

Electronic Supplementary Information

Assembly of twisted luminescent architectures based on acenaphtho[1,2-k]fluoranthene derivatives

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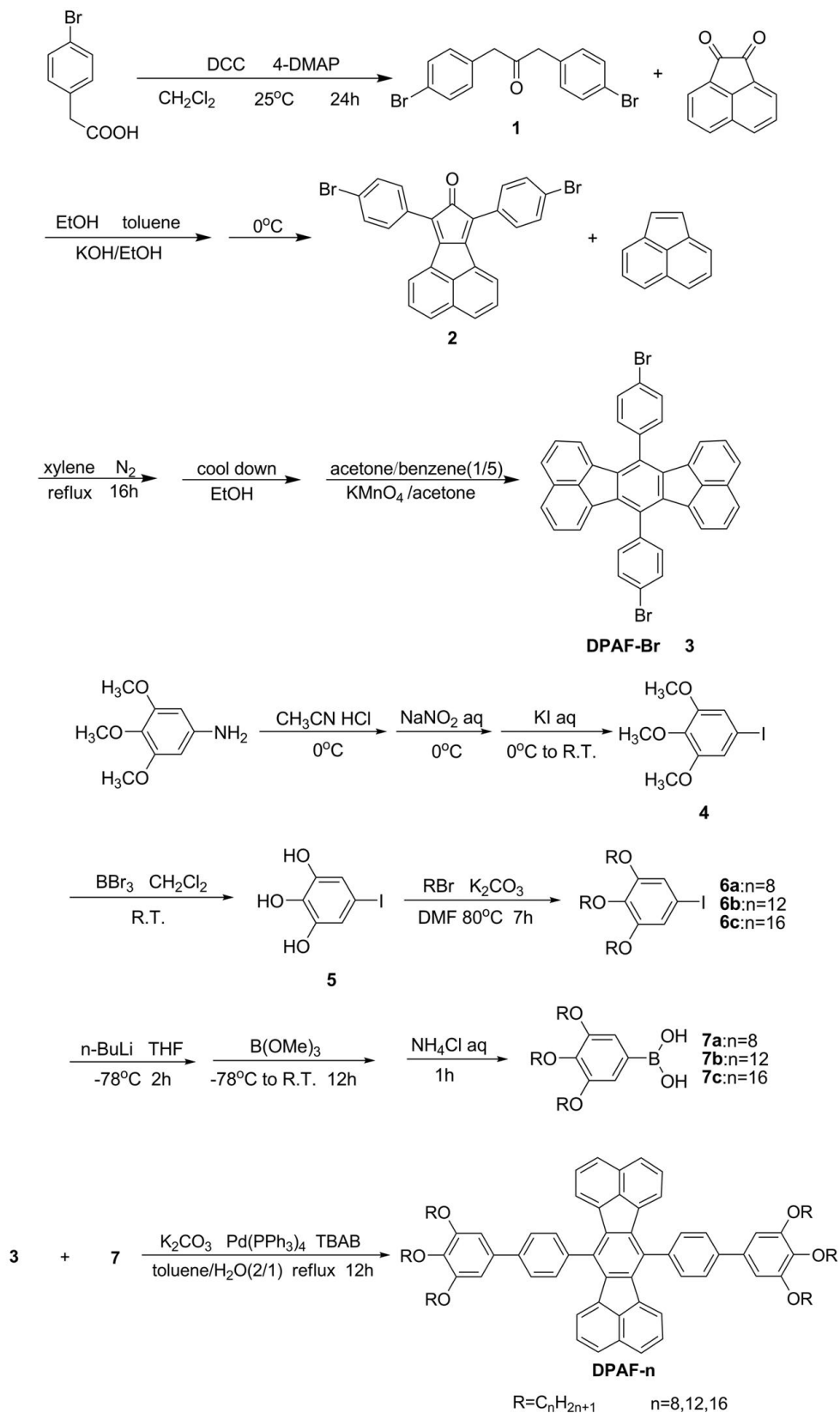
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1. Materials and Instruments

All reagents, starting materials and silica gel for TLC and column chromatography were obtained from the best known commercial sources and were used without further purification. The solvents of dichloromethane, N, N-dimethylformamide (DMF), tetrahydrofuran (THF), toluene and xylene used in the process of synthesis were purified using standard procedures, while other solvents were of AR quality and used without further purification. The solvents for the preparation of the assemblies were all spectral grade and used without further purification.

