

Electronic Supplementary Information

Unusual tubular organization with crystal stacks from new cyclic thiophene compound †

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Experimental section

General All reagents and chemicals were purchased from Aldrich, Alfa and used as received. Solvents and other common reagents were obtained from the Beijing Chemical Plant. Melting points were measured with a WRR melting point apparatus. ¹H NMR spectra were obtained on a Bruker DMX-300 NMR Spectrometer using tetramethylsilane as internal standard. MS spectra (MALDI-TOF-MS) were determined on Micromass GCT-MS spectrometer. Elemental analyses were performed on a Carlo Erba model 1160 elemental analyzer. Thermal gravimetric analysis (TGA) measurements were carried out on a TA SDT 2960 instrument under a dry nitrogen flow, heating from room temperature (R.T.) to 500 °C, with a heating rate of 10 °C /min. The products on the substrate were characterized by scanning electron microscopy (SEM, Hitachi S-4300, 10–15 kV).

Synthetic Details

3,3'-Dithienyl Sulfide (1). This compound was synthesized according to the literature procedure.¹ A solution of 3-thienyllithium was prepared at $-78\text{ }^{\circ}\text{C}$ from 16.3 g (0.1 mol) of 3-bromothiophene in 100 mL absolute ether and 40 mL 2.5 M *n*-BuLi (0.1 mol). In small portions of 15.6 g (0.049 mol) of $(\text{C}_6\text{H}_5\text{SO}_2)_2\text{S}$ was added. After stirring at $-78\text{ }^{\circ}\text{C}$ during 2 h, the reaction mixture was allowed to warm and at $0\text{ }^{\circ}\text{C}$, 10 mL water was added. The lithium sulfinate was filtered and washed with ether, the combined organic layers were extracted with water, dried with MgSO_4 , concentrated and the residue was distilled yielding the sulfide **1**. Yield: 71%; MS: $m/z = 198$; ^1H NMR (δ/ppm , CDCl_3): 7.60 (m, 2H), 6.92 (s, 2H), 6.71 (m, 2H); Anal. Calcd for $\text{C}_8\text{H}_6\text{S}_3$: C, 48.45; H, 3.05; Found: C, 48.38; H, 3.04.

2,2'-Dibromo-3,3'-dithienyl Sulfide (2). NBS (2.99 g, 16.8 mmol) was added to a solution of compound **1** (1.38g, 7 mmol) in a mixture of chloroform and acetic acid (50:50 v/v, 15 mL) in portions during 10 min at $25\text{ }^{\circ}\text{C}$. The mixture was stirred for 30 min. After being diluted with water, the mixture was extracted with chloroform. The organic layers were combined, washed with 10% sodium thiosulfate solution ($2 \times 15\text{ mL}$) and water (30 mL), and dried (MgSO_4). The solvent was removed and the residue was purified by column chromatography over silica gel eluting with hexane to give yellow oil as product **2**. Yield: 85%; MS: $m/z = 356$; ^1H NMR (δ/ppm , CDCl_3): 7.40 (d, 2H), 6.60 (d, 2H); Anal. Calcd for $\text{C}_8\text{H}_4\text{Br}_2\text{S}_3$: C, 26.98; H, 1.13; Found: C, 26.81; H, 1.30.

2,2'-Bis(tributylstannyl)-3,3'-dithienyl Sulfide (3). This compound was synthesized according to the literature procedure.² 2.5 M *n*-BuLi (1.5 mL, 3.6 mmol) was added dropwise to a solution of compound **2** (0.53 g, 1.5 mmol) in THF (40 mL) at $-78\text{ }^{\circ}\text{C}$ with stirring. After stirring for 1 h at $-78\text{ }^{\circ}\text{C}$, tri-*n*-butyltin chloride (1.17 g, 3.6 mmol)

was added. The reaction mixture was stirring at $-78\text{ }^{\circ}\text{C}$ for additional 3 h and was then gradually warmed to room temperature and stirred overnight. The clear solution was diluted with n-hexane (200 mL) and washed with water (20 mL). The organic layer was dried over MgSO_4 , and the solvents were concentrated on a rotary evaporation. The residue was collected as compound **3** without any purification.

