Electronic Supplementary Information for "Macroscopically Oriented Hierarchical Structure of the Amphiphilic Tetrathiafulvalene Molecule"

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Synthesis of amph-7TTF14

Compound 2: The mixture of compound 1 (1.33 g, 5.0 mmol), tetradecanoic acid (2.40 g, 10.5 mmol), DMAP (0.12 g, 1.0 mmol), and DCC (2.38 g, 11.5 mmol) and dried CH_2Cl_2 (50 mL) were stirred at room temperature for 12 h. The solvent was removed by rotating evaporation. The yellow solid (2.02 g) was obtained by column chromatography with mixture of PE and MC as the eluant. Yield: 58.8%. ^{1}H-NMR: 7.76 (dd, J = 6.3, 3.2 Hz, 2H), 7.57 (dd, J = 6.4, 3.2 Hz, 2H), 2.75 (t, J = 7.2 Hz, 4H), 1.87 (quint, J = 7.2 Hz, 4H), 1.51 (m, 4H), 1.45-1.16 (m, 36H), 0.88 (t, J = 6.8 Hz, 6H). ^{13}C-NMR: 210.47, 170.48, 136.27, 131.39, 127.68, 126.81, 121.25, 33.94, 31.93, 29.68, 29.65, 29.64, 29.60, 29.46, 29.36, 29.22, 29.20, 25.03, 22.69, 14.11. UV: 272.38nm, 329.47nm, 372.65 nm. HRMS calcd for $C_{39}H_{58}O_4S_3$ 686.35, found $(M + H)^+$ 687.33. Anal. Calcd for $C_{39}H_{58}O_4S_3$: C, 68.2; H, 8.5; S, 14.0. Found: 68.3%, 8.6%, 14.1%.

Compound 3: Mercury (II) acetate (1.53 g, 4.80 mmol) was added to a solution of compound **2** (1.32 g, 1.92mmol) in CH_2Cl_2. After stirring at room temperature for 1 h, the mixture became white from orange. The mixture was filtered through a celite, and the filtrate was washed with water (3 × 100 ml), dried with Na_2SO_4, the crude product was obtained after evaporating the solvent. White solid (1.21 g) was obtained by further purification of column chromatography. Yield: 93.9%. ^{1}H-NMR: 7.74 (dd, J = 6.4, 2.8 Hz, 2H), 7.57 (dd, J = 6.4, 3.2 Hz, 2H), 2.75 (t, J = 7.2 Hz, 4H), 1.87 (quint, J = 7.2 Hz, 4H), 1.51 (m, 4H), 1.45-1.16 (m, 36H), 0.88 (t, J = 6.4 Hz, 6H). ^{13}C-NMR: 187.45, 170.54, 138.43, 127.44, 126.42, 123.88, 120.99, 33.95, 31.91, 29.67, 29.65, 29.64, 29.60, 29.45, 29.34, 29.22, 29.18, 25.03, 22.68, 14.10. UV: 248.04nm, 303.42nm. HRMS calcd for $C_{39}H_{58}O_5S_2$ 670.37, found $(M + H)^+$ 671.35. Anal. Calcd for $C_{39}H_{58}O_5S_2$: C, 69.8; H, 8.7; S, 9.6. Found: 69.6%, 8.8%, 9.8%.

amph-7TTF14: The mixture of compound **3** (0.80 g, 1.19 mmol) and **4** (0.80 g, 1.63 mmol) and triethyl phosphate was heated to 120 ºC for 4 h. After the solution was cooled, triethyl phosphate was removed in the vacuum oven. Column chromatography was used to separate the product as a yellow solid (0.42 g). Yield: 31.7%. ^{1}H-NMR: 7.60 (dd, J = 6.5, 3.3 Hz, 2H), 7.45 (dd, J = 6.4, 3.2 Hz, 2H), 3.70-3.63 (m, 16H), 3.54 (t, J = 4.0 Hz, 4H), 3.37 (s, 6H), 3.03 (t, J = 6.6 Hz, 4H), 2.75 (t, J = 7.4 Hz, 4H), 1.88 (quint, J = 7.6, Hz, 4H), 1.51 (m, 4H), 1.45-1.21 (m, 36H), 0.88 (t, J = 6.8 Hz, 6H). ^{13}C-NMR: 170.58, 137.22, 134.22, 129.00, 128.01, 126.86, 126.82, 120.79, 114.14, 71.94, 70.62, 70.60, 70.57, 70.05, 59.03, 35.56, 34.00, 31.93, 29.71, 29.68, 29.66, 29.65, 29.54, 29.37, 29.30, 29.25, 25.07, 22.69, 14.11. UV: 251.03nm, 320.71nm, 385.04nm. LC-MS calcd for $C_{56}H_{88}O_{10}S_6$ 1112.5, found $(M + H)^+$ 1113.9. Anal. Calcd for $C_{56}H_{88}O_{10}S_6$: C, 60.4; H, 8.0; S, 17.3. Found: 60.4%, 8.2%, 17.2%.