^1H NMR spectra were recorded on Varian Mercury 300 MHz spectrometer and ^{13}C NMR spectra were recorded on Bruker AVANVE 500 MHz or 600 MHz spectrometers. Chemical shifts are reported in ppm (δ) with the signal of tetramethylsilane (TMS) or residual solvent as the internal standard. Mass spectra were recorded on a Shimadzu AXIMA-CFR MALDI-TOF or ITQ 1100 (Thermo Scientific) mass spectrometer. Elemental analyses were performed on a Vario Micro (Elementar) spectrometer. The emission spectrum of **DPAF-12** solution was recorded by a Shimadzu RF-5301 PC spectrometer. The emission spectra of **DPAF-12** solid samples (microstructures and crystal powder) were recorded by a Maya2000 pro CCD spectrometer. The absolute fluorescence quantum yields of **DPAF-12** samples in different states were measured on an Edinburgh FLS920 (excited at 425 nm). The fluorescence microscopy images were obtained on an Olympus BX51 fluorescence microscope. FESEM images were performed on a JSM 6700F field emission scanning electronic microscope. Power X-ray diffraction data were recorded by a PANalytical B.V. Empyrean diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$).

2. Synthesis and Characterization



Scheme 1. Synthetic Procedures of **DPAF-n** (n = 8, 12, 16).

The intermediate compounds 3,4,5-trialkyloxyphenylboronic acids (**7a**, **7b** and **7c**) and 7,14-Bis[4-bromophenyl]acenaphtho[1,2-k]-fluoranthene (**DPAF-Br**, **3**) were prepared according to the modified procedures reported in the literatures.^{S1, S2} The target product compounds DPAF-n were obtained by Suzuki cross-coupling of the **DPAF-Br** and the produced boronic acids.

1,3-Bis(4-bromophenyl)-2-propanone (1) A solution of 4-bromophenylacetic acid (6.45 g, 30 mmol) in CH₂Cl₂ (75 mL) was added dropwise to a mechanically stirred solution of dicyclohexylcarbodiimide (6.19 g, 30 mmol) and 4-(dimethylamino)pyridine (0.95 g, 7.53 mmol) in CH₂Cl₂ (70 mL). The reaction was allowed to proceed overnight under N₂ atmosphere at room temperature. The resulted mixture was filtered to remove dicyclohexylurea, and the filtrate was subjected by rotary evaporation under reduced pressure. Purification of the residue by flash chromatography (silica, CH₂Cl₂/petroleum ether 3:1), followed by crystallization from C₂H₅OH, gave 1,3-bis-(4-bromophenyl)-2-propanone (**1**; 2.49 g, 6.77 mmol, 45.11%) as a colorless solid. ¹H NMR (300 MHz, CDCl₃): δ 7.44 (d, 4H, J = 8.4 Hz), 7.01 (d, 4H, J = 8.4 Hz), 3.68 (s, 4H); MS m/z: 367.8 [M]⁺ (calcd: 367.9). Anal. Calcd (%) for C₁₅H₁₂Br₂O: C, 48.95; H, 3.29. Found: C, 48.85; H, 3.24.

