Electronic Supplementary Material (ESI) for CrystEngComm.


# Supporting Information

## Regulatable morphology and self-assembly of one-dimensional luminescence crystals based on alkyl-fluoro-substituted dithienophenazines

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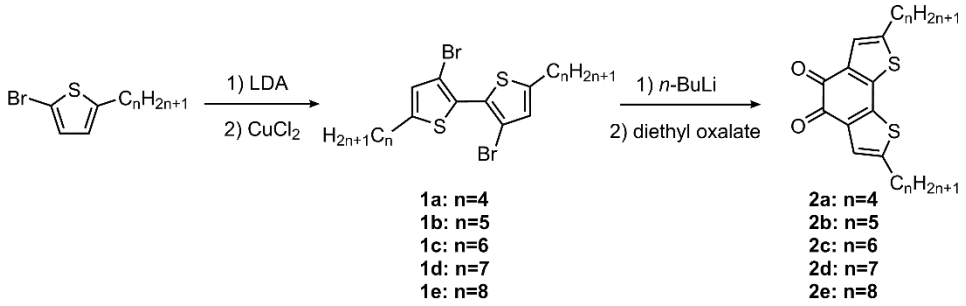
## Contents:

## 1. Synthesis and Characterization of Intermediate Products

The key intermediates of **1** and **2** prepared from alkyl substituted thiophenes are presented in **Scheme S1**.




**Scheme S1.** Synthesis procedure of compounds 1a-e and 2a-e.

*Synthesis of* **1a**: *n*-Butyllithium (20.8 mL, 2.4 M in hexane, 50 mmol) was added dropwise to the mixture of diisopropylamine (8.6 mL, 60 mmol) in anhydrous THF (80 mL) at 0°C under nitrogen gas. The mixture was stirred at 0°C for 1 hour. Then the mixture of 2-bromo-5-butylthiophene (9.8 g, 45 mmol) in anhydrous THF (10 mL) was added dropwise to the freshly prepared LDA at -78°C. The mixture was stirred at -78°C for 1 hour and then the temperature was allowed to rise slowly to -20°C for 1 hour and a dark red solution was observed. $CuCl_2$ (6.7 g, 50 mmol) powder was added in batches to the reaction below -78°C under nitrogen gas, and the mixture was stirred overnight at -78°C to room temperature. The dark brown mixture was quenched with saturated aqueous $NH_4Cl$ and a suspension was obtained. Aqueous HCl (20%) was added to the mixture until dissolution. The solution was extracted with ethyl ether (100 mL×3) and the combined organic layers were dried over $MgSO_4$. After removing the solvent, the residue was purified by column chromatography using petroleum ether as the eluent, affording white solid (6.6 g) in 67% yield. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 6.75 (s, 2H), 2.79 (t, $J$ = 7.7 Hz, 4H), 1.67 (dt, $J$ = 15.3, 7.6 Hz, 4H), 1.51 – 1.35 (m, 4H), 0.95 (t, $J$ = 7.4 Hz, 6H). MS: m/z 436.30 $[M]^+$ (calcd: 436.26).

*Synthesis of* **1b**: The synthesis was similar to that of compound **1a** but use 2-bromo-5-pentylthiophene as starting material. Colourless oil (yield: 65%). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 6.75 (s, 2H), 2.78 (t, $J$ = 7.7 Hz, 4H), 1.79-1.61 (m, 4H), 1.46-1.30 (m, 8H), 0.92 (t, $J$ = 7.0 Hz, 6H). MS: m/z 464.19 $[M]^+$ (calcd: 464.32).

