JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Communication

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J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.9b06908 • Publication Date (Web): 09 Aug 2019

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Three-Dimensional Tetrathiafulvalene-Based Covalent Organic Frameworks for Tunable Electrical Conductivity

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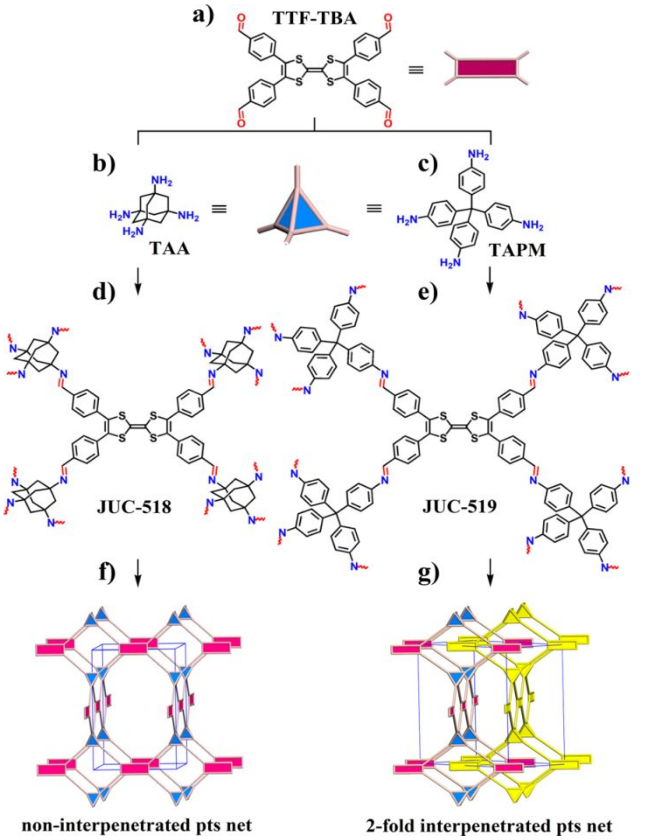
Supporting Information Placeholder

ABSTRACT: The functionalization of three-dimensional (3D) covalent organic frameworks (COFs) is essential to broaden their applications. However, the introduction of organic groups with electroactive abilities into 3D COFs is still very limited. Herein we report the first case of 3D tetrathiafulvalene-based COFs (3D-TTF-COFs) with non- or 2-fold interpenetrated **pts** topology and tunable electrochemical activity. The obtained COFs show high crystallinity, permanent porosity, and large specific surface area (up to 3000 m^2/g). Furthermore, these TTF-based COFs are redox active to form organic salts that exhibit tunable electric conductivity (as high as 1.4×10^{-2} S cm^{-1} at 120 °C) by iodine doping. These results open a way towards designing 3D electroactive COF materials and promote their applications in molecular electronics and energy storage.

Covalent organic frameworks (COFs), as an exciting new type of crystalline porous polymers, are made from light elements, typically H, B, C, N and O, which crystallize into periodic networks by the formation of reversible covalent bonds.[1-4] Owing to their high porosity, large specific surface area and good thermal/chemical stability, the COF materials have attracted much attention for considerable potential in gas storage and separation,[5-7] catalysis,[8-12] organic electronics,[13-16] and many others.[17-23] Over the past decade, most of the reported work on COFs, however, were focused on two-dimensional (2D) COFs with layered eclipsed structures. Three-dimensional (3D) COFs, especially 3D functionalized COFs, have recently attracted extensive interest due to their unique porous features and excellent performances.[24-29] We have synthesized a series of 3D functionalized COFs by the pre-synthesis or post-modification approach, including 3D Salphen-based COFs as catalytic antioxidants,[30] 3D ionic liquid-containing COFs for gas separation,[31] 3D carboxy-functionalized COFs with selective extraction of lanthanide ions,[32] and so on.[33-36] It must be noted, however, that the functionalization of 3D COFs remains largely unexplored, such as 3D electroactive COFs in particular. Thus, the development of new 3D functionalized COF materials is of critical importance for enriching the structural diversity and expanding their applications.

Scheme 1. Schematic representation of the strategy for preparing 3D-TTF-COFs[a]



[a]Molecular structures of TTF (a) as a planar 4-connected building unit, TAA (b) as a short tetrahedral building unit, and TAPM (c) as a long tetrahedral building unit. 3D-TFF-COFs, denoted as JUC-518 (d) and JUC-519 (e), are constructed by the condensation reaction of TTF and TAA or TAPM. Non- or 2-fold interpenetrated **pts** net in JUC-518 (f) and JUC-519 (g).