7,9-Bis(4-bromophenyl)-8H-cyclopenta[a]acenaphthylen-8-one (2) Compound **2** was synthesized by double Knoevenagel condensation reaction between 1,3-bis(4-bromophenyl)-2-propanone (**1**; 1.076 g, 2.92 mmol) and acenaphthylene-1,2-dione (0.54 g, 2.97 mmol) in mixture of ethanol (12 mL) and toluene (1.2 mL). A solution of KOH (0.2 g) in ethanol (1 mL) was added dropwise to the refluxing mixture, and the reaction went on refluxing for 5 min under vigorously stirring. Then the reaction mixture was cooled to 0 °C, and the black solid was filtered, washed with ethanol, and dried (**2**; 1.46 g, 2.84 mmol, 97.26%). The obtained compound was insoluble in common solvents. MS m/z: 514.6 [M]⁺ (calcd: 514.2). Anal. Calcd (%) for C₂₇H₁₄Br₂O: C, 63.07; H, 2.74. Found: C, 63.08; H, 2.75.

7,14-Bis[4-bromophenyl]acenaphtho[1,2-k]-fluoranthene (DPAF-Br) (3) A mixture of acenaphthylene (340 mg, 2.24 mmol) and 7,9-bis(4-bromophenyl)-8H-cyclopenta[a]acenaphthylene-8-one (**2**; 1.19 g, 2.32 mmol) in xylene (10 mL) was refluxed for 16 h under N₂ atmosphere. After cooling to room temperature, ethanol (150 mL) was added to the reaction mixture. The precipitated solid was filtered, washed with ethanol, and dried in vacuum. Subsequently, the solid was dissolved in a refluxing mixture of acetone/benzene (1:5, 60 mL) and treated with aliquots of a solution of KMnO₄ in acetone until the reaction mixture remained purple. After filtration over a column of silica gel to remove KMnO₄, evaporation of the solvent and drying in vacuum, a yellow strongly fluorescent solid **DPAF-Br** was obtained (**3**; 1.2g, 1.89 mmol, 84.38%). ¹H NMR (300 MHz, CDCl₃): δ 7.88 (d, 4H, J = 8.3 Hz), 7.76 (d, 4H, J = 8.2 Hz), 7.57 (d, J = 8.2 Hz, 4H), 7.39 (dd, 4H, J = 8.2, 7.1 Hz), 6.79 (d, 4H, J = 7.1 Hz). MS m/z: 636.1 [M]⁺ (calcd: 636.4). Anal. Calcd (%) for C₃₈H₂₀Br₂: C, 71.72; H, 3.17. Found: C, 71.68; H, 3.15.

5-Iodo-1,2,3-trimethoxybenzene (4) 3,4,5-Trimethoxyaniline (4.58 g, 25 mmol) was dissolved in 30 mL acetonitrile in a 250 mL flask. Then the flask was placed in an ice-bath and stirred with a mechanical stirrer. After 10 min, a mixture of hydrochloric acid (15 mL) and acetonitrile (25 mL) was added dropwise to the stirring solution. The resulting mixture went on stirring in ice-bath for 20 min, and a 15 mL aqueous solution of sodium nitrite (2.1g, 30.43 mmol) was slowly added to the mixture with the temperature maintained between 0 °C and 5 °C. After the mixture continued stirring for 1h in the ice-bath, a 25 mL aqueous solution of potassium iodide (12.5 g, 75.3 mmol) was added to the mixture, and the mixture kept on stirring at room temperature overnight. An aqueous solution of sodium thiosulfate was added to neutralize excess iodine until no further change in color was observed. After filtration, the precipitates obtained were purified by flash chromatography (silica, chloroform/ethyl acetate 60:1), followed by evaporation of the solvent and drying in vacuum, then a white solid (**4**; 6.54 g, 22.24 mmol, 88.98%) was obtained. ¹H NMR (300 MHz, CDCl₃): δ 6.89 (s, 2H), 3.84 (s, 6H), 3.81 (s, 3H). MS m/z: 293.8 [M]⁺ (calcd: 294.1).

Anal. Calcd (%) for C₉H₁₁IO₃: C, 36.76; H, 3.77. Found: C, 36.68; H, 3.73.

