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Metal-Driven Hierarchical Self-Assembled Zigzag Nanoarchitectures with Electrical Conductivity

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Notes.

The authors declare no competing financial interest.

Supporting Information

1. Experimental Section

Materials. Tetrathiafulvalene-tetracarboxylic ester was synthesized as previously reported.[1] A mixture of 27.4 g (0.20 mol) of ethylene trithiocarbonate, 28.4 g (0.20 mol) of dimethyl acetylenedicarboxylate, and 100 ml of toluene was heated at reflux for 4 h. After cooling to room temperature, the yellow solid was precipitated from the solution. The precipitated, dimethyl 1,3-dithiole-2-thione-4,5-dicarboxylate, was dried under vacuum and purified by column chromatography using ethyl acetate–petroleum ether as the eluent. Elemental analysis calcd (%): C, 33.59; H, 2.42; S, 38.43. Found: C, 33.97; H, 2.52; S, 38.68. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.88 (s). A mixture of 10.0 g (0.04 mol) of dimethyl 1,3-dithiole-2-thione-4,5-dicarboxylate, 10.0 g (0.06 mol) of triethyl phosphite, and 80 ml of benzene was refluxed for 10 h. The red solution was concentrated under vacuum to remove benzene. To the residue was added 50 ml of ethanol to precipitate tetrathiafulvalene-tetracarboxylic ester. Recrystallization from methanol gave red-purple products. Elemental analysis calcd (%): C, 38.52; H, 2.77; S, 29.38. Found: C, 38.33; H, 2.76; S, 30.05. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.85 (s).

The corresponding acid, tetrathiafulvalene-tetracarboxylate acid, was obtained by hydrolization of tetrathiafulvalene-tetracarboxylic ester in a NaOH alcoholic solution under reflux for 4 h. The resulting sodium salts were filtered, washed by ethanol and dissolved in 15 mL of water. Neutralization with hydrochloric acid yielded purple solids. These were filtered and dried. Recrystallization from DMF-ether gave purple crystals. Elemental analysis calcd (%): C, 31.57; H, 1.06; S, 33.72. Found: C, 31.59; H, 1.03; S, 33.78.

The stock solution of tetrathiafulvalene-tetracarboxylate sodium salt (Na_4(TTF-TC)) was obtained by neutralization of tetrathiafulvalene-tetracarboxylic acid with 4N of NaOH in water. All other reagents or solvents for syntheses and analyses were of analytical grade and obtained from Alfa Aesar used as received.

Preparation of TTF-TC/Metal Ion Zigzags: The TTF-TC/metal ion zigzag nanostructures were obtained by directly vortex mixing Na_4(TTF-TC) solution with desired amount of metal nitrates solution. In a typical procedure, the stock solutions of 20 mM Na_4(TTF-TC) and 20 mM copper nitrate were mixed in a molar ratio of 1:1 and the resulting mixture was kept at 25 ^{o}C in a thermostatted bath at least three days before further analysis. During this period, some brown precipitates can be observed at the bottom of test tubes. Then the brown precipitates were collected by centrifugation and washed with deionized water for several times.

Preparation of Gold Electrodes: The gold electrodes were prepared by thermal evaporation of gold through a shadow mask on silicon wafer. The silicon wafer was doped with 300 nm thick oxidized silicon on the surface. The gold electrodes were separated by ~20 μm (Figure 2a). To get individual zigzags, a short ultrasound (UP2200HB ultrasound mechine, 5 KHz, 20 W, 30 s) to the zigzag suspension was applied. Then a simple drop casting method was used to transfer the zigzags: a drop of dilute TTF-TC/Cu(Ⅱ) dispersion was poured over the electrodes, and the solvent evaporated at room temperature. This process transferred single and long zigzags onto substrate, some of which bridged across the micro-fabricated gold electrodes.