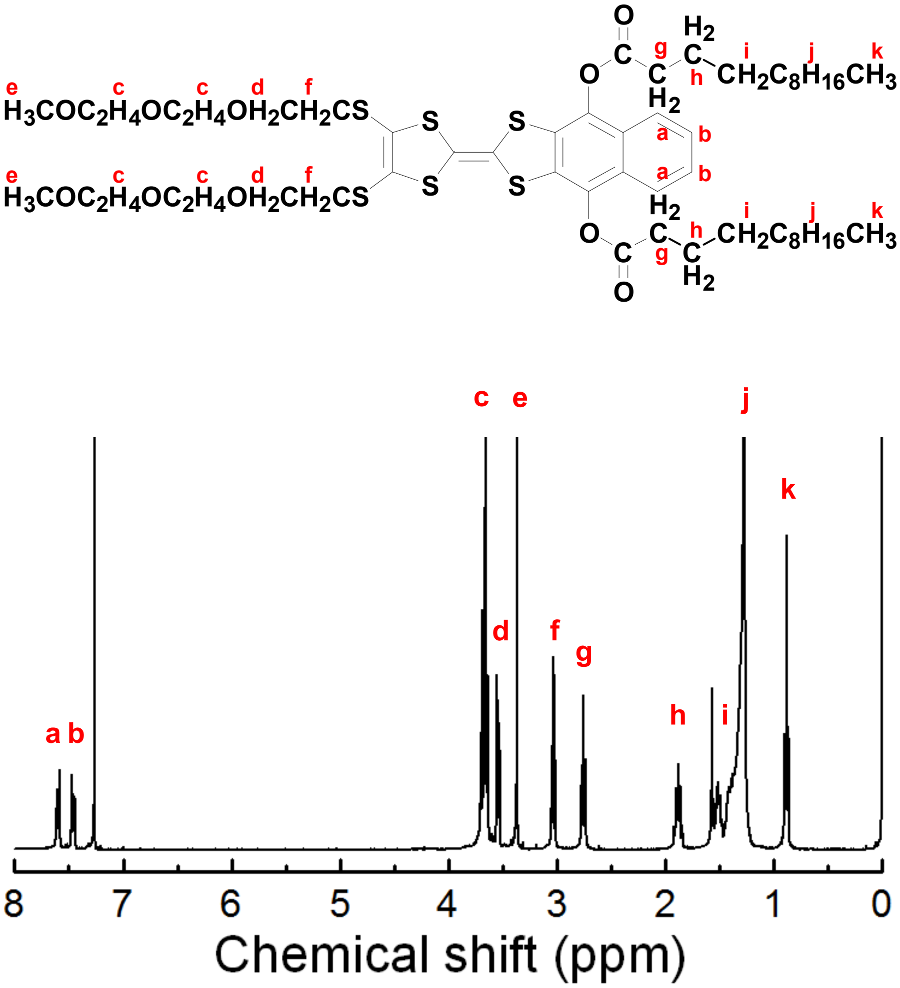

Fig. S1 The ^{1}H NMR spectrum of amph-7TTF14 in $CDCl_3$.