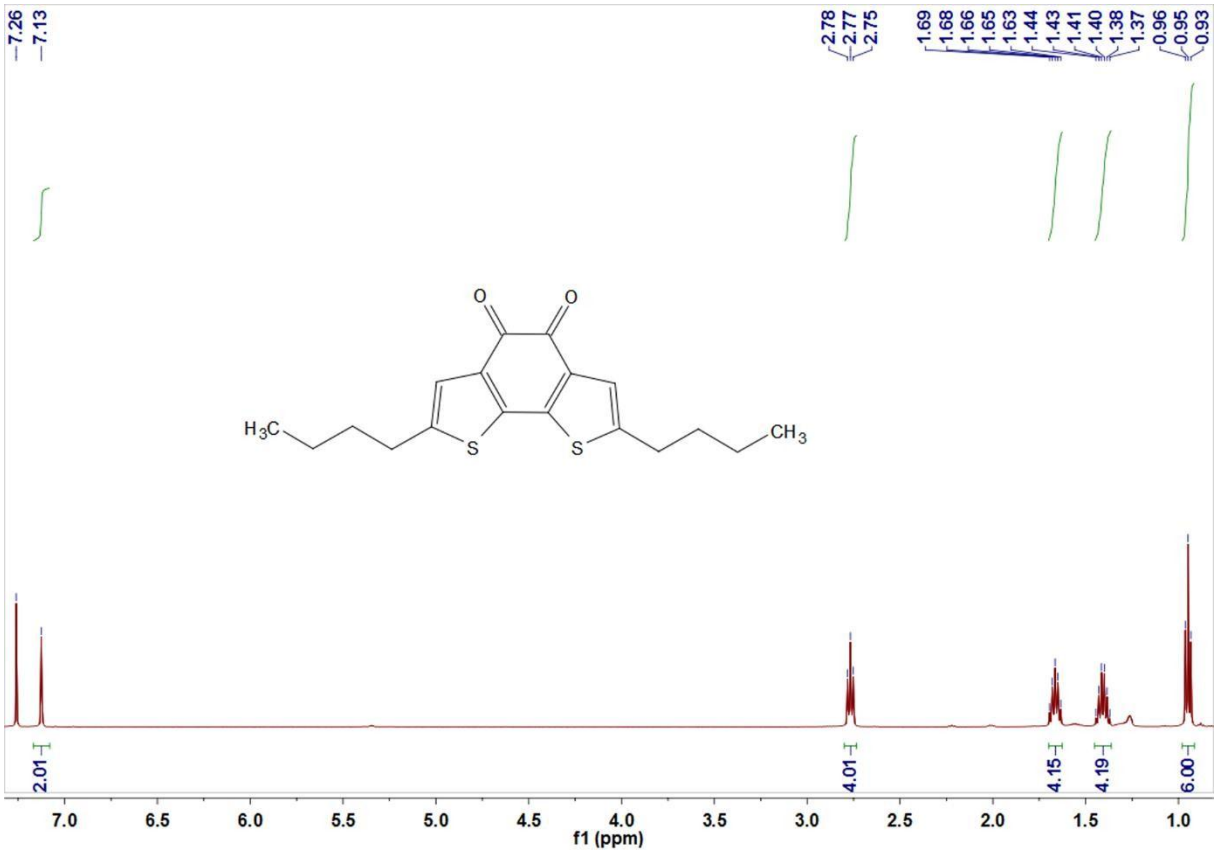
*Synthesis of* **1c**: The synthesis was similar to that of compound **1a** but use 2-bromo-5-hexylthiophene as starting material. White solid (yield: 61%). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 6.74 (s, 2H), 2.77 (t, $J$ = 7.7 Hz, 4H), 1.74-1.62 (m, 4H), 1.44-1.27 (m, 12H), 0.90 (t, $J$ = 6.2 Hz, 6H). MS: m/z 492.20 $[M]^+$ (calcd: 492.37).

*Synthesis of* **1d**: The synthesis was similar to that of compound **1a** but use 2-bromo-5-heptylthiophene as starting material. Colourless oil (yield: 58%). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 6.75 (s, 2H), 2.78 (t, $J$ = 7.7 Hz, 4H), 1.76-1.62 (m, 4H), 1.43-1.25 (m, 16H), 0.90 (t, $J$ = 6.9 Hz, 6H). MS: m/z 520.23 $[M]^+$ (calcd: 520.43).

*Synthesis of* **1e**: The synthesis was similar to that of compound **1a** but use 2-bromo-5-octylthiophene as starting material. White solid (yield: 67%). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 6.74 (s, 2H), 2.77 (t, $J$ = 7.6 Hz, 4H), 1.68 (dt, $J$ = 14.7, 7.5 Hz, 4H), 1.49 – 1.10 (m, 20H), 0.89 (t, $J$ = 5.7 Hz, 6H). MS: m/z 548.48 $[M]^+$ (calcd: 548.48).

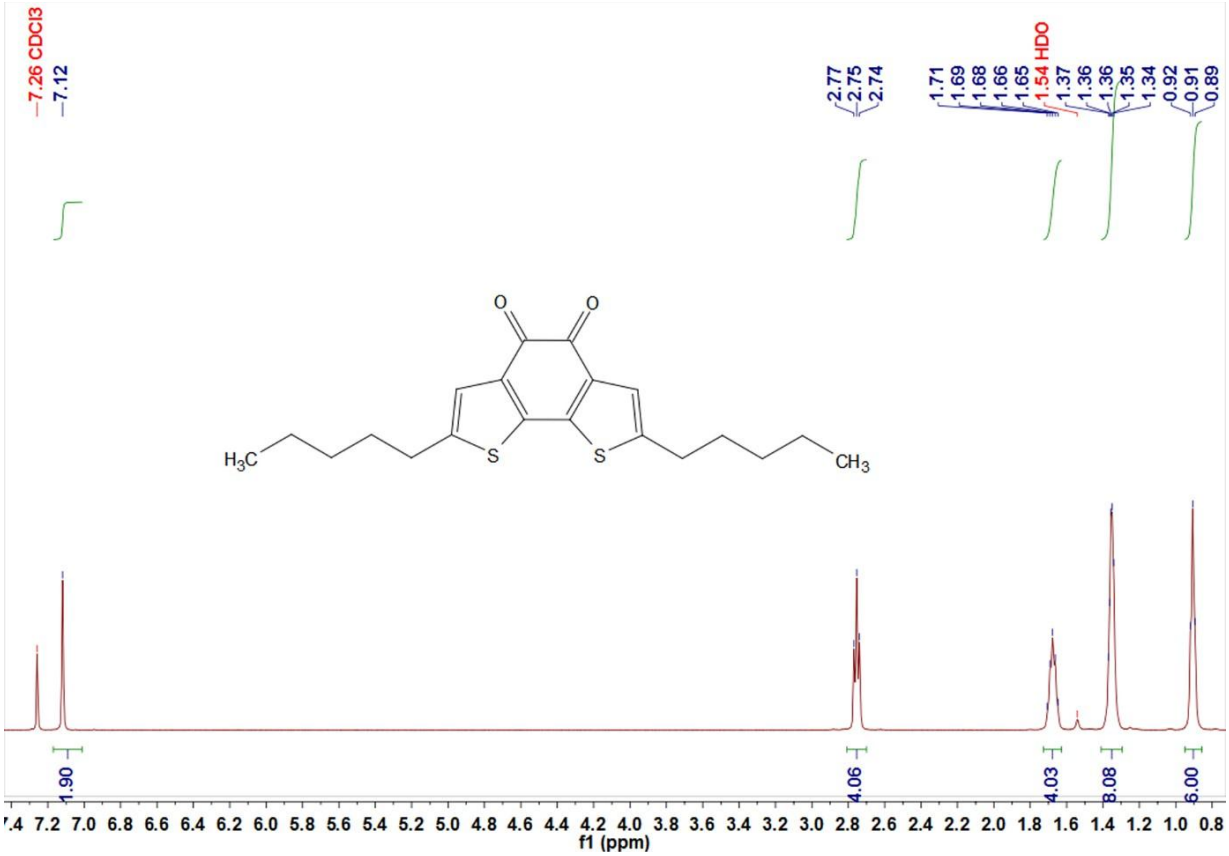
*Synthesis of* **2a**. *n*-Butyllithium (11.6 mL, 2.4 M in hexane, 28 mmol) was added dropwise to a mixture solution of compound **1a** (5.2 g, 12 mmol) in anhydrous THF (50 mL) at -78℃ under nitrogen gas. The mixture was stirred at -78℃ for 2 hour and diethyl oxalate (3.4 g, 24 mmol) was added to the mixture at -78℃. The mixture was stirred at -78℃ for 1 hours and then the temperature was allowed to slowly rise to 0℃. The obtained dark green mixture was