Taking these considerations in mind, we report herein the first case of 3D electroactive COFs containing tetrathiafulvalene (TTF) functional units, denoted as 3D-TTF-COFs. Our results demonstrate that the obtained COFs have rare non- or 2-fold interpenetrated **pts** topology, high crystallinity and large surface area (> 3000 m^2/g). More importantly, the TTF-based frameworks can be doped with electron acceptors (iodine, I_2), and their conducting properties can be tuned from 1.8×10^{-7} to 1.4×10^{-2} S cm^{-1} by the increasing amount of I_2. To the best of our knowledge, this study is the first example of 3D COFs with non-interpenetrated **pts** topology and the application of 3D COFs as charge-transfer materials.

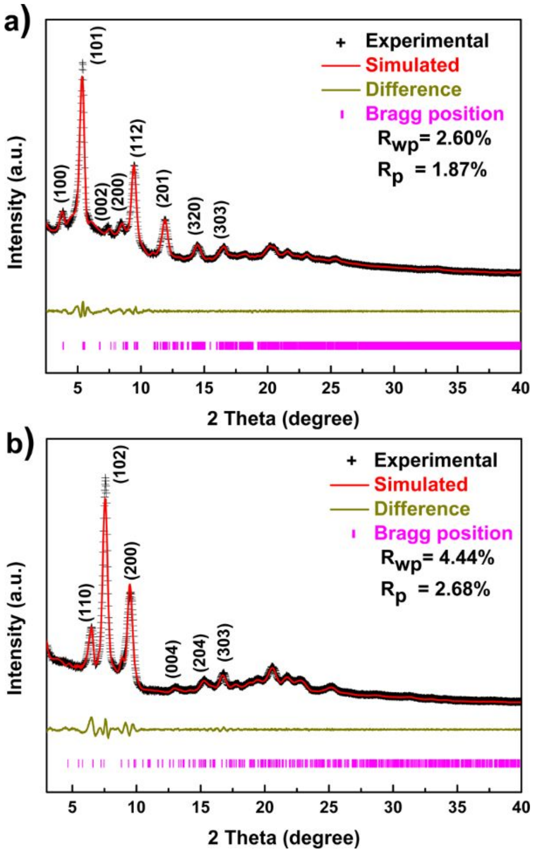


Figure 1. PXRD patterns of JUC-518 (a) and JUC-519 (b).

Our strategy for preparation of 3D electroactive COFs is based on a TTF derivative, tetrathiafulvalene-tetrabenzaldehyde (TTF-TBA, Scheme 1a). As we all know, due to their excellent electrical activities, TTF or TTF-based derivatives have played an important role in the development of organic conducting materials.[37-39] Therefore, by the incorporation of TTF units into 3D porous COFs, the resulting materials will not only promote electronic interactions between TTF molecules, but also enable doping with electron acceptors (e.g., I_2) to increase their conductivity. As shown in Scheme 1, TTF-TBA (Scheme 1a) was designed as a planar 4-connected building unit, and 1,3,5,7-tetraaminoadamantane (TAA, Scheme 1b) or tetra(4-aminophenyl)methane (TAPM, Scheme 1c) was chosen as a typical tetrahedral building unit. The condensation of TTF-TBA and TAA or TAPM produced 3D-TTF-COFs, termed as JUC-518 (JUC = Jilin University China, Scheme 1d) and JUC-519 (Scheme 1e). In light of the linking of tetrahedral and planar 4-connected building units, the structures of both COFs are expected to be the **pts** net (Scheme 1f and 1g). Since the TTF-TBA is connected by TAA as a short tetrahedral building unit (~ 3.1 Å) and TAPM as a long tetrahedral building unit (~ 5.9 Å, Figure S1), the resulting structures tend to be non- and 2-fold interpenetrated **pts** networks, respectively.[40]