For the calculation of conductivity, as shown in Figure 2b, the zigzag length L and cross sectional area S are 23.2 μm and 1.94×10^{-15} m^2, respectively. Meanwhile the value of I/V is calculated to be 2.09×10^{-8} S from Figure 2c. Hence the room temperature conductivity of TTF-TC/Cu(Ⅱ) is supposed to be $\sigma_{RT} = 0.025\ S\cdot cm^{-1}$.

Characterization of Zigzag Nanostructures: The zigzag nanostructures were characterized by scanning electron microscopy (SEM, Hitachi S4800, 5 kV, together with energy-dispersive spectroscopy (EDS) measurement), transmission electron microscopy (TEM, JEM-100CX, 100 kV), ultraviolet-visible spectrophotometry (UV-vis, Beijing Purkinje General Instrument Co., LTD. TU-1810), fluorescence spectrophotometer (Edinburgh FLS920), Fourier transform infrared spectrophotometry (FT-IR, NICOLET iN10 MX, Thermo Scientific), and X-ray diffraction (XRD, Rigaku Dmax-2000, Ni-filtered Cu K_{α} radiation). All measurements were conducted under ambient conditions at room temperature.

For SEM and TEM measurements, a drop of suspension was placed on clean silicon sheets or copper grids and then dried freely under ambient conditions. For UV-vis measurements, the precipitates in deioned water were used. Photoluminescent measurements were performed on an Edinburgh FLS920 lifetime and steady-state fluorescence spectrophotometer. For FT-IR, dry powder of precipitates was examined with micro-attenuated total reflection (ATR) method. For XRD measurements, several drops of the suspension were dropped on a clean glass slide, followed by drying in the air.

2. Molecular Structure of tetrathiafulvalene-tetracarboxylate (TTF-TC)

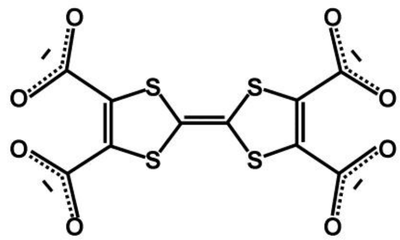

Figure S1. Molecular structure of tetrathiafulvalene-tetracarboxylate, TTF-TC.

