

Metal-driven hierarchical self-assembled zigzag nanoarchitectures with electrical conductivity†

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Quasi-one-dimensional electroactive materials with zigzag shape are fabricated by supramolecular self-assembly of a tetrathiafulvalene (TTF) derivative and metal ions under mild conditions. This is the first time that self-assembled organic conductors with zigzag shape are reported.

One-dimensional (1-D) materials have attracted considerable attention, largely due to their intriguing applications in device fabrication as connections and building blocks for nanocircuits and nanooptoelectronics. In addition to straight wires or tubes, novel geometric configurations or topological structures, such as zigzags, helices, and branches, are supposed to endow unprecedented functionalities, widen the applications, and fit the structural requirements of 1-D materials. Especially, zigzag-shaped nanomaterials with planar additional geometry-driven property tunability are expected to be used as turning building blocks in nanodevices.^{1–3} However, almost all of the research studies focus on inorganic zigzags, which are prepared under harsh conditions, such as extremely high temperatures.^{1–5}

Organic electrical materials with well-defined morphologies provide a link between molecules and solid-state physics, and possess the potential to reach far higher device densities than that is possible with conventional technology. TTF is a π -conjugated molecule that has been exploited as a conductive material and has become the most important electrical building block. The TTF-containing conductors and superconductors are obtained mainly in bulk and film states. Recently, spontaneous, but programmed supramolecular self-assembly has become a promising method to fabricate TTF conductive nanomaterials. Particularly, a series of 1-D nanostructures (e.g. fibers and ribbons) incorporating TTF are created.^{6–12}

Herein we report hierarchical zigzags based on molecular self-assembly of sodium tetrathiafulvalene-tetracarboxylate ($\text{Na}_4(\text{TTF-TC})$, Fig. S1, ESI†) and metal ions under mild conditions. A TTF-TC ligand is selected because: (1) four carboxyl groups on TTF-TC make it highly hydrophilic, allowing molecular

self-assembly in water; (2) carboxyl groups enable rich coordination modes with different kinds of metal ions; (3) TTF is an electron-rich moiety^{1,3} which is favorable for the fabrication of conductive materials; (4) planar TTF tends to adopt aromatic stacking, which is an important driving force for 1-D structures. In addition, metal ion-containing structures might achieve fascinating metallic conductivity and electrochemical redox activity.¹⁴

As shown in the scanning electron microscopy (SEM) image (Fig. 1a), massive zigzag-shaped structures are observed in TTF-TC/Cu(II) (10 mM/10 mM), which are tens of micrometers in length and 40–500 nm in width. These zigzags further assemble into hierarchical fan-shaped structures with the radiation of zigzag branches. As shown in Fig. 1b, the zigzags consist of segments and corners which repeat themselves in a periodically regular mode along the entire micron length of the wires. Although the length of a zigzag segment varies in a certain range, the turning angle of the corners remains approximately 125° (Fig. 1c). The transmission electron microscopy (TEM) image also confirms zigzag formation in TTF-TC/Cu(II) (Fig. 1d).

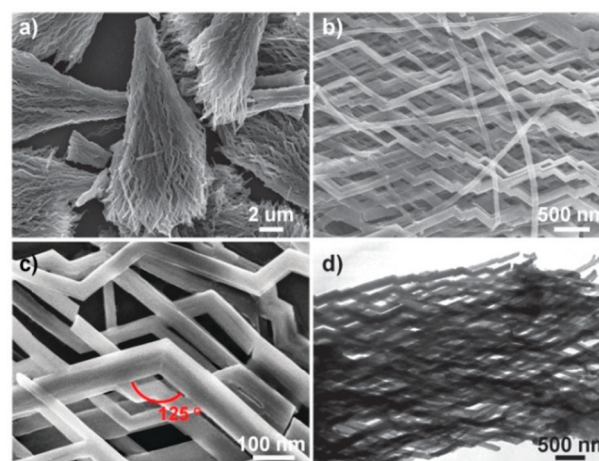


Fig. 1 (a–c) SEM and (d) TEM images of zigzags in the TTF-TC/Cu(II) (10 mM/10 mM) system at 25 °C.

