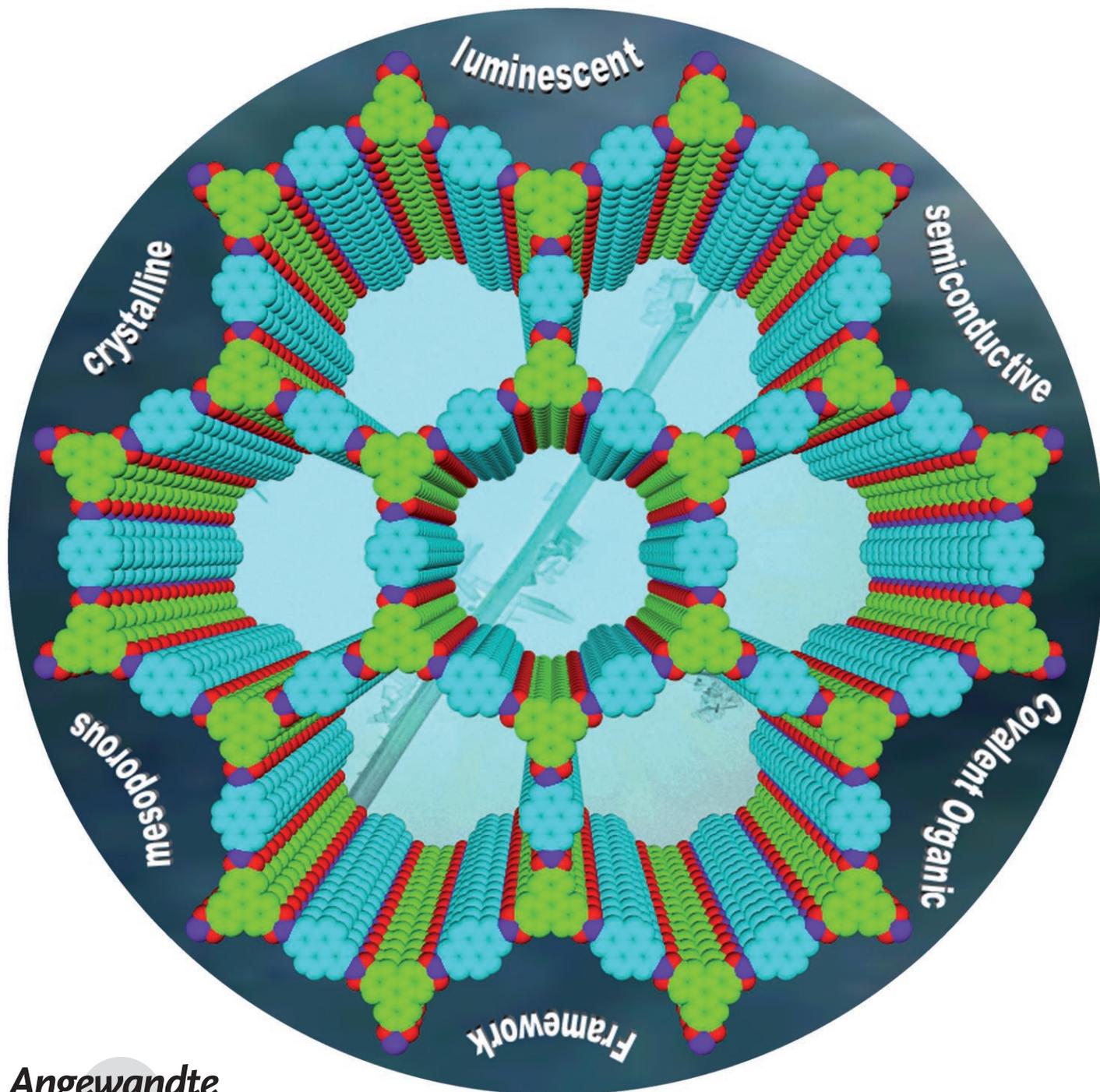


# A Belt-Shaped, Blue Luminescent, and Semiconducting Covalent Organic Framework\*\*

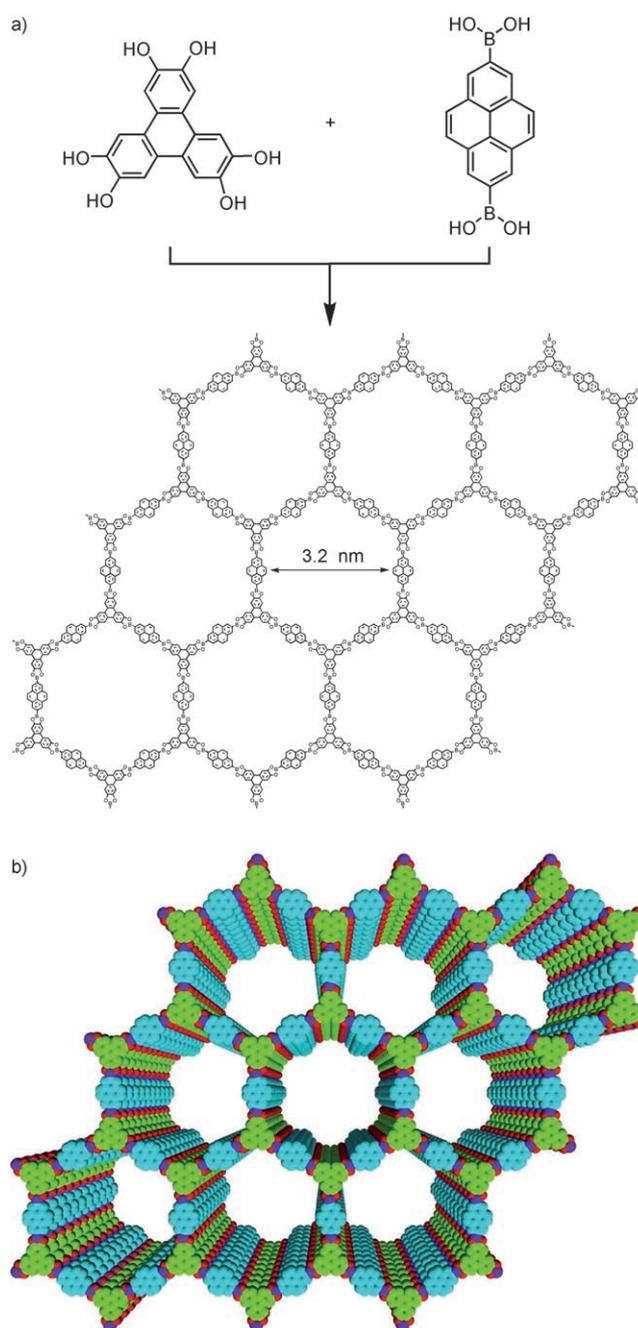
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Covalent organic frameworks (COFs) are porous and crystalline macromolecules with a well-defined and predictable network of building blocks.<sup>[1,2]</sup> Compared with inorganic porous materials, COFs are unique in that they are made from lighter elements, are robust towards air and organic solvents, and have tunable skeletons.<sup>[3]</sup> From a synthetic viewpoint, COFs are attractive motifs since they allow total control over structural parameters, including composition and porosity, after appropriate topological design. Most studies to date have focused on the development of synthetic methodologies with the aim of optimizing pore size and surface area.<sup>[4–9]</sup> In contrast, the functions of COFs, except for gas storage,<sup>[10]</sup> have not yet been well explored. This motivated us to explore the possibility of constructing functional COFs with novel properties by utilizing highly ordered  $\pi$ -conjugation systems. Herein, we report the first example of a luminescent and semiconducting COF, which adopts a belt shape and consists of pyrene and triphenylene functionalities alternately linked in a mesoporous hexagonal skeleton (TP-COF, Figure 1).

The structure of TP-COF was topologically designed so that  $D_{3h}$  symmetric monomers act as corners and  $D_{2h}$  symmetric monomers act as edges for pore hexagons. TP-COF was synthesized by a condensation reaction of 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) and pyrene-2,7-diboronic acid (PDBA). In a typical experiment, HHTP (74.58 mg, 0.23 mmol) and PDBA (100 mg, 0.345 mmol) were mixed in 1,4-dioxane/mesitylene (10 mL:10 mL) and stirred at 85 °C under Ar for 3 days.<sup>[5]</sup> The precipitate was collected by centrifugation, washed with anhydrous acetone, and dried at 150 °C under vacuum to give TP-COF (123 mg) as a pale yellow powder in 90 % yield. The FTIR spectrum of TP-COF shows vibrational bands arising from the boronate ester ring at 1345, 1328, 1246 and 1049  $\text{cm}^{-1}$ ; in contrast, the hydroxy bands of the starting materials are strongly attenuated in the FTIR spectrum of TP-COF, which indicates the condensation of two monomers (Figure S2 in the Supporting Information).<sup>[1]</sup> Field emission scanning electron microscopy (FESEM) images of TP-COF showed that the condensation polymerization of PDBA and HHTP afforded belts with