quenched with saturated aqueous $NH_4Cl$, extracted with ethyl ether (100 mL×3) and the combined organic layers were dried over $MgSO_4$. After removing the solvent, the residue was purified by chromatography, eluting with dichloromethane to afford 2.1 g of a dark purple solid (yield: 53%). $^1$H NMR (500 MHz, CDCl3) $\delta$ 7.13 (s, 2H), 2.77 (t, $J$ = 7.9 Hz, 4H), 1.74-1.59 (m, 4H), 1.40 (dq, $J$ = 14.4, 7.3 Hz, 4H), 0.95 (t, $J$ = 7.3 Hz, 6H); MS: m/z 331.98 [M]+ (calcd: 332.09).



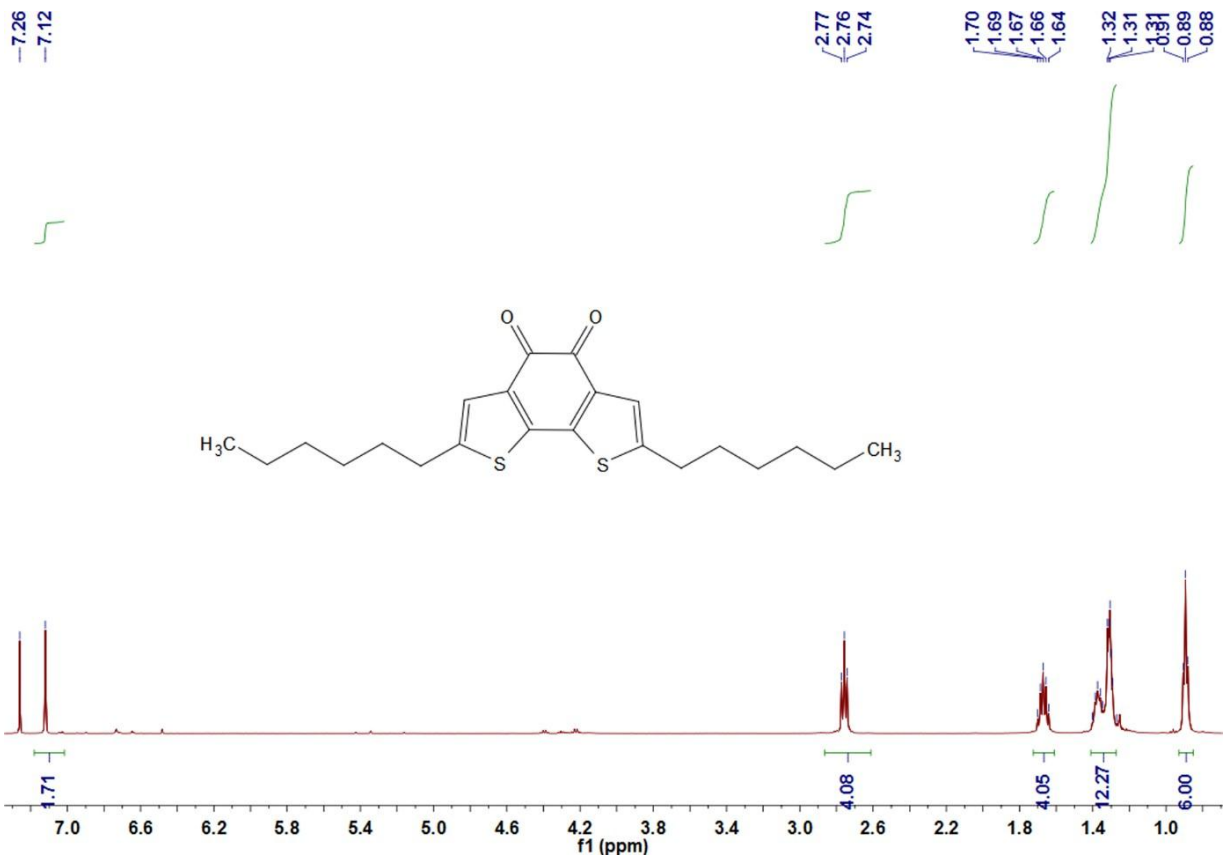

$^1$H NMR spectrum of **2a** (500 MHz, $CDCl_3$).