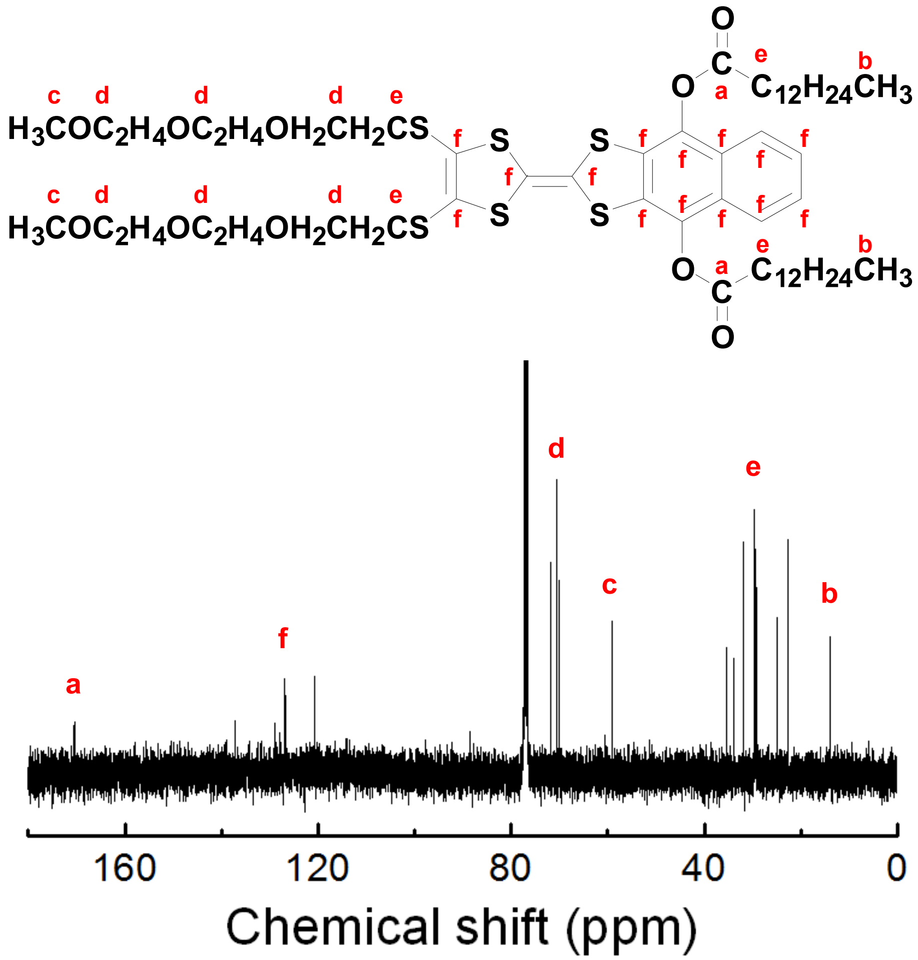

Fig. S2 The ^{13}C NMR spectrum of amph-7TTF14 in $CDCl_3$.