3. SEM images of different types of zigzags in TTF-TC/Cu(Ⅱ) system

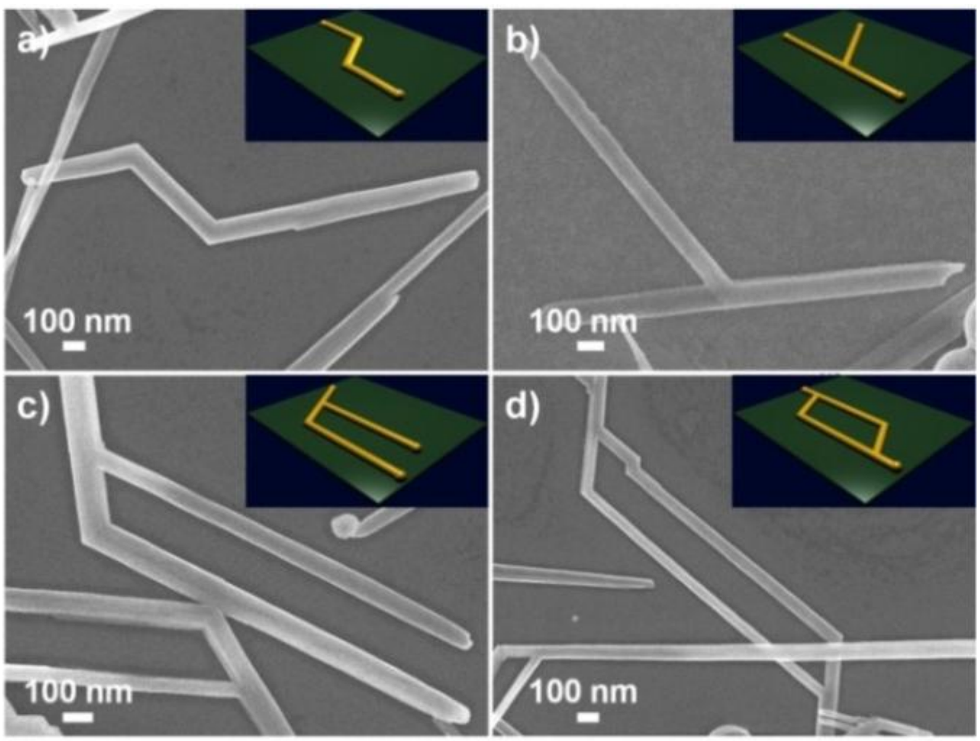

Figure S2. SEM images of different types of zigzags in TTF-TC/Cu(Ⅱ) system: a) Z-type; b) Y-type; c) U-type and d) O-type (closed type).

4. Elemental Analysis of Self-assembled Zigzags of TTF-TC/Cu(Ⅱ) 10 mM/10 mM System

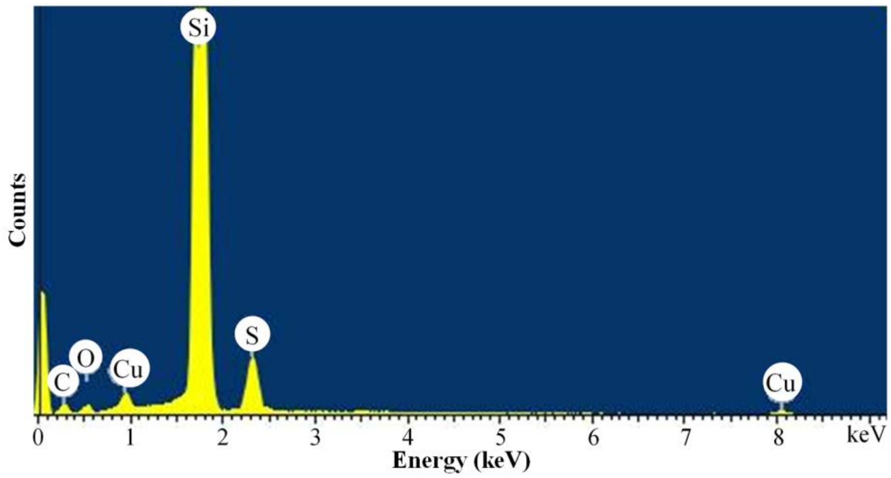

Figure S3. EDS result of self-assembled zigzags from TTF-TC/Cu(Ⅱ) 10 mM/10 mM mixture. The area integration shows the atomic compositions of element S and Cu are 7.13 and 1.62, respectively, which demonstrates that in the zigzag, the molar ratio of S to Cu is approximately 4:1 and TTF-TC to Cu(Ⅱ) is close to 1:1.

5. Interpretation of Metal-Ligand Coordination by FT-IR Spectra.

Direct evidence for TTF-TC/Cu(Ⅱ) coordination was obtained by Fourier transform infrared (FT-IR). For the FT-IR spectra of carboxyl acid, there is a single band around 1700 cm^{-1} due to the anti-symmetric C=O stretching mode. When carboxyl group interacts with metal, this singlet disappears and splits into a doublet, corresponding to the anti-symmetric and symmetric stretching modes, respectively. According to the literatures, the frequency separation $\Delta\nu=\nu_{as(COO)} - \nu_{s(COO)}$ can elucidate the coordination modes of metal carboxylates.[2, 3] Generally, monodentate complexes exhibit $\Delta\nu$ values much larger than that of the corresponding ionic structure (i.e.,

Na_4(TTF-TC) as shown in Figure 4). Bidentate chelating complexes exhibit $\Delta\nu$ values significantly smaller than the ionic values, and bidentate bridging complexes have values less than, but close to, the ionic value.