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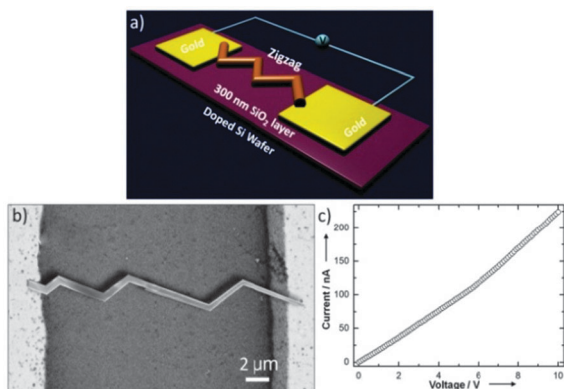


Fig. 2 (a) Scheme and (b) SEM image of electrodes connected by a zigzag, where the silicon wafer acts as a global back-gate; and (c) I - V curve of a TTF-TC/Cu(II) zigzag deposited across a pair of Au electrodes separated by $\sim 20 \mu\text{m}$ at a gate bias of 0 V.

Unlike the reported work, where 1-D conductive materials are obtained in a gel state and are difficult to isolate from solvent, the TTF-TC/Cu(II) zigzags are facilely separated.^{7,15,16} To measure the electrical properties, current-voltage (I - V) measurement is performed on a zigzag bridging two Au electrodes (Fig. 2a and b). The good performance of a I - V curve (Fig. 2c) indicates a good contact between zigzag and Au electrodes. The curve exhibits a nearly linear correlation in which larger current is generated when larger voltage is applied. It is found that the zigzag is a typical metal-like conductor, similar to previously reported 3,4,9,10-perylenetetracarboxylic acid potassium.¹⁷ The conductivity (σ) of a single zigzag is calculated by the following formula:

$$\sigma = \frac{I L}{V S}$$

Here V is the voltage, I is the current, S is the average cross sectional area which is estimated by assuming that the cross section of the zigzag is a square, and L is the length of a zigzag between electrodes. The room temperature conductivity is calculated to be 0.025 S cm^{-1} (ESI[†]), which is high compared to those of TTF-TCNQ fibers.^{7,15,18} This value is comparable with or higher than the electrical conductivities of copper/tetrakis(methylthio) tetrathiafulvalene doped by I_2 .¹⁹ This is the first time that organic conductors with zigzag shapes are prepared. In addition, some peculiar geometric configurations of zigzags, such as Z, Y, U and O-type (closed type), are obtained, which are segments of zigzags (Fig. S2, ESI[†]). They are anticipated to meet the special structural requirements for complicated electronic device fabrication.

In the absence of $\text{Cu}(\text{NO}_3)_2$, $\text{Na}_4(\text{TTF-TC})$ exhibits a high solubility in water and forms a homogeneous solution. Upon addition of Cu(II), $\text{Na}_4(\text{TTF-TC})$ self-assembles into well-defined zigzags which implies the indispensable role of Cu(II) in zigzag formation. Elemental analysis by energy-dispersive spectroscopy (EDS) demonstrates that the TTF-TC/Cu(II) zigzag contains S and Cu, with a S/Cu ratio of roughly 4 : 1, indicating that the TTF-TC/Cu(II) molar ratio is close to 1 : 1 (Fig. S3, ESI[†]). To reveal the intermolecular interactions, photoluminescence (PL), UV-vis, and Fourier transform-infrared spectroscopy (FT-IR) are performed. Fig. 3a shows UV-Vis spectra of zigzag and $\text{Na}_4(\text{TTF-TC})$ in water. The spectrum of $\text{Na}_4(\text{TTF-TC})$ displays two absorption peaks at