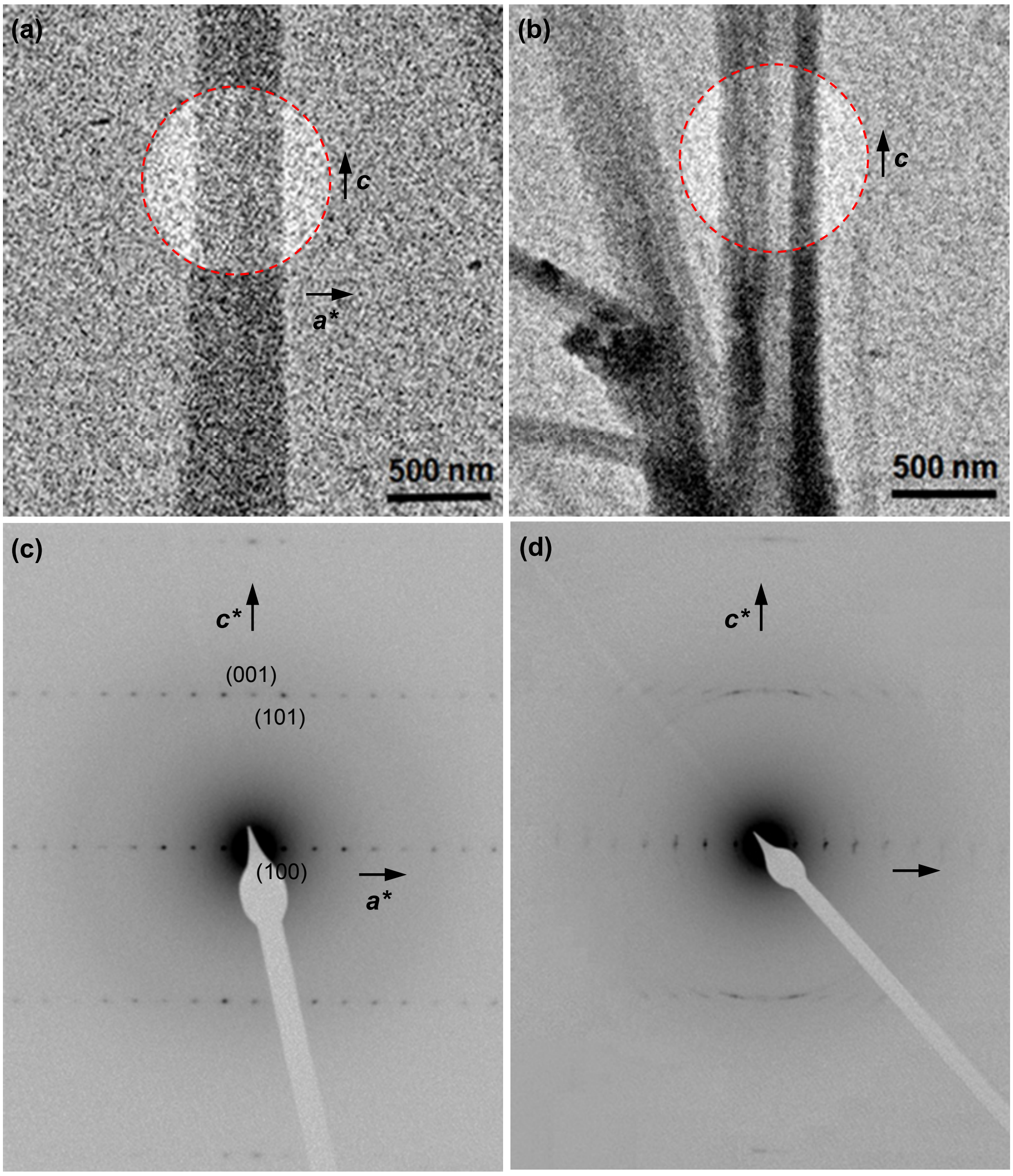

Fig. S3 Bight-field TEM images of the self-assembled amph-7TTF14 (a) flat and (b) scrolled ribbons with applying a low-dose technique. The arrow is pointing along the long axis of the flat ribbons (*c*-axis). SAED patterns from the circled areas of the bright-field TEM images in Figure (c) S3a and (d) S3b, respectively.

The optical properties of the amph-7TTF14 compound are investigated using UV-Vis spectroscopy (Fig. S4). The maximum absorption peak of the amph-7TTF14 compound in chloroform appears at around 384 nm and the optical band gap energy (E_g) is 2.73 eV from the absorption tail. The optical band gap energy of the amph-7TTF14 compound is higher than that of pentacene (2.2 eV), suggesting a better air stability.

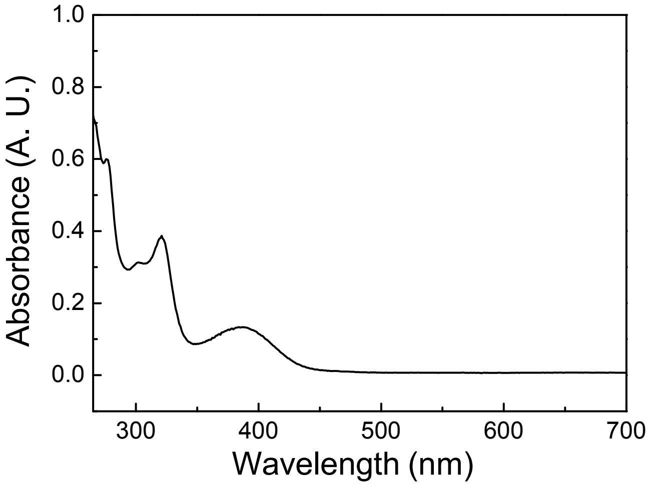

Fig. S4 UV-Vis spectrum of amph-7TTF14 in $CHCl_3$.

The amph-7TTF14 compound is chemically oxidized in dichloromethane solution (ca. 2 × 10^{-5} M) by a stepwise addition of $FeCl_3$ to explore the electronic transferring behavior and then the variation of UV-Vis absorption spectra is also monitored (Fig. S5). The absorption bands at 469 and 807 nm newly appear concomitantly and the intensity and area increase as oxidation proceeds. The absorption at 469 nm is ascribed to the intramolecular electron transfer of the radical cation, while the absorption band at 807 nm is due to the intermolecular electron transfer of the dicationic π-dimers.

