DOI: 10.1002/chem.201405330

Conducting Materials

A Tetrathiafulvalene-Based Electroactive Covalent Organic Framework

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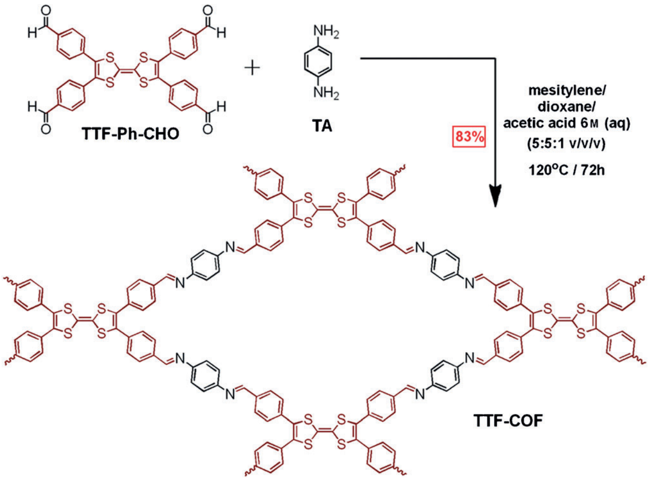
Abstract: Two-dimensional covalent organic frameworks (2D COFs) provide a unique platform for the molecular design of electronic and optoelectronic materials. Here, the synthesis and characterization of an electroactive COF containing the well-known tetrathiafulvalene (TTF) unit is reported. The TTF-COF crystallizes into 2D sheets with an eclipsed AA stacking motif, and shows high thermal stability and permanent porosity. The presence of TTF units endows the TTF-COF with electron-donating ability, which is characterized by cyclic voltammetry. In addition, the open frameworks of TTF-COF are amenable to doping with electron acceptors (e.g., iodine), and the conductivity of TTF-COF bulk samples can be improved by doping. Our results open up a reliable route for the preparation of well-ordered conjugated TTF polymers, which hold great potential for applications in fields from molecular electronics to energy storage.

Covalent organic frameworks (COFs), a class of crystalline porous materials composed of light-weight elements and connected through strong covalent bonds, have attracted[1] great attention in the past decade because of their usefulness for gas storage,[2] catalysis,[3] and optoelectronic devices.[4] Compared with three-dimensional COFs, two-dimensional (2D) COFs exhibit[5] unique eclipsed stacked structures, which can provide π–π interactions between monomers in adjacent layers, and thus, facilitate charge migration through the framework. Therefore, with certain photoelectric moieties embedded into well-defined 2D COFs, the corresponding COF materials are expected to possess unique optical and electrical properties. However, the incorporation of such moieties within 2D COFs is quite challenging. To date, successful attempts have been limited to a few electroactive monomers, including pyrene,[6] porphyrin,[4c,7] phthalocyanine,[4a,8] naphthalenetetracarboxy-diimide,[9] and thiophene.[10] Considering their interesting properties and promising applications, it would be highly desirable to have access to more 2D COFs with other photoelectric moieties.[11]

Tetrathiafulvalene (TTF) and its derivatives, well known for their π-electron-donating abilities and two reversible oxidation processes, have received[12–16] tremendous attention over the past forty years. Notably, owing to their electroactive abilities, TTF and its derivatives have played[17] a significant role in the development of organic conducting materials. For example, high conductivities can be expected for TTF-based nanofibers through the formation of charge-transfer (CT) complexes with electron acceptors.[18] Therefore, with the incorporation of TTF into a 2D COF, the resulting porous materials will not only facilitate electronic interactions between TTF units, but also allow doping with electron acceptors to increase conductivity. With these considerations in mind, we report herein the synthesis of a 2D COF containing the electroactive TTF unit (TTF-COF, Scheme 1) for the first time. Our results demonstrate clearly that the TTF-COF has permanent porosity with high thermal stability, and that the open frameworks are amenable to doping with electron acceptors (e.g., iodine). Moreover, the crystallinity of TTF-COF is retained in the doping process, and its conducting properties in the bulk state can be tuned by doping.