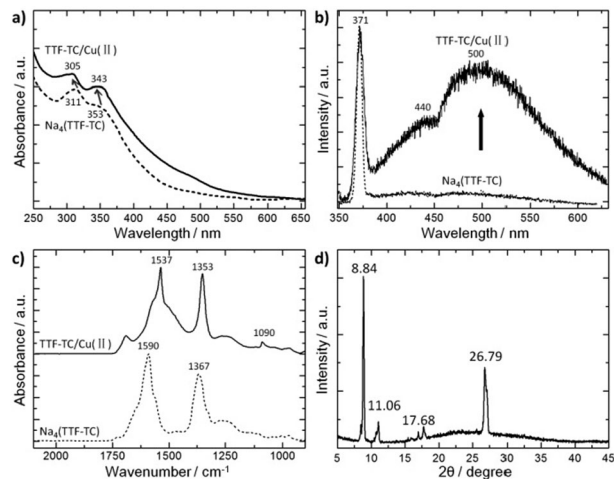


Fig. 3 (a) UV-vis absorption, (b) PL emission ($\lambda_{\text{ex}} = 330 \text{ nm}$) of TTF-TC/Cu(II) zigzag (solid line) and $\text{Na}_4(\text{TTF-TC})$ solution (dashed line). (c) FT-IR of TTF-TC/Cu(II) zigzag (solid line) and $\text{Na}_4(\text{TTF-TC})$ powder (dashed line). (d) XRD profile of zigzag.

311 nm and 353 nm, whereas the absorption maxima are observed at 312 and 369 nm in the case of TTF. These peaks correspond to π - π^* transition of TTF²⁰ and the blue shift comes from the electronic withdrawing effect of a carboxyl group. Upon coordination with Cu(II), the absorption peaks further blue-shift to 305 and 343 nm, respectively. This is a result of π - π interactions of TTF which lead to delocalization of the excited state.⁷ The PL emission spectrum (Fig. 3b) of $\text{Na}_4(\text{TTF-TC})$ gives a sharp fluorescent peak at 371 nm. Additional broad emission bands at 440 and 500 nm are significantly enhanced for the TTF-TC/Cu(II) zigzag, which are ascribed to delocalization of the excited state due to π - π interaction.²¹ Direct evidence for TTF-TC/Cu(II) coordination is obtained by FT-IR (Fig. 3c), which demonstrates Cu(II) coordinates with TTF-TC in a bridging fashion (ESI[†]). It is hence proposed that zigzags are constructed by metal-ligand coordination and π - π stacking.

In order to access the molecular packing within zigzags, X-ray diffraction (XRD) is employed. Sharp diffraction peaks are shown in Fig. 3d, suggesting a highly ordered molecular arrangement. The peaks at $2\theta = 8.84^\circ$ and 17.68° correspond to a d -spacing of 1.0 nm, which is equal to the molecular length of TTF-TC (Fig. 4a). Besides, a small peak of $2\theta = 11.06^\circ$ ($d = 0.80 \text{ nm}$) is also noticed, which is close to the width of a TTF-TC molecule. The peak located at $2\theta = 26.79^\circ$ corresponding to a d -spacing of 0.33 nm originates from π - π stacking.²² Based on these results, a possible molecular model of the TTF-TC/Cu(II) zigzag is proposed. As shown in Fig. 4b, one TTF-TC connects with four metal centers and each metal center interacts with four carboxyl groups, which is similar to the previous work.^{23,24} The TTF-TC/Cu(II) molar ratio is 1 : 1 as suggested by EDS. The distance between adjacent TTF-TC linked by copper ions is periodically 1.0 nm and 0.8 nm as indicated by XRD. The Cu-carboxyl coordination (with bridging mode) ultimately gives rise to supramolecular layers, which stack parallel to each other through π - π interactions with an inter-layer distance of 0.33 nm (Fig. 4c). As in Fig. 4, TTF-TC/Cu(II) zigzags are mainly constructed by the metal-ligand coordination and π - π stacking. An unsolved question still exists concerning how and why the kinked zigzags form. We tried to