5-Iodo-1,2,3-trihydroxybenzene (5) 5-Iodo-1,2,3-trimethoxybenzene (**4**; 1.5g, 5.10 mmol) was placed in a 100 mL three-neck round-bottom flask fitted with a condenser and CaCl₂ drying tube, dissolved in 10 mL freshly distilled CH₂Cl₂, degassed with nitrogen and cooled to -78 °C. Then boron tribromide (19 mL of 1M CH₂Cl₂ solution, 19 mmol) was added slowly via syringe. After the addition was completed, the mixture was allowed to warm to room temperature and further stirred for 24 h. The reaction was then carefully quenched with ice-water (10 mL) and stirred for 30 min. Then the mixture was extracted with ethyl acetate (3 x 25 mL), and the organic phase was washed with aqueous Na₂SO₃. After dried with MgSO₄, the solvent was removed to give a brown oil. Finally, the product was precipitated from the crude oil by addition of CHCl₃, collected by filtration, washed with cold CHCl₃ and dried overnight. The obtained product was an off-white solid (**5**; 610 mg, 2.42 mmol, 47.46%). ¹H NMR (300 MHz, DMSO): δ 9.16 (s, 2H), 8.31 (s, 1H), 6.57 (s, 2H). MS m/z: 251.8 [M]⁺ (calcd: 252.0). Anal. Calcd (%) for C₆H₅IO₃: C, 28.60; H, 2.00. Found: C, 28.58; H, 1.99.

1,2,3-Trioctyloxy-5-iodo-benzene (6a) 5-Iodo-1,2,3-trihydroxybenzene (**5**; 1.806 g, 7.17 mmol) was dissolved in DMF (37 mL) and the solution was degassed with nitrogen for 15 min. Then K₂CO₃ (7.9 g, 57.16 mmol) was added and the mixture was stirred at room temperature for 30 min. Then 1-bromooctane (5.0 g, 25.89 mmol) was added and the mixture was stirred at 80 °C for 7 h. After cooling down, the brown crude solid was removed by filtration and filtrate was evaporated under reduced pressure. Then chromatography (silica gel, CH₂Cl₂/hexane 1:2) gave the desired product as a colorless liquid (**6a**; 2.92 g, 4.96 mmol, 69.22%). ¹H NMR (300 MHz, CDCl₃): δ 6.84 (s, 2H), 3.94-3.89 (m, 6H), 1.86-1.64 (m, 6H), 1.55-1.39 (m, 6H), 1.26 (br, 24H), 0.87 (t, 9H). MS m/z: 588.8 [M]⁺ (calcd: 588.6). Anal. Calcd (%) for C₃₀H₅₃IO₃: C, 61.21; H, 9.08. Found: C, 61.08; H, 9.01.

1,2,3-Tridodecyloxy-5-iodo-benzene (6b) According to the procedure described for the synthesis of **6a**, the mixture of 5-Iodo-1,2,3-trihydroxybenzene (**5**; 2.38 g, 9.44 mmol), K₂CO₃ (9.7 g, 70.18 mmol) and 1-bromododecane (8.35 g, 33.45 mmol) was stirred in DMF (50 mL) at 80 °C for 7 h under nitrogen atmosphere. A white solid (**6b**; 3.87 g, 5.12 mmol, 54.24%) was obtained after column chromatography (silica gel, CH₂Cl₂/hexane 2:5). ¹H NMR (300 MHz, CDCl₃): δ 6.84 (s, 2H), 3.94-3.88 (m, 6H), 1.86-1.64 (m, 6H), 1.53-1.39 (m, 6H), 1.26 (br, 48H), 0.87 (q, 9H). MS m/z: 756.8 [M]⁺ (calcd: 757.0). Anal. Calcd (%) for C₄₂H₇₇IO₃: C, 66.64; H, 10.25. Found: C, 66.48; H, 10.17.