*Synthesis of* **2b**. The synthesis was similar to that of compound **2a** but use **1b** as starting material. Dark purple solid (yield: 45%). $^1$H NMR (500 MHz, CDCl3) $\delta$ 7.12 (s, 2H), 2.75 (t, $J$ = 7.5 Hz, 4H), 1.72-1.61 (m, 4H), 1.43-1.27 (m, 8H), 0.91 (t, $J$ = 6.9 Hz, 6H). MS: m/z 360.15 [M]+ (calcd: 360.12).



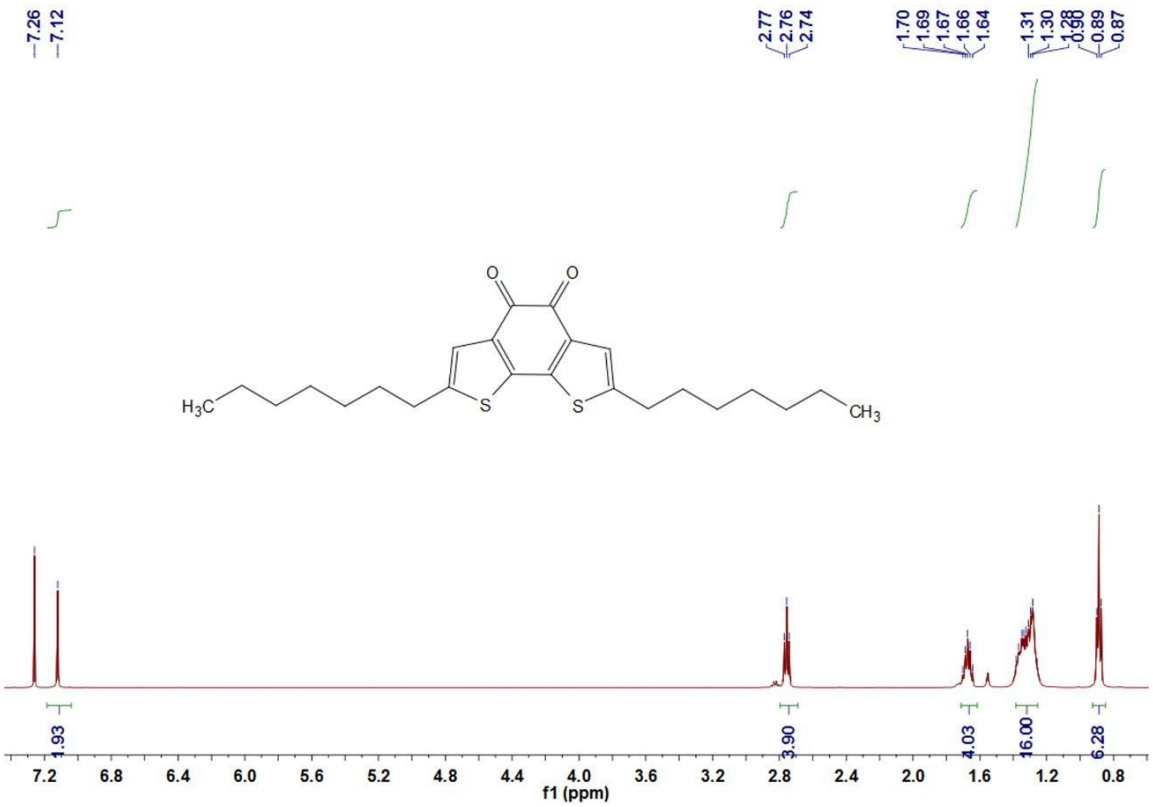

$^1$H NMR spectrum of **2b** (500 MHz, $CDCl_3$).

*Synthesis of* **2c**. The synthesis was similar to that of compound **2a** but use **1c** as starting material. Dark purple solid (yield: 48%). $^1$H NMR (500 MHz, CDCl3) $\delta$ 7.12 (s, 2H), 2.76 (t, $J$ = 7.5 Hz, 4H), 1.71-1.62 (m, 4H), 1.41-1.25 (m, 12H), 0.89 (t, $J$ = 6.9 Hz, 6H). MS: m/z 388.04 $[M]^+$ (calcd: 388.15).