In Figure 4, the IR spectrum of Na_4(TTF-TC) exhibits two absorbance bands at 1590 and 1367 cm^{-1}, corresponding to C=O anti-symmetric and symmetric stretching modes. With the incorporation of Cu(Ⅱ), these two peaks shift to 1537 and 1353 cm^{-1}, respectively. The frequency separation of TTF-TC/Cu(Ⅱ) 175 cm^{-1} (1537－1353), which is less than 223 cm^{-1} (1590－1367) of Na_4(TTF-TC), indicate that the Cu(Ⅱ) binds to carboxyl group in a bridging fashion. The new peak at 1090 cm^{-1} in TTF-TC/Cu(Ⅱ) system, is ascribed to $Cu(NO_3)_2$.

6. Self-assembled Zigzags in the Mixture of Na_4(TTF-TC)/$Cu(NO_3)_2$ (10 mM/20 mM).

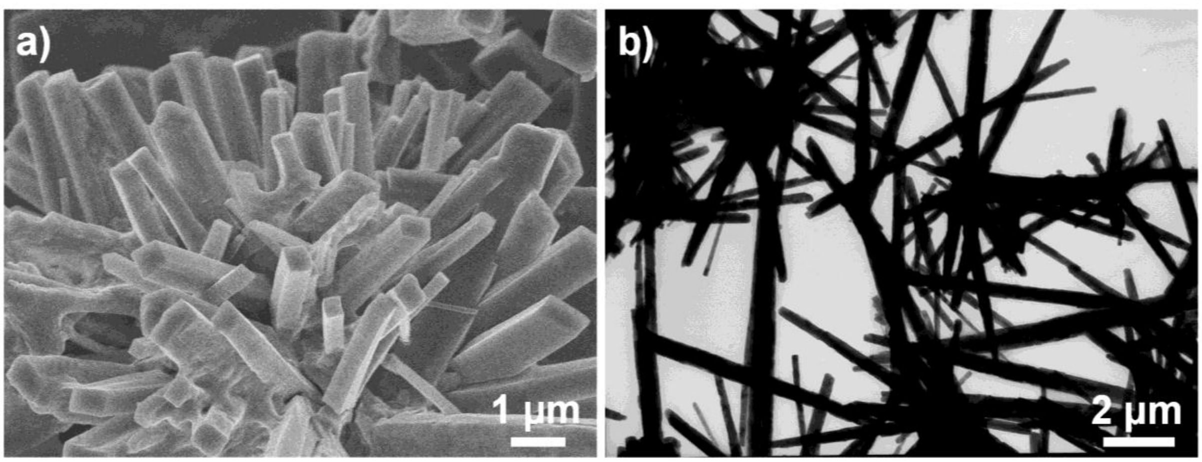

Figure S4. a) SEM and b) TEM images of zigzag structures in the mixture of 10 mM Na_4(TTF-TC) and 20 mM $Cu(NO_3)_2$ at 25 ^{o}C.