1,2,3-Trihexadecyloxy-5-iodo-benzene (6c) According to the procedure described for the synthesis of **6a**, the mixture of 5-Iodo-1,2,3-trihydroxybenzene (**5**; 2.96 g, 11.77 mmol), K₂CO₃ (13.1 g, 94.78 mmol) and 1-bromohexadecane (13.3 g, 43.55 mmol) was stirred in DMF (60 mL) at 80 °C for 7 h under nitrogen atmosphere. A white solid (**6c**; 7.345 g, 7.99 mmol, 67.88%) was obtained after column chromatography (silica gel, CH₂Cl₂/hexane 1:3). ¹H NMR (300 MHz, CDCl₃): δ 6.84 (s, 2H), 3.94-3.88 (m, 6H), 1.86-1.64 (m, 6H), 1.53-1.39 (m, 6H), 1.26 (br, 72H), 0.87 (t, 9H). MS m/z: 925.0 [M]⁺ (calcd: 925.3). Anal. Calcd (%) for C₅₄H₁₀₁IO₃: C, 70.10; H, 11.00. Found: C, 70.06; H, 10.99.

3,4,5-Trioctyloxyphenylboronic acid (7a) A solution of **6a** (620 mg, 1.05 mmol) in dry THF (20 mL) was stirred under N₂ at -78 °C. After 10 min, a solution of n-BuLi (0.8 mL, 1.92 mmol) in hexane was added dropwise. The mixture kept on stirring for 90 min at -78 °C, then the formed organolithium derivative was quenched by trimethylborate (0.307 mL). The reaction mixture continued stirring at room temperature for 12 h. An excess aqueous solution of ammonium chloride was added and the mixture was extracted with Et₂O. The organic layer was washed with saturated salt water, and evaporated to dryness. The crude liquid was obtained as **7a** and used directly for next Suzuki cross-coupling reaction.

3,4,5-Tridodecyloxyphenylboronic acid (7b) According to the procedure described for the synthesis of **7a**, a solution of n-BuLi (1.5 mL, 3.75 mmol) in hexane was added dropwise to a stirring solution of **6b** (1.512 g, 2 mmol) in dry THF (40 mL) under N₂ at -78 °C and the mixture was quenched by trimethylborate (0.615 mL). An excess aqueous solution of ammonium chloride was added to the resulting mixture, and the crude liquid was obtained by evaporating the extracted organic layer of the mixture as **7b** and used directly for next Suzuki cross-coupling reaction.

3,4,5-Trihexadecyloxyphenylboronic acid (7c) According to the procedure described for the synthesis of **7a**, a solution of n-BuLi (3.3 mL, 8.25 mmol) in hexane was added dropwise to a stirring solution of **6c** (2.772 g, 3 mmol) in dry THF (40 mL) under N₂ at -78 °C and the mixture was quenched by trimethylborate (1.384 mL). An excess aqueous solution of ammonium chloride was added to the resulting mixture, and the crude liquid was obtained by evaporating the extracted organic layer of the mixture as **7c** and used directly for next Suzuki cross-coupling reaction.

DPAF-8 To a 250 mL two-neck flask, 7,14-Bis[4-bromophenyl]acenaphtho[1,2-k]fluoranthene (**3**, 827 mg, 1.3 mmol), potassium carbonate (2.21 g, 16 mmol), tetrabutyl ammonium bromide (500 mg), excess crude boronic acid **7a**, toluene (100 mL) and water (50 mL) were added. The mixture was degassed by a repeated procedure of freeze-pump-thaw and then Pd(PPh₃)₄ (40mg, 0.032 mmol, 2.5%) was added. The mixture was refluxed for 12 hours under nitrogen atmosphere, then poured into water (200 mL) and extracted three times with toluene (3 x 75 mL). The combined extracts were washed with brine (20 mL) and dried with MgSO₄. After the solvent was removed by rotary evaporation, the residue was purified by column chromatography (silica gel, CH₂Cl₂/petroleum ether 1:2). The solvent was removed by rotary evaporation to give a green oil. Finally, the product was precipitated from the green oil by addition of methanol, collected by filtration and dried overnight, which give the desired product **DPAF-8** as a green solid (1.47 g, 1.05 mmol, 80.77%). ¹H NMR (300 MHz, CDCl₃): δ 7.96 (d, J = 8.1 Hz, 4H), 7.75 (d, J = 8.2 Hz, 4H), 7.74 (d, J = 8.2 Hz, 4H), 7.36 (dd, J = 8.0, 7.3 Hz, 4H), 7.09 (s, 4H), 6.88 (d, J = 7.0 Hz, 4H), 4.17 (t, J =