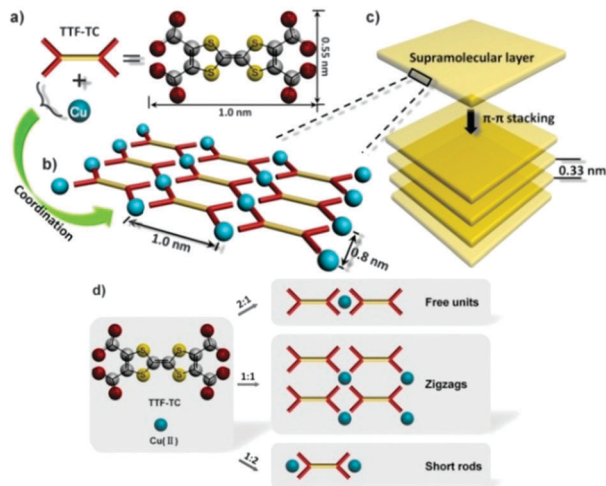


Fig. 4 Schematic illustration of possible molecular packing: (a) TTF-TC molecule; (b) arrangement in a supramolecular layer and (c) inter-layer stacking. (d) Possible mechanism of molecular self-assembly with different TTF-TC/Cu(II) composition.

get hints from superstructure analysis by high-resolution TEM and unfortunately this attempt failed.

It is noted that zigzags are observed only in TTF-TC/Cu(II) with a molar ratio of 1 : 1. When the molar ratio is 2 : 1, the sample remains a stable solution and no aggregates are found. In contrast, when the molar ratio is 1 : 2, short thick micro-rods rather than long zigzags are observed (Fig. S4, ESI[†]). The diameter of micro-rods is $\sim 1 \mu\text{m}$ while most of the rods are shorter than $5 \mu\text{m}$, namely, the aspect ratio is low. EDS analysis of these micro-rods gives a S/Cu ratio of roughly 2 : 1 which indicates that the TTF-TC/Cu(II) molar ratio is 1 : 2 (Fig. S5, ESI[†]). The concept of a *coordination supramolecule* is borrowed to illustrate the self-assembly behavior of TTF-TC/Cu(II) (Fig. 4d).²⁵ It is suggested that the coordination of TTF-TC/Cu(II) (1 : 1) generates coordination supramolecules or a polymer network, in which TTF-TC serves as a multiple ligand with four chelating heads and Cu(II) as linkers. The polymerization degree of coordination supramolecules is highly dependent on the mixing ratio. Long chains and networks can be formed only at a 1 : 1 ligand/metal ratio. In the system of TTF-TC-Cu(II) (2 : 1), metal ions are not sufficient to coordinate TTF-TC into a linear polymer or network. In this case, most of the TTF-TC molecules are in a free state. Consequently, the sample remains a stable solution. In the system of TTF-TC-Cu(II) (1 : 2), however, metal ions are in excess and such deviation from 1 : 1 leads to formation of chain ends, which stops the directional growth of the chain and results in lower aspect-ratio rods.

Moreover, TTF-TC/metal ion self-assembly is proven to be a general route to fabricate zigzags by using different metal ions. The SEM images in Fig. S6 (ESI[†]) provide convincing evidence of zigzags constructed by $\text{Na}_4(\text{TTF-TC})$ and various metal ions including Fe(III), Co(II), Ni(II), and Zn(II). The incorporation of different metal centers is anticipated to endow versatile functionalities to zigzags in diverse subjects such as catalysis and photoluminescence devices.

Hierarchical zigzags with good electrical conductivities are constructed by TTF-TC/Cu(II) self-assembly. The cooperative

effect of molecular interactions (*i.e.* coordinating interaction and π - π stacking) is accounted for zigzags. The metal/ligand ratio plays an important role in zigzag formation and the concept of *coordination supramolecule* is exploited to understand TTF-TC/Cu(II) self-assembly. Compared to nanowires and nanobelts reported previously, zigzags exhibit unique structural characteristics and high conductivity, which may lead to novel applications in miniaturized optoelectronic devices. We hope that this study may shed light on rational design of structural molecular materials, especially 1-D architectures with special geometries.

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