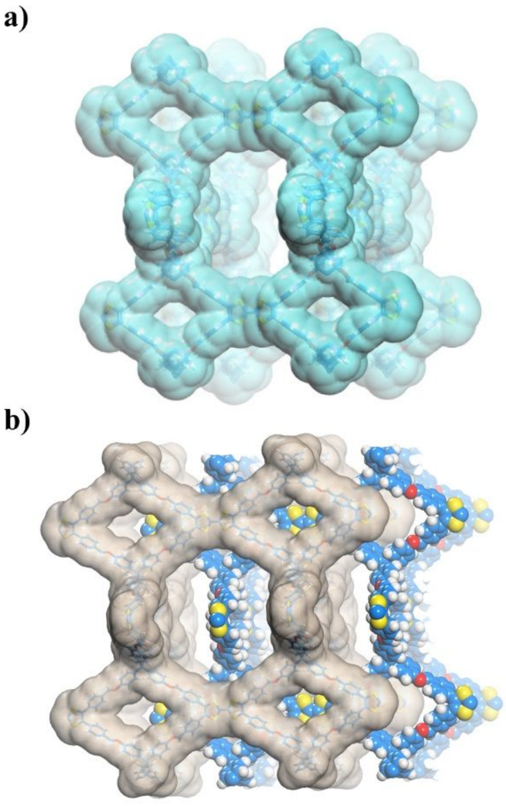


Figure 2. Extended structures of non-interpenetrated JUC-518 (a) and 2-fold interpenetrated JUC-519 (b). C, blue; H, gray, N, red; S, yellow.

The synthesis of 3D-TTF-COFs was carried out by suspending TTF-TBA and TAA or TAPM in the mixed solvent of *o*-dicholobenzene (*o*-DCB) and n-butanol (n-BuOH) in the presence of acetic acid followed by heating at 120 °C for 3 days. A variety of methods were employed for structural characterizations of 3D-TTF-COFs. The morphology was examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM, Figures S2 and S3), which showed isometric crystals with a size of 0.2 μm. The Fourier transform infrared (FT-IR) spectrum exhibited a new peak at 1637 cm^{-1} for JUC-518 or 1625 cm^{-1} for JUC-519, which is a typical characteristic of C=N bond. The concomitant disappearance of the C=O stretching vibration (1701 cm^{-1} for TTF-TBA) and the N-H stretching vibration (~3324 cm^{-1} for TAA and ~3348 cm^{-1} for TAPM), confirmed the complete transformation of aldehyde and amine groups (Figures S4 and S5). The solid-state ^{13}C cross-polarization magic-angle-spinning (CP/MAS) NMR spectroscopy confirmed the presence of carbons from the imine groups by the peak at 154 ppm for JUC-518 or 158 ppm for JUC-519 (Figures S6 and S7). Both 3D-TTF-COFs had high thermal stability (~400 °C) as shown by the thermogravimetric analysis (TGA, Figures S8 and S9), and can be preserved in different organic solvents and aqueous solutions of 1 M HCl or 1 M NaOH (Figures S10 and S11).

The crystal structures of 3D-TTF-COFs were analyzed by the powder X-ray diffraction (PXRD) measurements in conjunction with structural simulations (Figure 1). After a geometrical energy minimization by the Materials Studio software package[41] on the basis on non- or 2-fold interpenetrated **pts** net, their unit cell parameters were acquired ($a = b = 21.528$ Å, $c = 25.743$ Å and α

$= \beta = \gamma = 90°$ for JUC-518; $a = b = 18.673$ Å, $c = 30.679$ Å and $\alpha = \beta = \gamma = 90°$ for JUC-519). Moreover, full profile pattern matching (Pawley) refinements were applied to their experimental PXRD patterns. Peaks at 3.78, 5.40, 7.43, 8.39, 9.44, 11.89, 14.36 and 16.57° for JUC-518 belong to the (100), (101), (002), (200), (112), (201), (320) and (303) Bragg peaks of space group $P4_2/m$ (No. 84); peaks at 6.51, 7.45, 9.48, 12.99, 15.19 and 16.68° for JUC-519 correspond to the (110), (102), (200), (004), (204) and (303) Bragg peaks of the space group $P4_2/m$ (No. 84). The refinement results can match well with the observed ones with good agreement factors (Rp = 1.87% and ωRp = 2.60% for JUC-518; Rp = 2.68% and ωRp = 4.44% for JUC-519). In addition, we tried alternative structures, such as 2-fold interpenetrated **pts** net for JUC-518 and non-interpenetrated **pts** net for JUC-519; however, their simulated PXRDs did not match to the experimental ones (Figures S12-15). In consideration of these results, the obtained COFs were proposed to have the expected frameworks with non- or 2-fold interpenetrated **pts** topology, which show microporous cavities with ~ 1.62 nm for JUC-518 and ~ 0.81 nm for JUC-519 (Figure 2). Remarkably, all the previous COFs with **pts** topology show interpenetrated structures and small dominated pores (~ 0.60 nm),[42-44] and thus the successful preparation of JUC-518 with non-interpenetrated nets will benefit the development of 3D COFs with large pores.