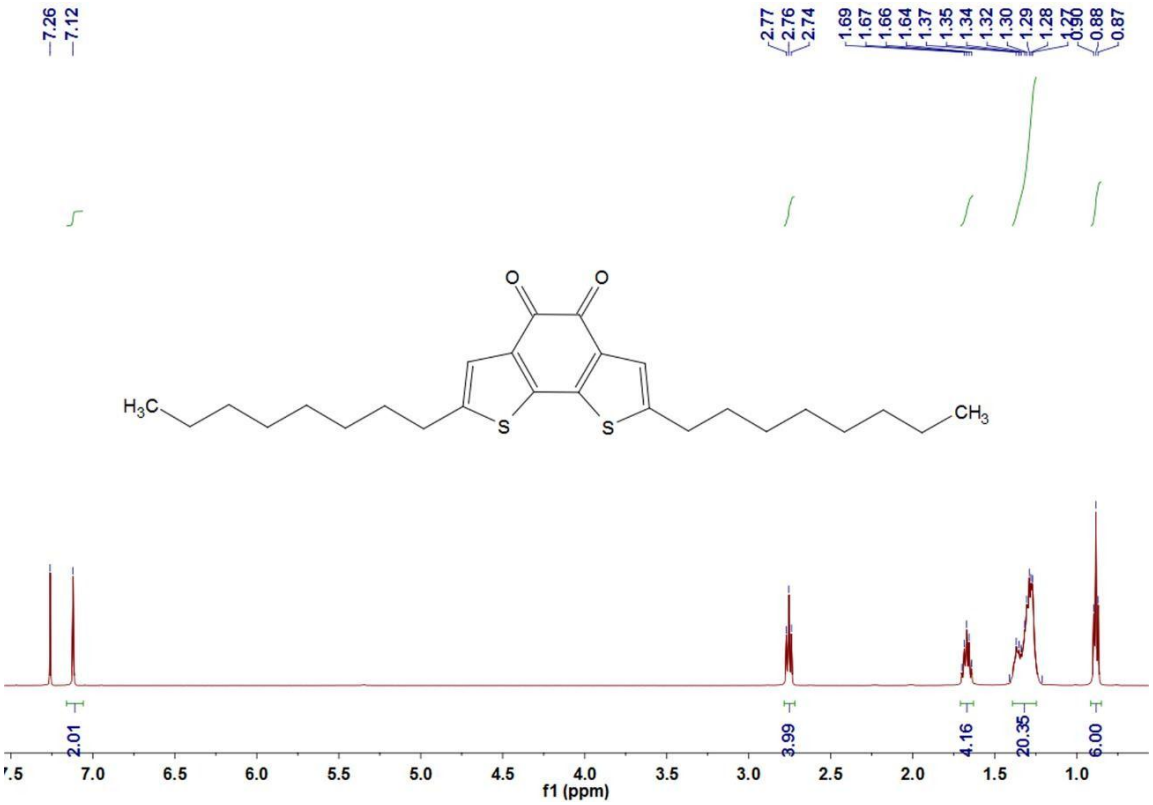

$^1$H NMR spectrum of **2c** (500 MHz, $CDCl_3$).

*Synthesis of* **2d**. The synthesis was similar to that of compound **2a** but use **1d** as starting material. Dark purple solid (yield: 41%). $^1$H NMR (500 MHz, CDCl3) $\delta$ 7.12 (s, 2H), 2.76 (t, $J$ = 7.5 Hz, 4H), 1.75-1.62 (m, 4H), 1.43-1.21 (m, 16H), 0.89 (t, $J$ = 6.9 Hz, 6H). MS: m/z 416.23 $[M]^+$ (calcd: 416.18).




$^1$H NMR spectrum of **2d** (500 MHz, $CDCl_3$).

*Synthesis of* **2e**. The synthesis was similar to that of compound **2a** but use **1e** as starting material. Dark purple solid (yield: 51%). $^1$H NMR (500 MHz, CDCl3) $\delta$ 7.12 (s, 2H), 2.75 (t, $J$ = 7.5 Hz, 4H), 1.70-1.62 (m, 4H), 1.42-1.18 (m, 20H), 0.88 (t, $J$ = 6.9 Hz, 6H). MS: m/z 444.19 $[M]^+$ (calcd: 444.22).




$^{1}$H NMR spectrum of **2e** (500 MHz, $CDCl_3$).

## 2. Supplementary Figures

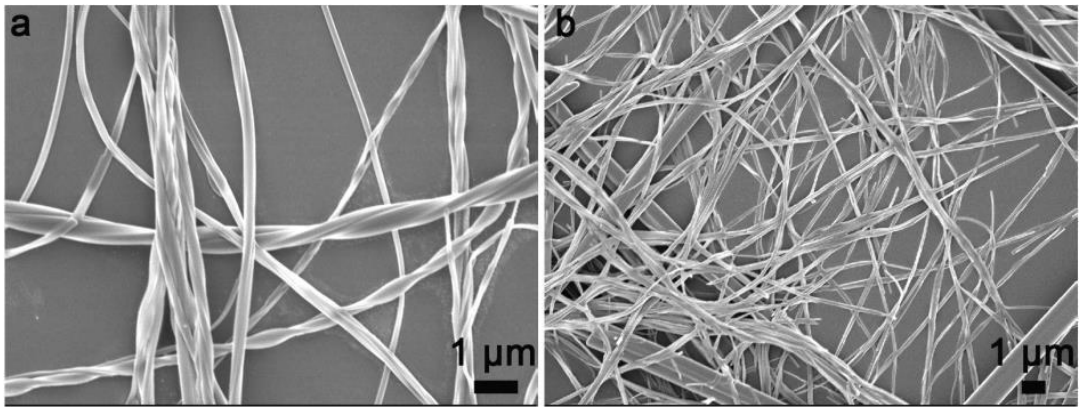



**Fig. S1.** High magnification SEM images of (a) F-7 and (b) F-8 based microstructures prepared by crystallization from ethanol.