Scheme 1. Schematic representation of the synthesis of TTF-COF. The wavy lines imply the extension of periodic structures.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201405330.

TTF-COF was synthesized by the condensation reaction between tetrathiafulvalene-tetrabenzaldehyde (TTF-Ph-CHO, Scheme 1)[19] and *p*-phenylenediamine in mixtures of mesitylene/dioxane/AcOH (5:5:1, by volume) at 120 °C for 3 days. The selection of TTF-Ph-CHO and *p*-phenylenediamine for the preparation of TTF-COF was based on the following considerations: 1) by using a combination of 2D blocks (e.g., 2D C_2 + 2D C_2), the 2D COF was expected to be obtained with the designed topology and pore structure;[1,6b] and 2) the imine bonds may be stable after doping with iodine. The resulting precipitate was collected by filtration, washed with anhydrous tetrahydrofuran, acetonitrile, and acetone, and dried at 120 °C under vacuum to provide TTF-COF as a dark maroon powder in 83 % yield. The formation of imine bonds in TTF-COF was assessed by Fourier-transform infrared (FTIR) and ^{13}C cross-polarization with total suppression of sidebands (CP-TOSS) NMR spectroscopic methods. The FTIR spectrum (Figure S1, Supporting Information) exhibited a stretching vibration band at 1621 cm^{-1} assignable to the C=N band, whereas the ^{13}C CP-TOSS NMR spectrum (Figure S2) showed a resonance at 157 ppm for the carbon of the C=N bond. Thermogravimetric analysis (TGA) showed that TTF-COF is stable up to 350 °C (Figure S3).

Powder X-ray diffraction (PXRD) was used to determine the crystallinity of the synthesized TTF-COF. As shown in Figure 1 a (red curve), TTF-COF exhibited an intense diffraction peak at 3.7° as well as weak peaks at 5.9° and 7.5°, which can be assigned to the (110), (200), and (220) facets, respectively. To elucidate the lattice packing, we constructed the crystal models using the *Materials Studio* software package (see Supporting Information for details).[20] The eclipsed AA stacking mode (Figure 1 b) can reproduce the XRD pattern (Figure 1 a, blue curve), whereas the staggered AB stacking mode (Figure 1 c) gives an XRD pattern (Figure 1 a, orange curve) that deviates significantly from the experimentally obtained profile. Furthermore, the experimental powder XRD pattern of TTF-COF was subjected to refinement by the Pawley method. The refined XRD curve (Figure 1 a, green curve) shows a small difference (Figure 1 a, black curve) from the experimental data. A monoclinic unit cell (C_2/m) with the parameters $a = 29.7532$ Å, $b = 37.9189$ Å, $c = 4.281$ Å, $\alpha = \gamma = 90.0°$, and $\beta = 92.7256°$ was deduced, which are very similar to the dimensions of the eclipsed model ($a = 29.6321$ Å, $b = 37.8481$ Å, $c = 4.2997$ Å, $\alpha = \gamma = 90.0°$, and $\beta = 92.8785°$). The final R_{WP} and R_P values were converged to 6.71 % and 5.41 %, respectively.