Compound A. $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (70 mg, 0.1 mmol), compound **2** (1.153 g, 4.25 mmol), compound **3** (3.298 g, 4.25 mmol) were put into a three-neck flask. The mixture was flushed with argon for 10 min and then 20 mL toluene was added. At the protection of argon, the reactant was heated to reflux for 24 h. The mixture was cooled to room temperature and was diluted with 50 mL water. Then the mixture was washed with aqueous potassium fluoride solution (5%, 20 mL), and water (20 mL). The organic layers were dried over MgSO_4 and the solvents were concentrated on a rotary evaporation. The residue was purified by column chromatography over silica gel eluting with hexane to give the compound **A** as pale white powder. Yield: 21%; Mp: 263–264 $^{\circ}\text{C}$; MS: $m/z = 392$; ^1H NMR (δ/ppm , CDCl_3): 7.34 (d, 4H), 6.92 (d, 4H); ^{13}C NMR (δ/ppm , CDCl_3): 130.7, 130.5, 125.0, 124.3; Anal. Calcd for $\text{C}_{16}\text{H}_8\text{S}_6$: C, 48.95; H, 2.05; Found: C, 49.06; H, 2.19.

Sample Preparation Methods

The micro-sticks and macroscopic tubular crystals of compound **A** were synthesized through a simple solution procedure. In a typical preparation, 100 μL DMF solutions [$(2\text{--}10) \times 10^{-3}\text{ M}$] of compound **A** was injected into 10 mL of continuously stirred methanol at room temperature ($25\text{ }^{\circ}\text{C}$), then the micro-sticks were obtained. When 100 μL DMF solutions [$(35\text{--}50) \times 10^{-3}\text{ M}$] of compound **A** was dropped into 10 mL of methanol and lay-aside about 2 days, discrete macroscopic tubular crystals were found in the bottom of solution.

For the characterization of scanning electron microscopy observation, the solution including micro-sticks was deposited onto silicon wafer substrate. Besides, the macroscopic crystals were transferred to the silicon wafer using fine pin smearing with Vaseline and adhered to carbon adhesive.

Thermal property characterization

The thermal property of the collected crystal tubes was evaluated by TGA (Fig. S4). Thermal decomposition of A starts at about 240 °C, and decomposition temperature is recorded at 291 °C. The weight loss starts at 140 °C is believed to be the solvent (DMF) contained in the crystals. The results indicate that the thermal stability of the tubular crystals is very good.

References

- 1 F. De Jone and J. M. Janssen, *J. Org. Chem.*, 1971, **36**, 1645–1648.
- 2 Y. Wei, Y. Yang and J. M. Yeh, *Chem. Mater.*, 1996, **8**, 2659–2666.

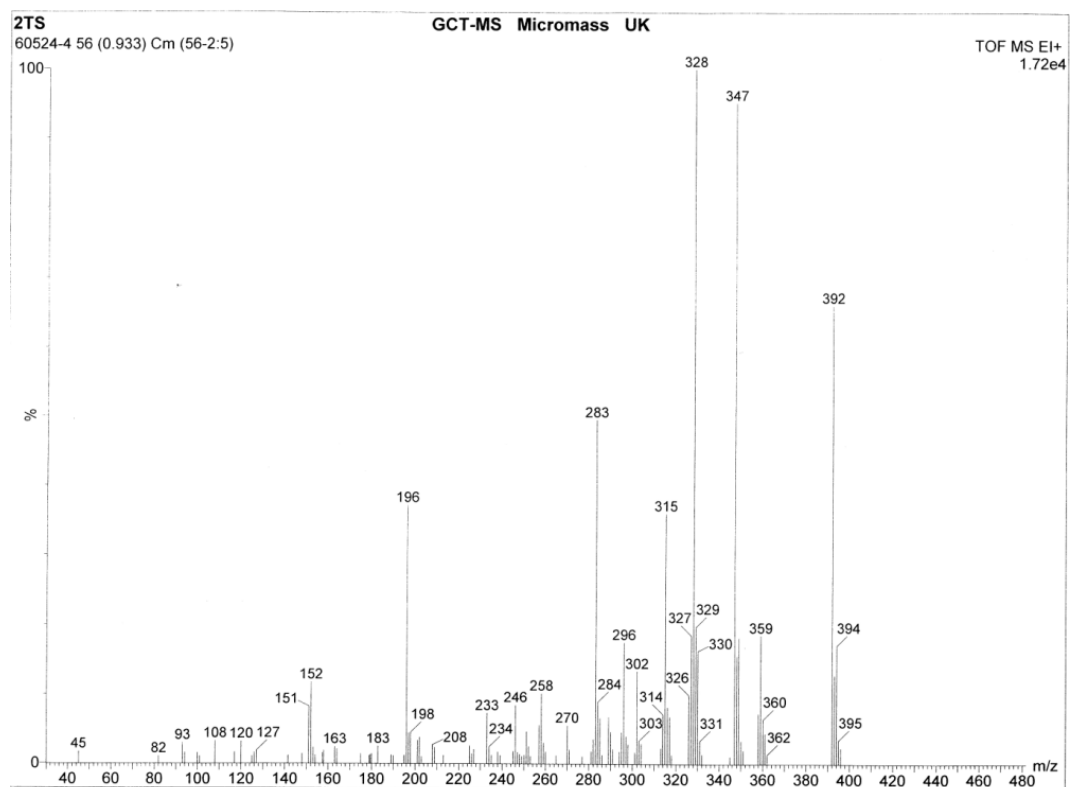


Fig. S1 EIMS of compound A.