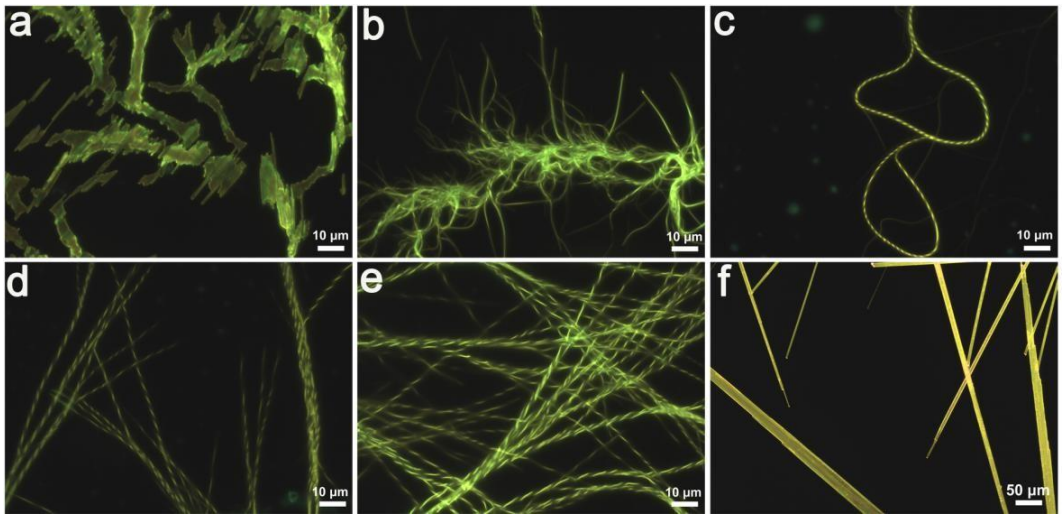



**Fig. S2.** Fluorescence microscopy images of F-4 based microstructures prepared by natural evaporation of chloroform/ethanol solutions (0.5 mg/mL) with different volume ratios (v/v): (a) 5/1, (b) 4/1, (c) 3/1, (d) 2/1, (e) 1/1, and (d) 1/2.

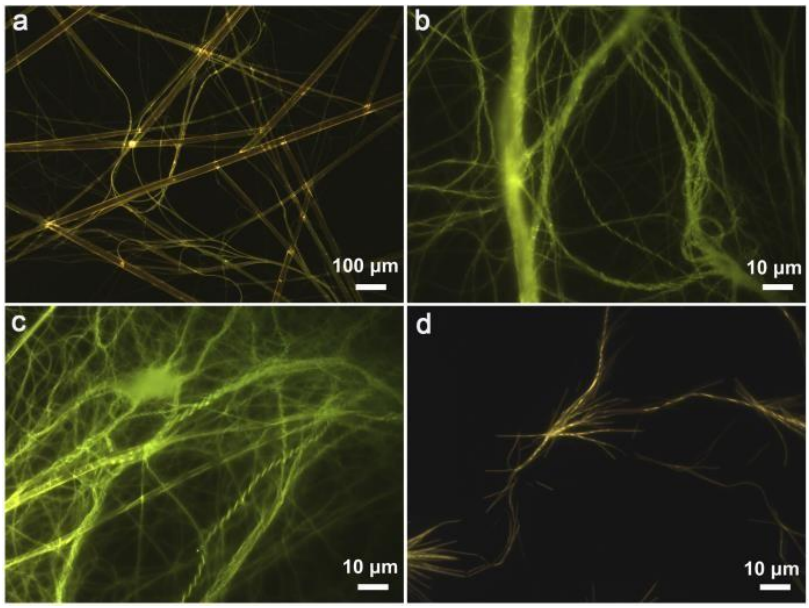



**Fig. S3.** Fluorescence microscopy images of F-6 based microstructures prepared by natural evaporation of chloroform/ethanol (V:V = 2:1) solutions with different concentrations: (a) 1.0 mg/mL, (b) 0.5 mg/mL, (c) 0.25 mg/mL, and (d) 0.1 mg/mL.

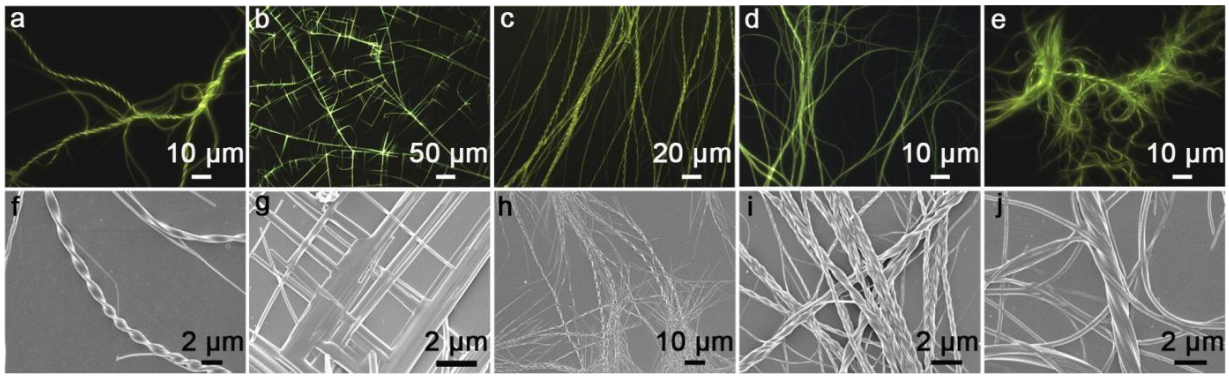



**Fig. S4.** Fluorescence microscopy and FESEM images of F-n based microstructures prepared by natural evaporation of chloroform/ethyl acetate solutions (V:V = 1:1, 0.5 mg/mL): (a, f) F-4, (b, g) F-5, (c, h) F-6, (d, i) F-7, and (e, j) F-8.