**Figure 1.** a) Synthesis of TP-COF. b) Schematic representation of TP-COF (structure is based on quantum calculation and crystal lattice parameters; B purple, O red, triphenylene green, pyrene blue, H atoms are omitted for clarity).

length in the micrometer range, width of about 300 nm, and thickness of 100 nm (Figure 2 a). The belt morphology is quite uniform in terms of width and thickness, no other morphologies are observable (Figure 2 b). To further investigate the COF structure, high resolution transmission electron microscopy (TEM) was performed. As shown in Figure 2 c, 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

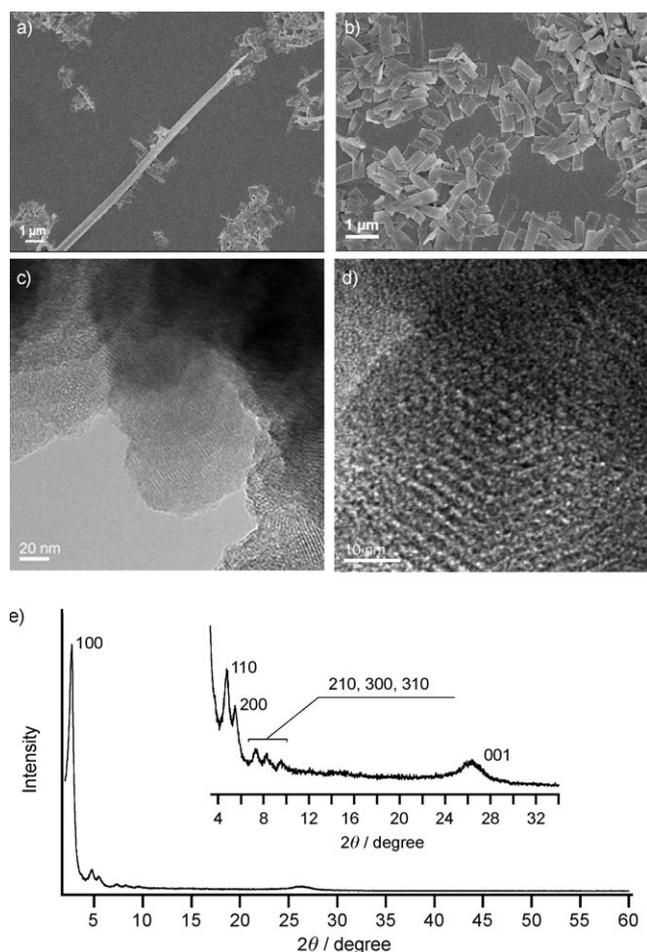
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[\*\*] This work was supported by Precursory Research for Embryonic  
 Science and Technology (PRESTO) and the Japan Science and  
 Technology Agency (JST). D.J. thanks the JSPS Asian core program.  
 J.G. was supported by a JSPS Fellowship for Young Scientists.

Supporting information for this article is available on the WWW  
 under <http://dx.doi.org/10.1002/anie.200803826>.



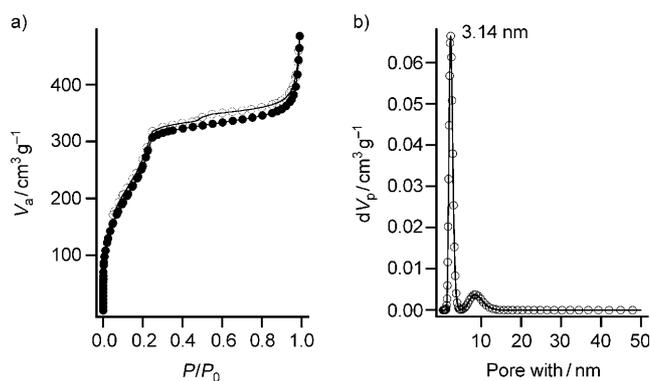
**Figure 2.** a) and b) FE SEM images of TP-COF. c) and d) HR TEM images of TP-COF. e) PXRD pattern of TP-COF.

visualization of a stacked sheet structure are unprecedented for COFs. To our surprise, the hexagonal mesostructure can be observed along the (001) facet, which enabled us to estimate the center-to-center distance between the neighboring pores to be approximately 3.3 nm (Figure 2d).