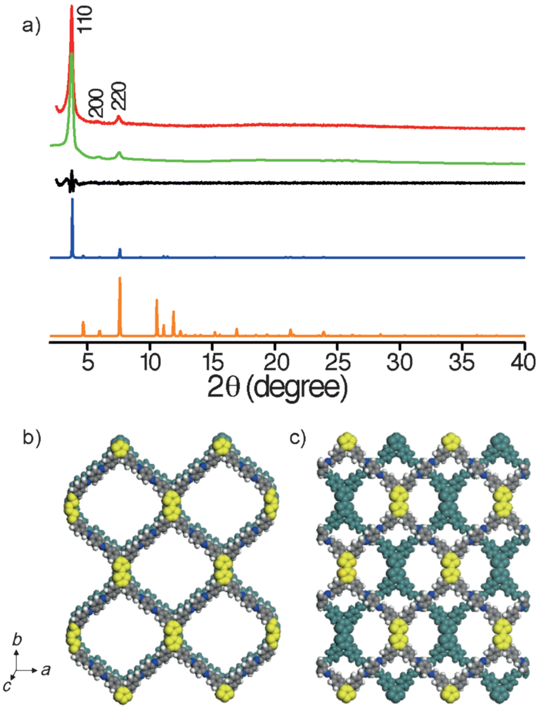

Figure 1. a) PXRD pattern of TTF-COF: experimental (red), Pawley refined (green), difference between experimental and calculated data (black), calculated for AA stacking (blue), and calculated for AB stacking (orange). Space-filling models of TTF-COF in b) AA and c) AB stacking modes.

The permanent porous structure of TTF-COF was investigated by using its nitrogen sorption isotherm at 77 K. Prior to the measurement, the sample was degassed at 100 °C and 1×10^{-5} torr for 10 h. As shown in Figure 2 a, the isotherm of TTF-COF showed a significant uptake in the low-pressure region ($P/P_0 < 0.1$). This sorption curve is best described as a typical type I isotherm, which is characteristic of microporous materials. The Brunauer–Emmett–Teller (BET) surface area and pore volume were calculated to be 955 $m^2 g^{-1}$ and 0.64 $cm^3 g^{-1}$, respectively. The pore size distribution calculated using the nonlocal density functional theory (NLDFT) method

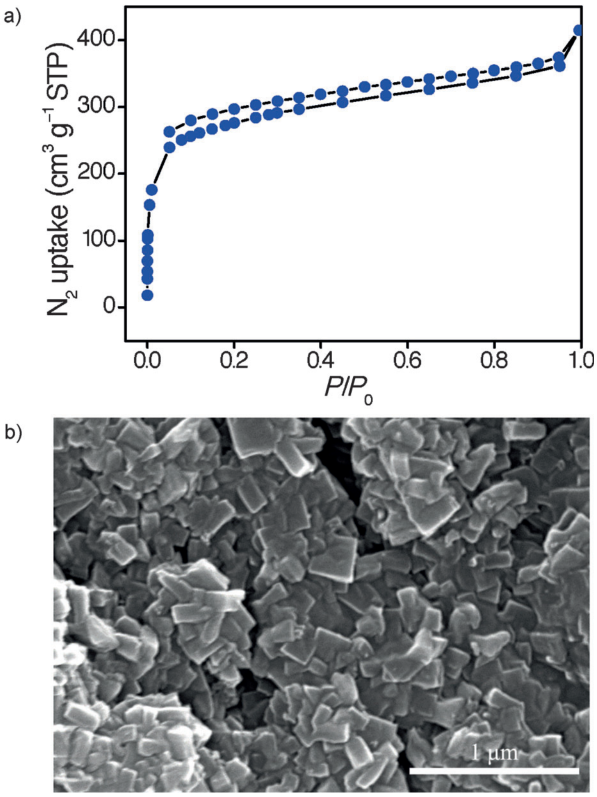

Figure 2. a) Nitrogen sorption isotherm profiles for TTF-COF measured at 77 K. b) SEM image of TTF-COF.

was 1.41 nm (Figure S4), which was close to the value obtained from theoretical calculation (1.6 nm).[21] Furthermore, scanning electron microscopy (SEM) revealed that TTF-COF has a flake morphology (Figure 2b).