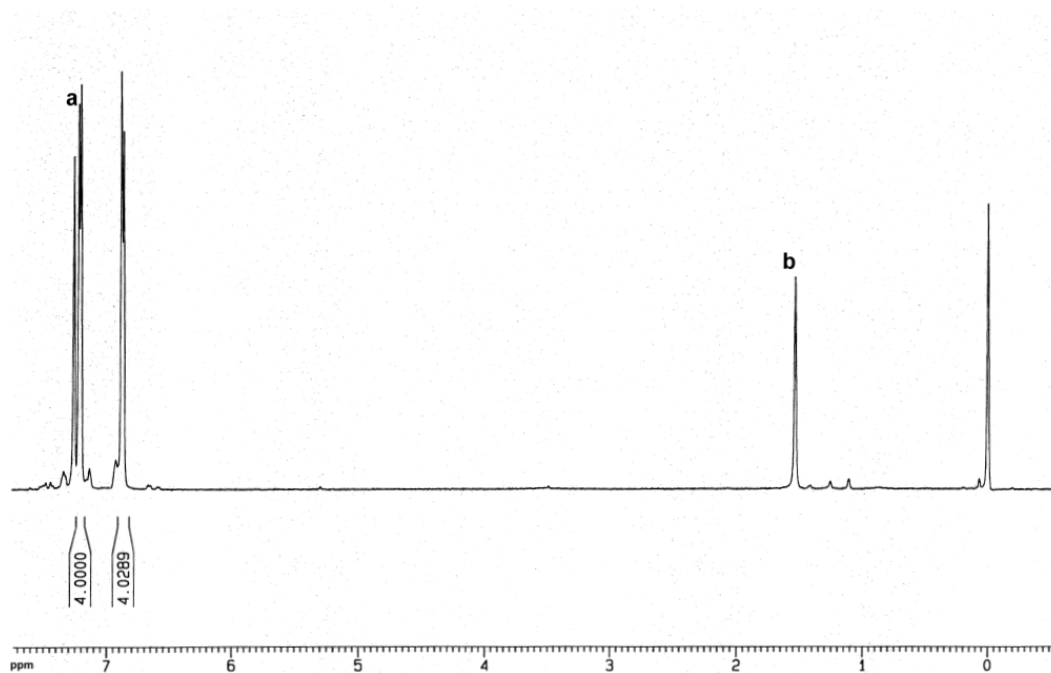


Fig. S2 The ^1H NMR spectra of compound A (a = CDCl_3 , b = H_2O).

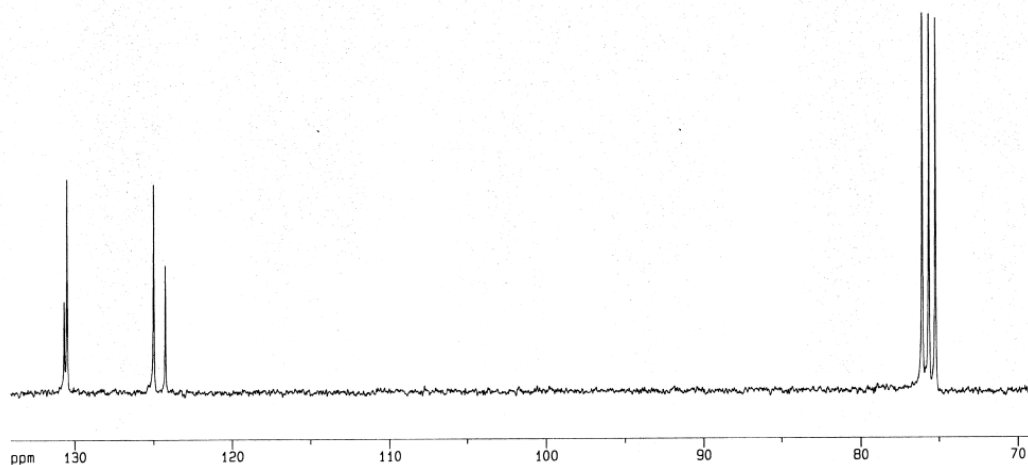


Fig. S3 The ^{13}C NMR spectra of compound A in CDCl_3 .