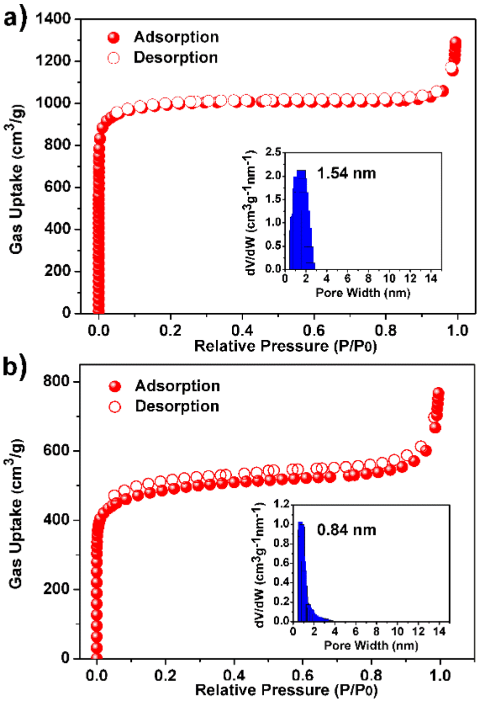


Figure 3. N_2 adsorption-desorption isotherms for JUC-518 (a) and JUC-519 (b) at 77 K. Inset: pore-size distribution calculated by fitting on the NLDFT model to the adsorption data.

The porosity and specific surface areas of 3D-TTF-COFs were determined by N_2 adsorption analysis at 77 K (Figure 3). Both materials show a sharp uptake at a low pressure of $P/P_0 < 0.05$, which is a typical characteristic of the microporous material. The inclination of isotherms in the 0.9-1.0 P/P_0 range and slight desorption hysteresis can be attributed to the presence of textural mesopores, which is from the agglomeration of COF crystals.[34] The Brunauer-Emmett-Teller (BET) equation was carried out in the $0.05 < P/P_0 < 0.30$ range of their isotherms, indicating BET surface areas of 3018 $m^2\ g^{-1}$ for JUC-518 and 1513 $m^2\ g^{-1}$ for JUC-519 (Figures S18 and S19). Obviously, owing to the non-interpenetrated structure, JUC-518 shows a high porosity (88.8%) and low crystalline density (0.19 g cm^{-3}, Table S1), and thus its BET surface area is much higher than those from all reported 3D COFs with the **pts** topology (< 1400 $m^2\ g^{-1}$).[42-44] Pore size distributions of 3D-TTF-COFs calculated based on the nonlocal density functional theory (NLDFT) demonstrated pores with the size of 1.54 nm for JUC-518 and 0.84 nm for JUC-519 (Figure 3, inset), which are in good agreement with those of the proposed model (1.62 nm for JUC-518 and 0.81 nm for JUC-519).

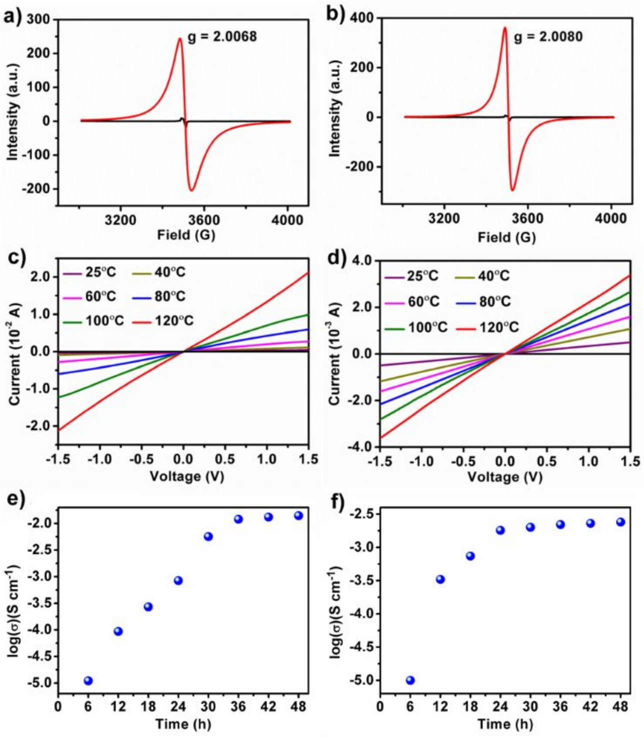


Figure 4. Solid-state EPR spectrum of JUC-518 (a) or JUC-519 (b) before (black) and after (red) I_2 doping. Temperature-dependent I–V curves of JUC-518 (c) and JUC-519 (d) upon I_2 oxidation (black curves: pristine COFs at 25 ºC). Time-dependent electrical conductivities of JUC-518 (e) and JUC-519 (f) upon I_2 oxidation.