The presence of TTF units should benefit TTF-COF as an electron donor. Cyclic voltammetry (CV) was used to investigate the electrochemical behavior of TTF-COF. TTF-COF is insoluble in common organic solvents, so we modified the working electrode for CV measurements. TTF-COF (6 mg) and carbon black (4 mg) were ground in an agate mortar and pestle for 10 min, the ground powder was subjected to CH_2Cl_2 (1 mL), and the electrode was prepared by drop-casting a supersonicated CH_2Cl_2 suspension onto the tip of the Pt working electrode. As shown in Figure 3, TTF-COF shows a typical surface-confined voltammetric profile with two reversible redox processes at 0.69[22] and 1.07 V, indicating the electron-donating character of TTF-COF. Both oxidation steps are shifted to higher potentials compared with TTF-Ph-CHO and the model compound (see Supporting Information for details), so it is difficult to oxidize the TTF units oxidized in the COF state.

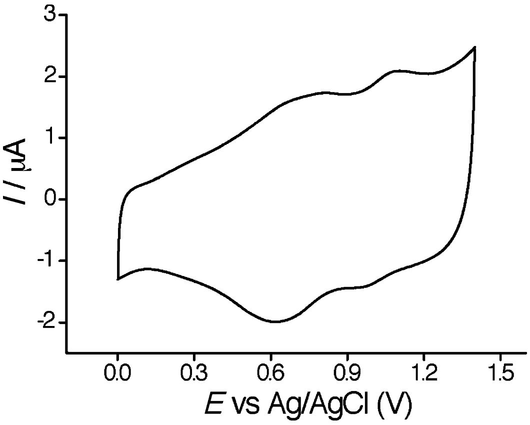

Figure 3. Cyclic voltammogram of TTF-COF (counter electrode: Pt; reference electrode: Ag/AgCl; scan rate 50 mV s^{-1}; 0.1 M NBu_4PF_6 in CH_2Cl_2). The electrode was prepared by drop-casting a supersonicated CH_2Cl_2 suspension of TTF-COF and carbon black onto the tip of the Pt working electrode.

The electron-donating nature of TTF-COF could allow us to prepare TTF-based CT complexes for the development of organic conducting materials. Therefore, we pursued the doping experiment with TTF-COF with the aim of inducing high electrical conductivity. TTF-COF was doped (oxidized) by exposure to iodine vapor. Before any further experiments, the as-doped samples were dried in vacuum at 50 °C to remove the iodine absorbed in the pores. Figure 4a shows the electron paramagnetic resonance (EPR) spectrum of TTF-COF after iodine doping. A very sharp peak was found at $g = 2.0094$, which is typical of the TTF radical cation, and suggests that the TTF units are oxidized. More importantly, the TTF-COF after iodine doping exhibits intense XRD patterns (Figure 4b), indicating that the crystallinity of TTF-COF is retained[23] in the doping process.

We further investigated the electrical conductivities of the bulk samples of TTF-COF and its doped state. We measured the resistance using silver paste contacts in a constant-voltage two-probe configuration. The compressed pellet was cut into rectangular bars with dimensions of 0.5 × 0.2 × 0.1 cm (see Supporting Information for details). We were not able to measure[24] the conductivity of TTF-COF bulk sample in the temperature range 0 to 40 °C because the resistance is greater than 2 GΩ, beyond the range of instrument. However, for the as-doped samples, a significant increase in conductivity was observed (Figure 5). A conductivity of 2.1×10^{-7} S cm^{-1} at 25 °C