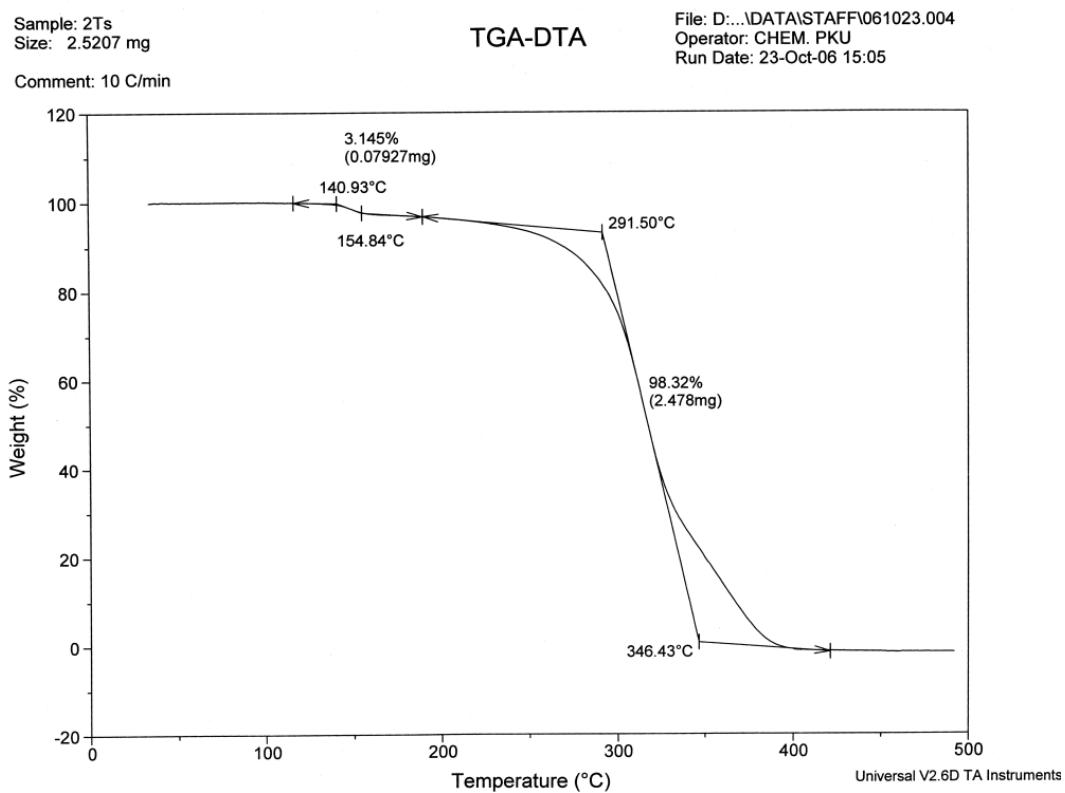


Fig. S4 TGA plot of the compound A with heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under an inert atmosphere.

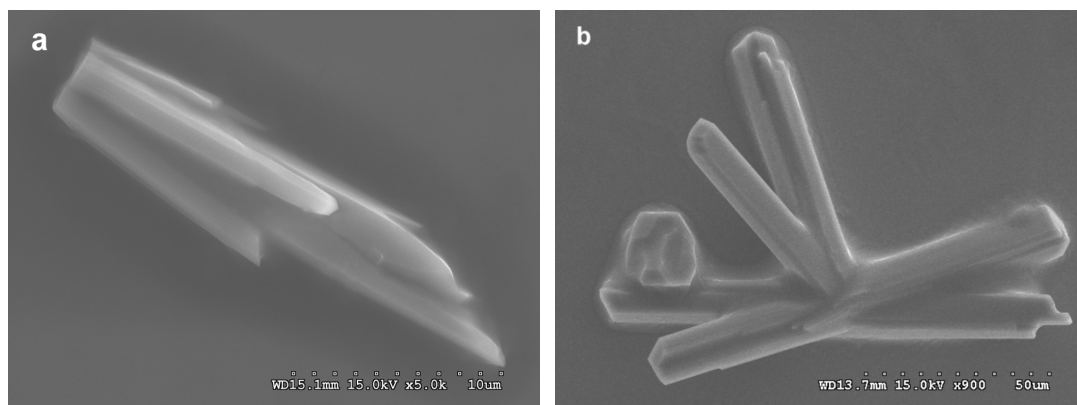


Fig. S5 The representative SEM images of samples which deposited solutions onto silica substrates. The solutions were obtained from injecting 100 μL DMF solutions with different concentrations: (a) 20 and (b) 25×10^{-3} M into 10 mL stirred methanol for 10 min and stored for about 5 h.