7. Elemental Analysis of Self-assembled Zigzags of TTF-TC/Cu(Ⅱ) 5mM/ 10 mM System

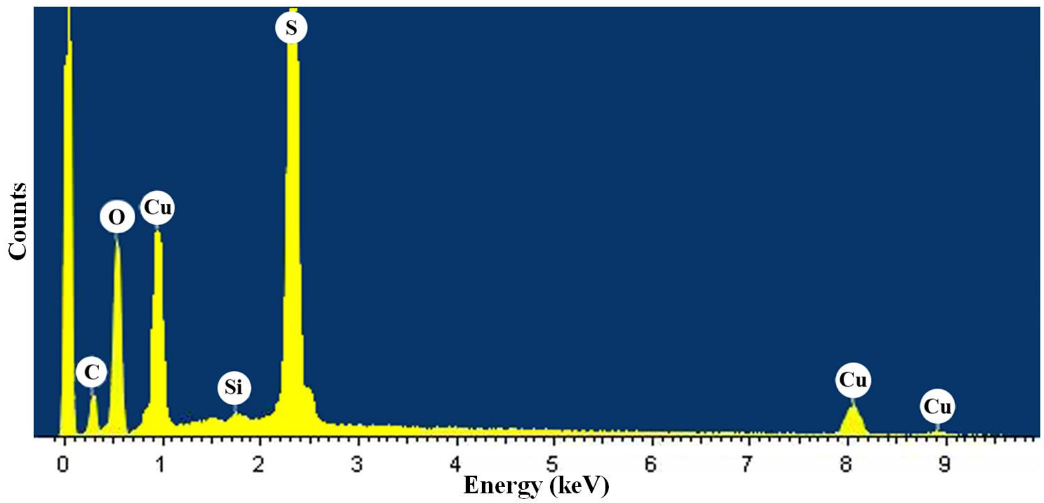

Figure S5. EDS result of self-assembled zigzags from TTF-TC/Cu(Ⅱ) 10 mM/5 mM mixture. The area integration shows the atomic compositions of element S and Cu are 7.13 and 1.62, respectively, which demonstrates that in the zigzag, the molar ratio of S to Cu is approximately 4:1 and TTF-TC to Cu(Ⅱ) is close to 1:1.

8. SEM Images of Self-assembled Zigzags in Na_4(TTF-TC)/Metal Ions.

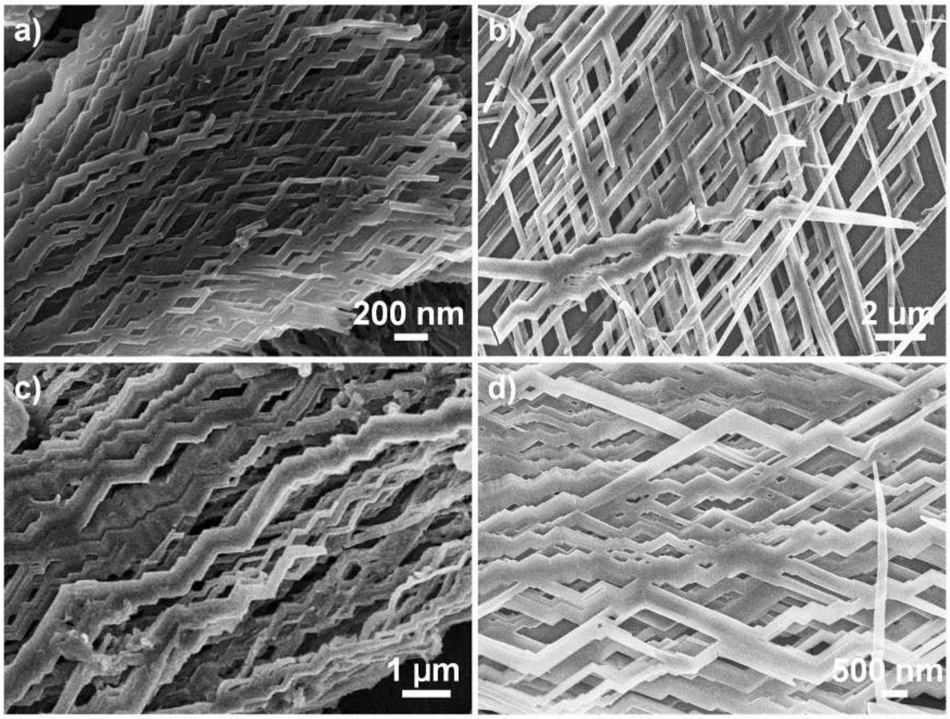

Figure S6. SEM images of self-assembled zigzags in Na_4(TTF-TC) solution in the presence of: (a) Fe(III), (b) Co(II), (c) Ni(II), and (d) Zn(II). The concentration of Na_4(TTF-TC)/metal ion mixture is 10 mM/10 mM.

9. References

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