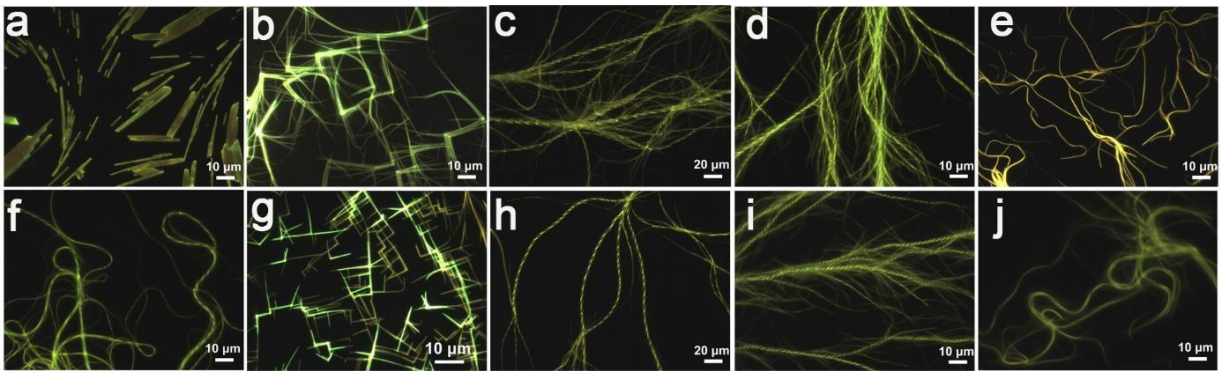



**Fig. S5.** Fluorescence microscopy of F-n based microstructures prepared by natural evaporation of chloroform/ethyl acetate solutions with ratio (V:V) of 3:1 (**top**) and 1:2 (**bottom**), respectively: (a, f) F-4, (b, g) F-5, (c, h) F-6, (d, i) F-7, and (e, j) F-8.

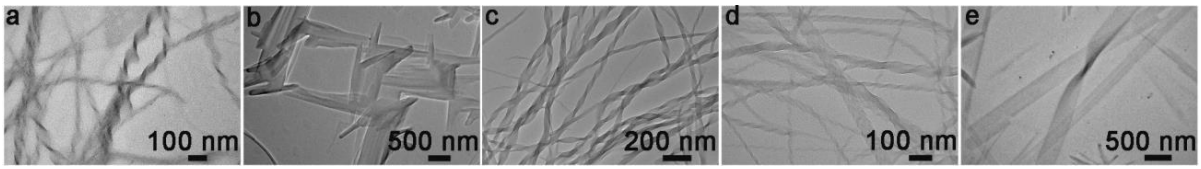



**Fig. S6.** The TEM images of nanostructures prepared by solvent diffusing for 2 h in chloroform solutions (0.5 mg/mL, 2 mL) and ethanol (4 mL): (a) F-4, (b) F-5, (c) F-6, (d) F-7, and (e) F-8.

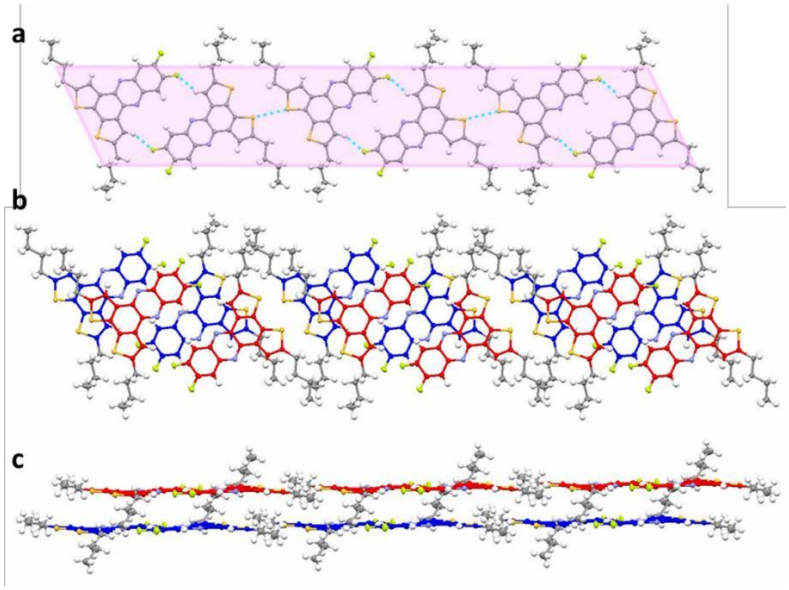



**Fig. S7.** Arrangement of π···π stacking structures in the F-4 crystal: (a) top view of a molecular layer, (b) top view of two stacking layers, and (c) side view of the π···π stacking feature. The aromatic regions of two layers are marked with red and blue color, respectively.