6.5 Hz, 8H), 4.07 (t, J = 6.6 Hz, 4H), 1.98-1.77 (m, 12H), 1.62-1.48 (m, 12H), 1.47-1.24 (m, 48H), 0.88 (q, 18H). ¹³C NMR (500 MHz, CDCl₃): δ 153.69, 140.87, 138.38, 138.10, 137.16, 136.51, 135.80, 133.79, 133.24, 129.67, 129.55, 128.02, 127.83, 126.54, 123.29, 105.96, 73.68, 69.47, 31.97, 31.88, 30.43, 29.63, 29.57, 29.44, 29.35, 29.20, 22.75, 22.71, 14.13. MS (MALDI-TOF) m/z: 1439.35 [M+K]⁺ (calcd: 1439.05). Anal. Calcd (%) for C₉₈H₁₂₆O₆: C, 84.07; H, 9.07. Found: C, 84.06; H, 9.05.

DPAF-12 According to the procedure described for the synthesis of **DPAF-8**, 7,14-Bis[4-bromophenyl]acenaphtho[1,2-k]fluoranthene (**3**, 190 mg, 0.3 mmol), potassium carbonate (415 mg, 3 mmol), tetrabutyl ammonium bromide (50 mg), excess crude boronic acid **7b**, toluene (20 mL), water (10 mL) and Pd(PPh₃)₄ (20mg, 0.016 mmol, 5.3%) were refluxed for 12 hours under nitrogen atmosphere to afford the desired product **DPAF-12** as a yellow solid (368 mg, 0.21 mmol, 70.66%) after column chromatography (silica gel, CH₂Cl₂/petroleum ether 1:2). ¹H NMR (300 MHz, CDCl₃): δ 7.96 (d, J = 8.1 Hz, 4H), 7.75 (d, J = 8.2 Hz, 4H), 7.74 (d, J = 8.2 Hz, 4H), 7.36 (dd, J = 7.8, 7.5 Hz, 4H), 7.09 (s, 4H), 6.88 (d, J = 7.1 Hz, 4H), 4.17 (t, J = 6.4 Hz, 8H), 4.07 (t, J = 6.7 Hz, 4H), 1.99-1.72 (m, 12H), 1.60-1.49 (m, 12H), 1.47-1.17 (m, 96H), 0.88 (q, 18H). ¹³C NMR (600 MHz, CDCl₃) δ 153.69, 140.86, 138.35, 138.09, 137.15, 136.50, 135.79, 133.78, 133.24, 129.66, 129.54, 128.01, 127.83, 126.53, 123.29, 105.92, 73.68, 69.45, 31.98, 31.94, 30.44, 29.82, 29.80, 29.79, 29.74, 29.71, 29.69, 29.57, 29.50, 29.43, 29.39, 26.23, 26.20, 22.73, 22.70, 14.14, 14.13. MS (MALDI-TOF) m/z: 1775.37 [M+K]⁺ (calcd: 1775.68). Anal. Calcd (%) for C₁₂₂H₁₇₄O₆: C, 84.37; H, 10.10. Found: C, 84.26; H, 10.03.

DPAF-16 According to the procedure described for the synthesis of **DPAF-8**, 7,14-Bis[4-bromophenyl]acenaphtho[1,2-k]-fluoranthene (**3**, 406 mg, 0.638 mmol), potassium carbonate (882 mg, 6.38 mmol), tetrabutyl ammonium bromide (110 mg), excess crude boronic acid **7c**, toluene (40 mL), water (20 mL) and Pd(PPh₃)₄ (35 mg, 0.031 mmol, 4.8%) were refluxed for 12 hours under nitrogen atmosphere to afford the desired product **DPAF-16** as a yellow solid (431 mg, 0.21 mmol, 32.92%) after