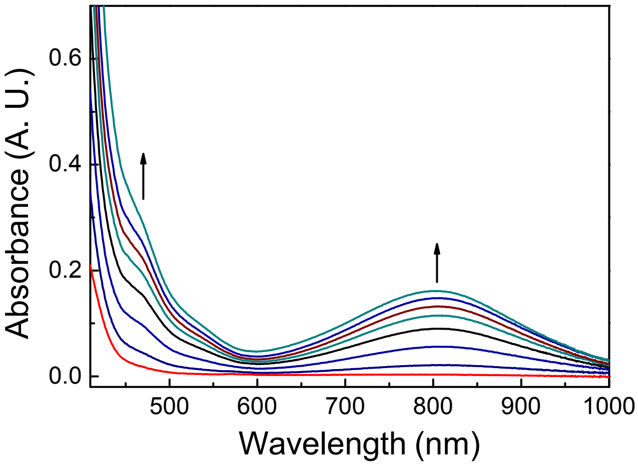

Fig. S5 UV-Vis absorption spectra of amph-7TTF14 (2×10^{-5} M) in dichloromethane solutions with addition of $FeCl_3$.

The mechanically oriented amph-7TTF14 film is examined using linear polarized UV-Vis spectroscopy (Fig. S6). Absorption maximum of the amph-7TTF14 solid film is red-shifted, which is slightly different from that of amph-7TTF14 in solution. It may be attributable to the π-π interactions between TTF groups in the self-assembled amph-7TTF14 columns. As increasing the angle between the polarizer and SD from 0° to 90°, the absorption intensity at 409 nm increases, indicating that the long axis of TTF group is perpendicular to the fiber direction. This conclusion is well matched with the results obtained from 2D WAXD, SAED and POM.

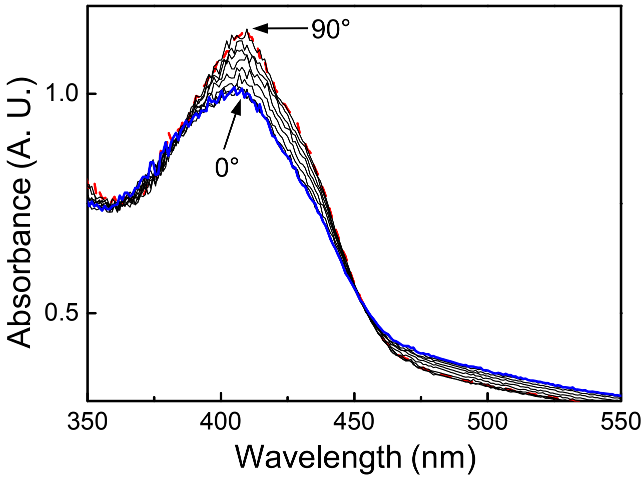

Fig. S6 Polarized UV-Vis spectra of the uniaxially oriented amph-7TTF14 film with the polarized radiation from 0 to 90° with respect to the long axis of columns.

The electrochemical property of the amph-7TTF14 compound is also studied using CV. The CV measurements are performed in a dry dichloromethane solution of Bu4NBF4 (0.1 M) with a scan rate of 100 mV·s^{-1} at room temperature (Fig. S7). The amph-7TTF14 compound exhibit two irreversible single-electron oxidation peaks at 0.89 and 1.20 V which correspond to the radical cations and dications, respectively. Both oxidation potentials of amph-7TTF14 are higher than those of the pristine TTF molecules presumably due to the electron-withdrawing ester linkages.

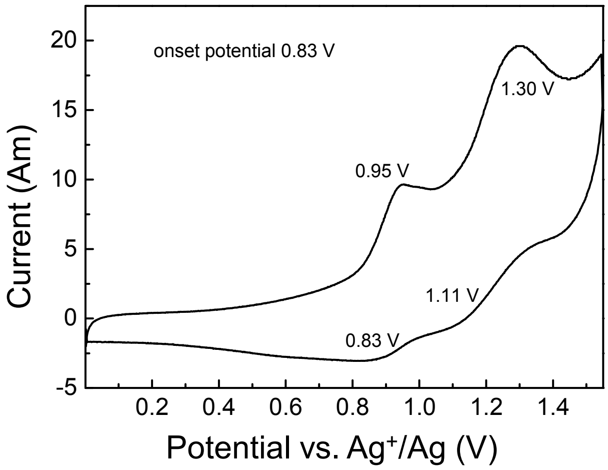

Fig. S7 CV of amph-7TTF14 in a solution of Bu_4NBF_4 (0.1 M) in water-free dichloromethane with a scan rate of 100 mV·s^{-1} at RT.