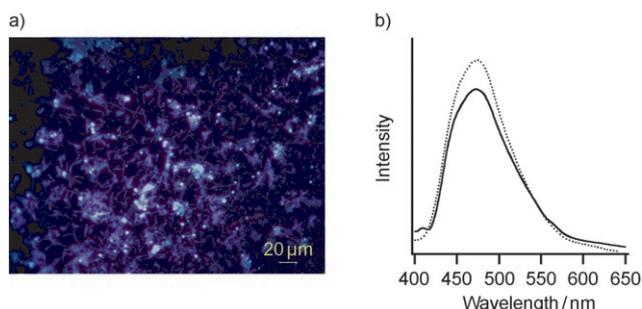
Powder X-ray diffraction (PXRD) patterns show a main diffraction peak arising from 100 at  $2.70^\circ$ , as well as diffractions from 110 ( $4.74^\circ$ ), 200 ( $5.46^\circ$ ), 210 ( $7.26^\circ$ ), 300 ( $8.24^\circ$ ), and 310 ( $9.54^\circ$ ) and 001 ( $26.32^\circ$ ; Figure 2e and Figure S3 in the Supporting Information). To elucidate the lattice packing, we first carried out semiempirical calculations at the PM3 level to optimize the geometry of the whole pore unit structure, and further optimized the molecular geometry of the repeating unit in the single unit cell at B3LYP/6-31G(d) by using the Gaussian 03 program (see the Supporting Information). Final lattice parameters were determined after Pawley refinement using Reflex, a software package for crystal structure determination from the PXRD pattern, implemented in MS modeling (version 4.2; see the Supporting Information). 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 pattern (Figure S4 in the Supporting Information). All the diffraction peaks can be reasonably assigned. On the

other hand, a staggered model using the space group of *P63/mmc* (no. 194) does not reproduce the experimental PXRD pattern (Figure S5 in the Supporting Information). Therefore, the 2D sheets crystallize in an eclipsed fashion to give a perfect superimposition of the triphenylene and pyrene units on themselves (Figure 1b and Figure S4 in the Supporting Information). Such a crystalline structure would provide open and aligned mesopores of 3.26 nm in diameter (Figure S4 in the Supporting Information). Thus, we carried out nitrogen sorption isotherm measurement to investigate the porosity of TP-COF. As shown in Figure 3a, TP-COF exhibits a typical type IV nitrogen sorption curve, which is indicative of a mesoporous character.<sup>[11]</sup> A Brunauer–Emmett–Teller (BET) calculation gives specific surface area and pore volume values for TP-COF as  $868 \text{ m}^2 \text{ g}^{-1}$  and  $0.7907 \text{ cm}^3 \text{ g}^{-1}$ , respectively. Estimation of the pore size from a density functional theory (DFT) model shows a diameter of 3.14 nm (Figure 3b), which is close to the theoretical value. The pore distribution profile shows that the specific surface area of TP-COF originates predominately from the persistent mesopores, whereas the contribution of other pores formed between belts or from defects is small (Figure 3b). All the above results indicate that TP-COF is a crystalline material with a uniformly sized mesopore formed from the eclipsed packing of the polymeric sheets.

Fluorescence microscopy shows that the belts of TP-COF have an intense blue luminescence (Figure 4a). Condensed poly(boronate ester)s bearing fluorene units have been reported to be blue-emissive materials.<sup>[12,13]</sup> Fluorescence spectroscopy shows that, upon excitation of the pyrene units at 376 or 417 nm, TP-COF displays an emission signal at 474 nm, (Figure 4b, dotted curve). On the other hand, when a solid sample of the HHTP monomer was excited at 340 nm, an emission signal at 402 nm with a shoulder at 424 nm was observed. Since this emission partially overlaps with the absorption band of the pyrene moiety, the triphenylene units in TP-COF have a chance to communicate photochemically with the pyrene moieties by energy transfer from the excited state. Excitation of the triphenylene units in TP-COF at



**Figure 3.** a) Nitrogen adsorption (●) and desorption (○) isotherm profiles of TP-COF measured at 77 K. b) Pore size distribution of TP-COF by DFT modeling on the  $\text{N}_2$  adsorption isotherms.  $V_a$  = adsorbed pore volume at standard temperature and pressure,  $P/P_0$  = relative pressure,  $P_0$  = saturated vapor pressure of the gas at 77K,  $dV_p$  = differential pore volume.

