blue curve: with PPy-COF; red curve: with iodine-doped PPy-COF). b) Electric current when the 2 V bias voltage was turned on or off. c) *I*–*V* profile of PPy-COF between sandwich-type Al/Au electrodes (black curve: without light irradiation; red curve: upon light irradiation). d) Photocurrent when the light was turned on or off.

With the above results in mind, we investigated the photoconductivity of PPy-COF by casting a thin film of PPy-COF on an Al electrode and covering the film with a 30 nm thick layer of Au by vapor deposition to fabricate sandwich-type electrodes. Indeed, on irradiation from the Au side with visible light (> 400 nm) from a xenon lamp, PPy-COF was highly responsive; a sharp rise in photocurrent generation gave a linear *I*–*V* profile (Figure 4c). Moreover, the photocurrent can be switched repetitively many times without deterioration at an on–off ratio over 8.0×10^4 (Figure 4d). The quick response, together with the large on–off ratio, is most likely related to the facilitated exciton migration and carrier transportation in PPy-COF. In sharp contrast, PDBA hardly showed any response to light irradiation under otherwise identical conditions (see Figure S6b in the Supporting Information). On the other hand, TP-COF, which consists of a network of cocondensed triphenylene and pyrene, showed a low photocurrent with a significantly (fourfold) decreased on–off ratio relative to that observed for PPy-COF (see Figure S7 in the Supporting Information). Although 1,4-

benzenediboronic acid forms a crystalline COF, the structure is staggered and hardly absorbs any photons in the visible region.[1a]

In summary, we have reported the first example of a photoconductive COF, which we synthesized by the self-condensation of pyrenediboronic acid under solvothermal conditions. The alignment of 2D polypyrene sheets in a 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 significant photocurrent generation, displays quick response to light irradiation, and is capable of repetitive on–off photocurrent switching with a large on–off ratio. These unique properties are unprecedented and thus represent an important step toward the use of COFs in optoelectronics and photovoltaics.

Received: February 13, 2009

Keywords: conducting materials · covalent organic frameworks · exciton migration · microporous materials · photoswitches

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