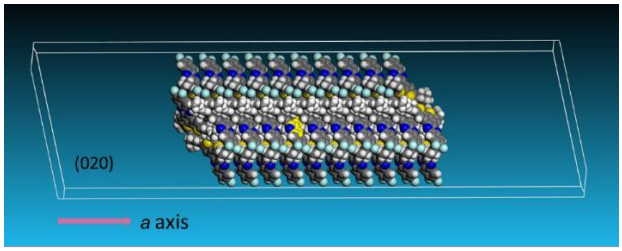



**Figure S8.** The growth morphology of the F-8 crystal predicted based on the attachment energies calculated with the Material Studio package.

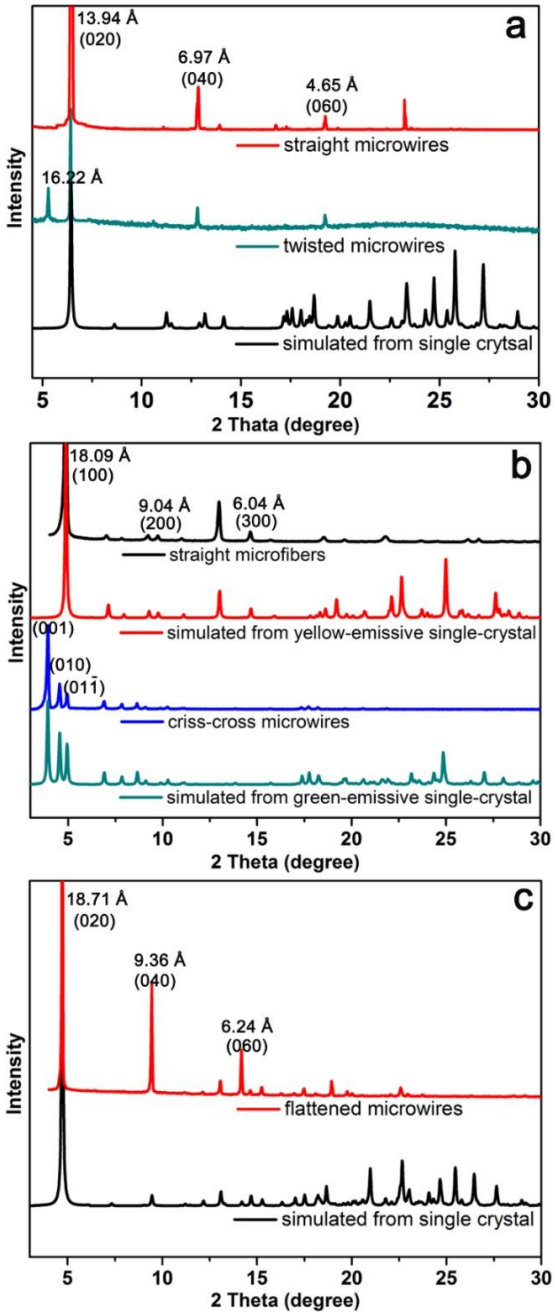



**Fig. S9** Powder XRD patterns recorded for (a) F-4, (b) F-5 and (c) F-8 based micromaterials and simulated patterns from corresponding single crystal data.

## 3. Supplementary Tables

**Table S1** Calculated attachment energies (EA) for different lattice planes of the F-5 green emissive crystal.

| *hkl* | $d_{hkl}$/Å | *EA (total)/kcalmol* $^{-1}$ | *% Total facet area* |
|---|---|---|---|
| (0 0 1) | 22.524 | -26.771 | 39.045 |
| (0 1 0) | 19.403 | -27.896 | 34.399 |
| (0 1 $\bar{1}$) | 17.862 | -32.869 | 18.234 |
| (1 $\bar{1}$ 0) | 4.872 | -158.804 | 4.474 |
| (1 0 $\bar{1}$) | 4.886 | -159.751 | 3.848 |
| (1 $\bar{3}$ $\bar{2}$) | 3.579 | -175.262 | Near to 0 |

**Table S2** Calculated attachment energies (EA) for different lattice planes of the F-8 crystal.

| *hkl* | $d_{hkl}$/Å | *EA (total)/kcalmol* $^{-1}$ | *% Total facet area* |
|---|---|---|---|
| (0 2 0) | 18.693 | -53.376 | 40.095 |
| (0 0 1) | 15.768 | -55.449 | 30.164 |
| (0 $\bar{1}$ $\bar{1}$) | 14.528 | -64.931 | 8.098 |
| (0 1 1) | 14.528 | -64.931 | 8.098 |
| (1 1 $\bar{1}$) | 4.751 | -184.844 | 5.548 |
| (1 $\bar{1}$ $\bar{1}$) | 4.751 | -184.844 | 5.548 |
| (1 0 $\bar{1}$) | 4.789 | -185.618 | 1.225 |
| (1 0 0) | 4.865 | -199.646 | 1.223 |

The growth morphology method was applied to investigate the shapes of organic molecular crystals in this study. In general, the growth rate of one crystal face is assumed to be proportional to its attachment energy (*EA*). The face with lower attachment energy is slower growing and hence has more morphological importance. The attachment energy can be calculated by:

$$EA = E_{lattice} - E_{slice}$$

Where $E_{lattice}$ is the lattice energy of the crystal and $E_{slice}$ is the energy for a growth slice of thickness $d_{hkl}$.