column chromatography (silica gel, CH₂Cl₂/petroleum ether 1:2). ¹H NMR (300 MHz, CDCl₃): δ 7.96 (d, J = 8.2 Hz, 4H), 7.75 (d, J = 8.2 Hz, 4H), 7.74 (d, J = 8.2 Hz, 4H), 7.36 (dd, J = 7.8, 7.5 Hz, 4H), 7.09 (s, 4H), 6.88 (d, J = 7.1 Hz, 4H), 4.17 (t, J = 6.5 Hz, 8H), 4.07 (t, J = 6.6 Hz, 4H), 1.95-1.79 (m, 12H), 1.61-1.50 (m, 12H), 1.45-1.21 (m, 144H), 0.88 (q, 18H). ¹³C NMR (500 MHz, CDCl₃) δ 153.69, 140.87, 138.38, 138.10, 137.16, 136.51, 135.80, 133.78, 133.25, 129.67, 129.55, 128.01, 127.82, 126.53, 123.29, 105.95, 77.27, 77.02, 76.76, 73.68, 69.46, 31.96, 31.94, 30.44, 29.82, 29.80, 29.75, 29.72, 29.70, 29.69, 29.58, 29.51, 29.41, 29.38, 26.24, 26.21, 22.72, 22.70, 14.13. MS (MALDI-TOF) m/z: 2111.74 [M+K]⁺ (calcd: 2111.32). Anal. Calcd (%) for C₁₄₆H₂₂₂O₆: C, 84.58; H, 10.79. Found: C, 84.46; H, 10.73.

3. Preparation and Characterization of Supramolecular Structures

To investigate the assembly properties of **DPAF-n** molecules, a phase transfer (PT) method involved in literatures^{S3} with different binary solvent systems was adopted. **DPAF-n** samples were dissolved in good solvents (about 1 mL) such as dioxane, chloroform, toluene and tetrahydrofuran. Then the **DPAF-n** solution was added into test tube, and sequentially poor solvent (about 5 mL) such as methanol, ethanol and isopropanol was carefully covered on top surface of **DPAF-n** solution. Slow diffusion of poor solvent into **DPAF-n** solution resulted in 1D nano/micro-materials with luminescent characteristic in the interlayer between good and poor solvent phases. The forming self-assembling suspensions of microstructures were transferred onto clean glass, quartz, or silicon substrates and dried in air for morphology and spectroscopy measurements.

The other method employed to fabricate the microstructure samples is direct vaporization.^{S4} Various of **DPAF-n** solutions in different solvents were dropped on the clean glass, quartz or silicon substrates located in glass containers with covers, and self-assembly structures were generated after slow vaporization of the solutions.

The additional characteristic data of **DPAF-n** microstructures are shown below.