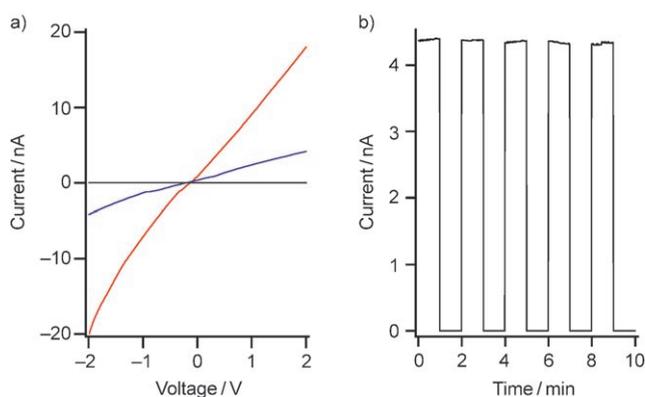


**Figure 4.** a) Fluorescence image of TP-COF. b) Fluorescence spectra of TP-COF upon excitation at 340 nm (black curve) and 376 nm (dotted curve) at 25 °C.

340 nm resulted in negligible emission at 402 nm from the triphenylene units but a strong emission from the pyrene moieties at 474 nm (Figure 4b, black curve), where the ratio of the fluorescence intensities at 474 and 402 nm ( $I_{474\text{nm}}/I_{402\text{nm}}$ ) was as high as 16. In sharp contrast, excitation of a mixture of HHTP and PDBA (2:3) at 340 nm predominately resulted in emission at 402 nm to give a low  $I_{474\text{nm}}/I_{402\text{nm}}$  ratio (0.6). Therefore, the strong pyrene fluorescence, observed for TP-COF upon excitation at 340 nm, is clearly due to an intramolecular singlet energy transfer from the triphenylene units to pyrene units. Comparison of the excitation spectrum with the diffuse reflectance UV/Vis spectrum (Kubelka–Munk spectrum; Figure S6 in the Supporting Information), the quantum yield of energy transfer was estimated to be 60%. Therefore, the presence of the triphenylene units means that TP-COF can harvest photons over a wide wavelength range—from the ultraviolet to the visible regions—and convert them to blue emission.

We further investigated the fluorescence anisotropy of TP-COF upon excitation with polarized light. When a chromophore with restricted Brownian motion is excited with polarized light, it emits a polarized fluorescence. However, the fluorescence should be depolarized when the excitation energy migrates randomly within the lifetime of the excited state. Here, fluorescence anisotropy ( $p$ ) is defined by  $(I_{\parallel} - GI_{\perp}) / (I_{\parallel} + GI_{\perp})$ , where  $I_{\parallel}$  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. The mixture of HHTP and PDBA (2:3) 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 demonstrates 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.<sup>[14,15]</sup> The ultimate  $\pi$  stacking of these large  $\pi$ -conjugated components means that TP-COF may have a high probability of becoming electrically semiconducting. We investigated this possibility by measuring the electrical conductivity across a 10  $\mu\text{m}$  width Pt gap using a two-probe method. TP-COF shows an almost linear  $I$ - $V$  profile in air at 25 °C (Figure 5a, blue curve), while the gap itself is silent, irrespective of voltage bias (black



**Figure 5.** a)  $I$ - $V$  profile of a 10  $\mu\text{m}$  width Pt gap (black curve: without TP-COF; blue curve: with TP-COF; red curve: with iodine-doped TP-COF). b) Electric current when 2 V bias voltage is turned on or off.

curve). For example, at 2 V bias voltage, the electric current is 4.3 nA (Figure 5b). In contrast, a mixture of HHTP and PDBA (2:3) shows a low current (79 pA) under otherwise identical conditions. Moreover, the electric current can be on-off switched repeatedly many times without significant deterioration (Figure 5b). 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 (Figure 5a, red curve), which suggests that TP-COF has a  $p$ -type semiconductor character.

Exploration of functional COFs is a subject that has a high probability to lead to the development of new materials. In summary, we have reported 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 characteristics are unique and clearly originate from the highly ordered structure of TP-COF. By filling the mesopores with photoactive molecules such as electron acceptors, we expect the formation of COF-based optoelectronic devices, which will be a target of further investigation.

Received: August 4, 2008

Published online: September 30, 2008

**Keywords:** conducting materials · energy transfer · luminescence · mesoporous materials · organic frameworks

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