Inspired by the abundant presence of TTF functional units, we firstly investigated the electrochemical behavior of 3D-TTF-COFs by cyclic voltammetry (CV). As shown in Figures S20 and S21, both COFs showed a reversible CV profile with two clear redox processes at 0.776 and 1.162 V vs Ag/AgCl for JUC-518 and 0.752 and 1.133 V vs Ag/AgCl for JUC-519 respectively, revealing that TTF units in COF frameworks retain their redox activities. Furthermore, the electron-donating nature of TTF units and permanent porosity of 3D-TTF-COFs could endow us to develop TTF-based charge-transfer (CT) materials. It is known that I_2 can act as a suitable oxidant due to its reduction potentials at 0.784 V for I_3^-.[45] Compared with the potentials between 3D-TTF-COFs and I_2, only the first redox process for both COFs can be happened by using I_2 as an oxidant. Typically, both COFs were doped (oxidized) by exposure to I_2 vapor. Figure 4a and 4b showed electron paramagnetic resonance (EPR) spectra of JUC-518 and JUC-519 before and after I_2 doping. Obviously, the pristine samples had very weak EPR spectra; however, the doped samples exhibited a significant paramagnetic intensity increased by approximately two orders of magnitude. After I_2 doping, the sharp peaks were observed at g = 2.0068 for JUC-518 and 2.0080 for JUC-519, clearly confirming the enhancing concentration of TTF radical cations.[37-39] The PXRD patterns showed that 3D-

TTF-COFs after I_2 doping for 48 hrs remained highly crystalline and structurally intact (Figures S16 and S17).

We further investigated the electrical conductivities of I_2 doped 3D-TTF-COFs. Typically, the doped samples were compressed into cylindrical pellets with a diameter of 0.5 cm and a thickness of 0.2 cm. The conductivities were conducted by using gold paste contacts in a two-probe configuration. As shown in Figures 4c-f and S22-37, the temperature dependences of the conductivities in the range of 25 to 120 ºC could be observed. Further analysis, including Arrhenius plots with linear relationship (Figures S38 and S39) and activation energy (0.42 eV for JUC-518 and 0.20 eV for JUC-519), indicated the semiconductor-like behavior of these materials. The conducting properties of 3D-TTF-COFs could be tuned with doping time from 6 to 48 hrs, which can be attributed to the increasing amount of I_2 with the extension of the doping time (Table S4). These results are summarized in Tables S2 and S3. For example, the conductivity of 2.9×10^{-7} S cm^{-1} for JUC-518 at 25 °C is obtained after doping for 6 hrs, which could be increased to 2.7×10^{-4} S cm^{-1} at 25 °C upon extending the doping time to 48 hrs. Subsequently, the conductivity of JUC-518 can be extremely enhanced to 1.4×10^{-2} S cm^{-1} by raising the temperature up to 120 ºC. Notably, the electrical conductivities of 3D-TTF-COFs is higher than those from 2D TTF-based COF powders (~ 10^{-5} S cm^{-1})[46,47] and TTF-based MOFs (~ 10^{-7} S cm^{-1}).[48] Compared with 2D-TTF-COFs, the higher conductivities in 3D-TTF-COFs can be attributed to the fact that more I_2 are doped and TTF units are fully oxidized into TTF radical cations due to interconnected channels and higher surface areas in 3D COFs. As for TTF-based MOFs, the carboxyl units are strong electron-withdrawing groups, which will reduce the ability of TTF units to donate electrons and thus decrease their conductivities. Furthermore, the electrical conductivities of 3D-TTF-COFs with I_2 doped can be tested repeatedly at least four times without obvious electroactive loss (Figures S40 and S41).

In summary, we report 3D electroactive TTF-based COFs with non- or 2-fold interpenetrated **pts** topology, high crystallinity and large permanent porosity. Furthermore, these 3D-TTF-COFs are redox active to form organic salts that exhibit outstanding electric conductivity by doping I_2. This study not only develops a way towards designing 3D electroactive COF materials, but also promotes their applications in molecular electronics and energy storage.

ASSOCIATED CONTENT

Supporting Information

Methods and synthetic procedures, SEM, FTIR, solid state ^{13}C NMR, TGA, BET plots, and unit cell parameters. This material is available free of charge via the internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was supported by National Natural Science Foundation of China (21571079, 21621001, 21390394, 21571076, and 21571078), ″111″ project (B07016 and B17020), and the program for JLU Science and Technology Innovative Research Team. Q.F. and V.V. acknowledge the Thousand Talents program (China).

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