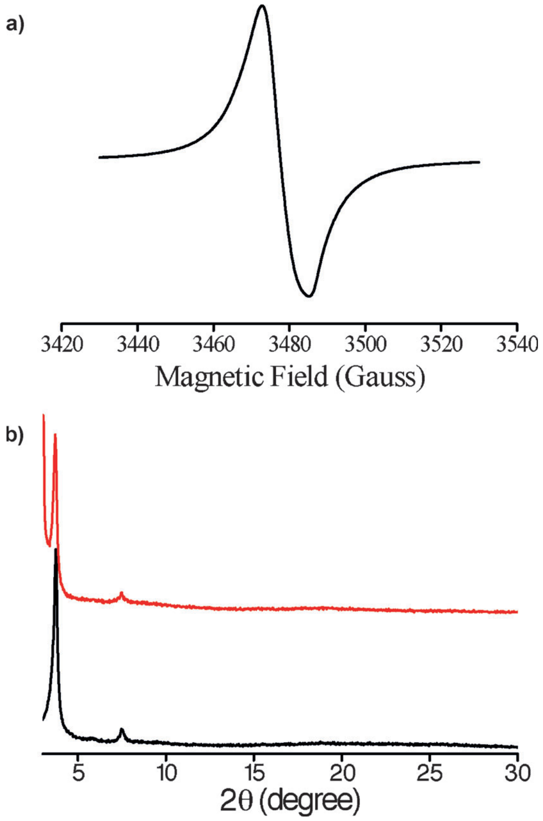

Figure 4. a) Solid-state EPR spectrum of TTF-COF after iodine doping for 2 days. b) PXRD patterns of TTF-COF before (black line) and after (red line) iodine doping for 2 days.

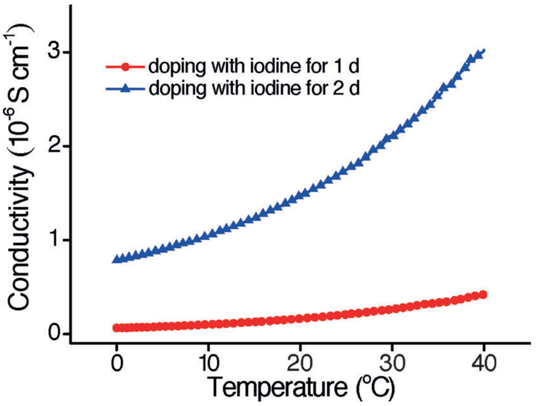

Figure 5. Electrical conductivities of TTF-COF after doping with iodine for 1 day (red curve) and 2 days (blue curve) in the temperature range 0 to 40 °C.

was obtained after doping for 1 day, and this value could increase to 1.8×10^{-6} S cm^{-1} upon extending the doping time to 2 days.[25] Furthermore, the temperature dependences of the resistance in the range 0 to 40 °C revealed the semiconductor-like behavior of TTF-COFs after doping with iodine. Therefore, the conducting properties of the bulk TTF-COF sample could be tuned by iodine doping.

In conclusion, we have described the synthesis of an electroactive COF containing the TTF monomer for the first time. Our results clearly demonstrate that the well-defined TTF-COF shows high thermal stability and permanent porosity, and is amenable to doping with iodine, which could improve the conductivity of TTF-COF bulk samples. This novel system provides a new way to prepare well-ordered conjugated TTF materials, and may find applications in various fields from electronic devices to energy storage. Furthermore, this system may provide a way to obtain single-layer 2D COFs, owing to the charge repulsion between TTF^{2+} in the adjacent layer as soon as the TTF units are fully oxidized. Further investigations are now underway in our laboratory.

Experimental Section

Preparation of TTF-Ph-CHO

The synthesis was performed according to the reported method.[19] A 50 mL two-neck bottle flask was filled with Pd(OAc)$_2$ (84 mg, 0.38 mmol), P(tBu)$_3$·HBF$_4$ (326 mg, 1.1 mmol), Cs$_2$CO$_3$ (2.45 g, 7.5 mmol), and THF (10 mL). The mixture was stirred for 10 min under nitrogen. Then, a solution of tetrathiafulvalene (307 mg, 1.5 mmol) and 4-bromobenzaldehyde (2.78 g, 15 mmol) in THF (10 mL) was added, and the mixture was heated to reflux for 2 days. After the reaction was cooled down, chloroform (100 mL) was added. The organic layer was washed with brine and dried over Na$_2$SO$_4$. Subsequently, the solvents were evaporated under reduced pressure and the resulting residue was subjected to column chromatography [SiO$_2$ (200–300):PE/CH$_2$Cl$_2$ (1:2, by vol.)$\rightarrow$CH$_2$Cl$_2$]. The product was isolated and recrystallized from CH$_3$OH and CHCl$_3$ as a maroon solid (0.35 g, yield, 38 %). ^{1}H NMR (CDCl$_3$, 300 MHz, 298 K): $\delta=9.97$ (s, 1 H), 7.78 (d, $J=7.8$ Hz, 2 H), 7.37 ppm (d, $J=7.9$ Hz, 2 H); ^{13}C NMR (CDCl$_3$, 100 MHz, 98 K): $\delta=191.5$, 138.3, 136.6, 130.7, 130.5, 130.1, 109.2 ppm; GC-MS: m/z calcd for C$_{34}$H$_{20}$O$_4$S$_4$: 620.0244 [M]$^+$; found: 620.0253 [M]$^+$; elemental analysis calcd (%) for (C$_{34}$H$_{20}$O$_4$S$_4$ + 0.22 CHCl$_3$): C 63.52, H 3.15, S 19.82; found: C 63.00, H 2.95, S 20.28.

Preparation of TTF-COF

A 10 mL Pyrex glass tube was charged with TTF-Ph-CHO (0.022 mmol, 13.6 mg), p-phenylenediamine (0.044 mmol, 4.8 mg), mesitylene (0.5 mL), dioxane (0.5 mL), and 6 M aqueous acetic acid (0.1 mL). The tube was degassed by three freeze-pump-thaw cycles, sealed under vacuum, and heated at 120 °C for 3 days. The reaction mixture was cooled to room temperature, and the precipitate was collected by centrifugation, washed with anhydrous tetrahydrofuran, acetonitrile, and acetone. The resulting dark maroon powder was dried at 120 °C under vacuum overnight to give the corresponding TTF-COF in 83 % isolated yield. Elemental analysis calcd (%): C 72.22, H 3.69, N 7.32, S 16.77; found: C 68.48, H 4.18, N 6.96, S 15.37.

Acknowledgements

C.W. is grateful for financial support from the National Natural Science Foundation of China (21203140), the Research Fund for the Doctoral Program of Higher Education of China (20130141110008), and Wuhan University (203273642). D.Z. acknowledges financial support from NSFC, the State Basic Program, and the Chinese Academy of Sciences. We thank Prof. Wei Wang (Lanzhou University) for kind discussions and Prof. Bo Wang (Beijing Institute of Technology) for nitrogen sorption measurements.

Keywords: conducting materials · covalent organic frameworks · electron donor · microporous materials · tetrathiafulvalene

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[19] The TTF-Ph-CHO was synthesized in one step and with reasonable yield directly from commercially available TTF, by applying Yorimitsu's method (Y. Mitamura, H. Yorimitsu, K. Oshima, A. Osuka, *Chem. Sci.* **2011**, *2*, 2017 – 2021).

[20] From theoretical optimization, the obtained eclipsed AA stacking mode represents the lowest energy structure. By increasing monotonically the slipped distances, the energies of the slipped structures increased, and finally, the energy of the AB model was 78 kcal mol^{-1} higher than that of the AA model.

[21] Yaghi and Goddard's method was applied to calculate the theoretical pore size (J. L. Mendoza-Cortés, S. S. Han, H. Furukawa, O. M. Yaghi, W. A. Goddard III, *J. Phys. Chem. A* **2010**, *114*, 10824 – 10833)

[22] The first redox wave appears broadened, which may originate from the stacking of TTF units in the adjacent layer.

[23] Previous results demonstrated that boronate-ester-linked COFs became amorphous after doping with iodine (Ref. [10a]). Our experiments indicate that the C=N bond is stable in this doping process.

[24] The calculated distance between two TTF planes (4.3 Å) is larger than that of π–π interaction, which may explain the low electrical conductivity of TTF-COF. Besides, as we measured the conductivity of TTF-COF in the bulk state, the intergrain boundaries and electrode contact resistances may also have some effects on this phenomenon.

[25] We measured more than five samples and the experiments were reproducible.

Received: March 21, 2014
Revised: June 19, 2014