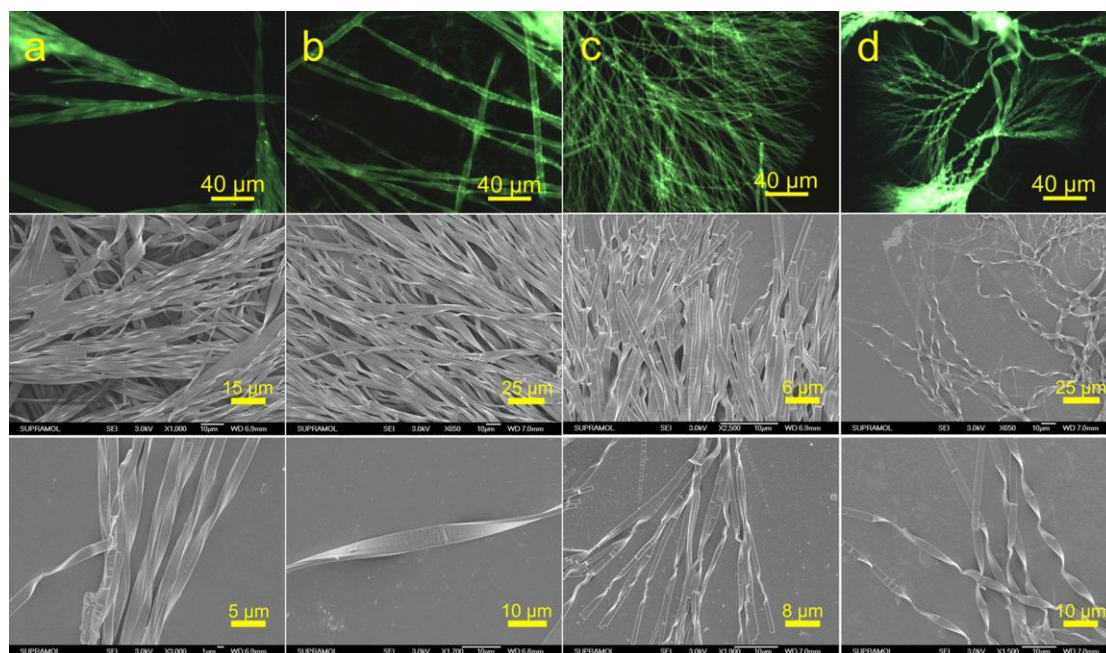


Figure S1. Fluorescence microscopy and FESEM images of **DPAF-12** twisted microstructures prepared by phase transfer methods from binary solvents systems: (a) chloroform solution (1 mg mL^{-1})/methanol; (b) chloroform solution (1 mg mL^{-1})/ethanol; (c) chloroform solution (1 mg mL^{-1})/isopropanol; (d) THF solution (1 mg mL^{-1})/ethanol.

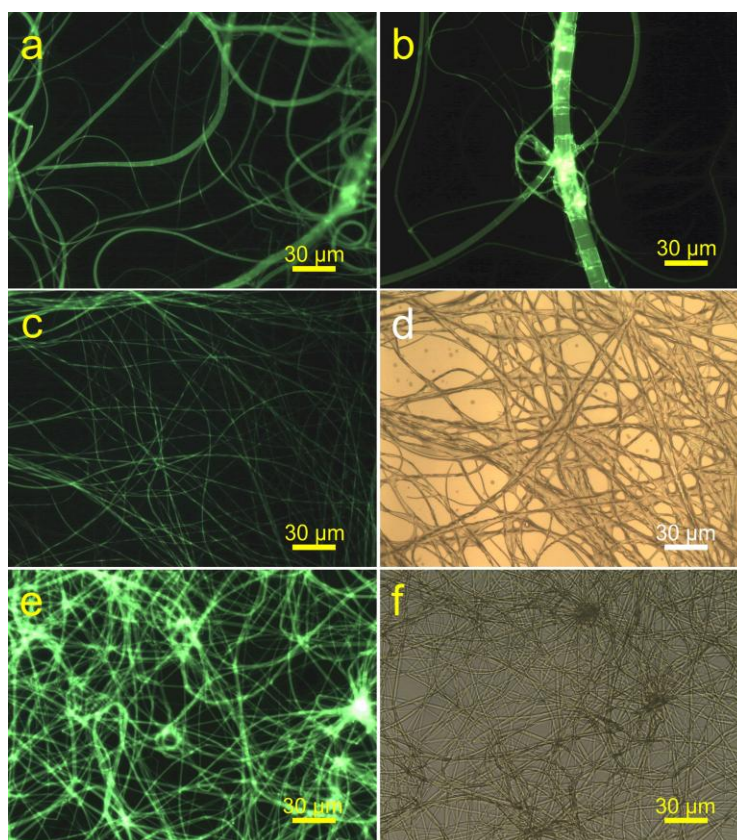


Figure S2. Fluorescence microscopy and bright-field optical images of **DPAF-12** morphologies prepared by slow evaporation of the solutions in mixed solvents of dioxane and ethanol with different ratios: (a) 3:1; (b) 2:1; (c) (d) 1:1; (e) (f) 1:2. The twisted architectures were only generated in the ratio of 1:1.

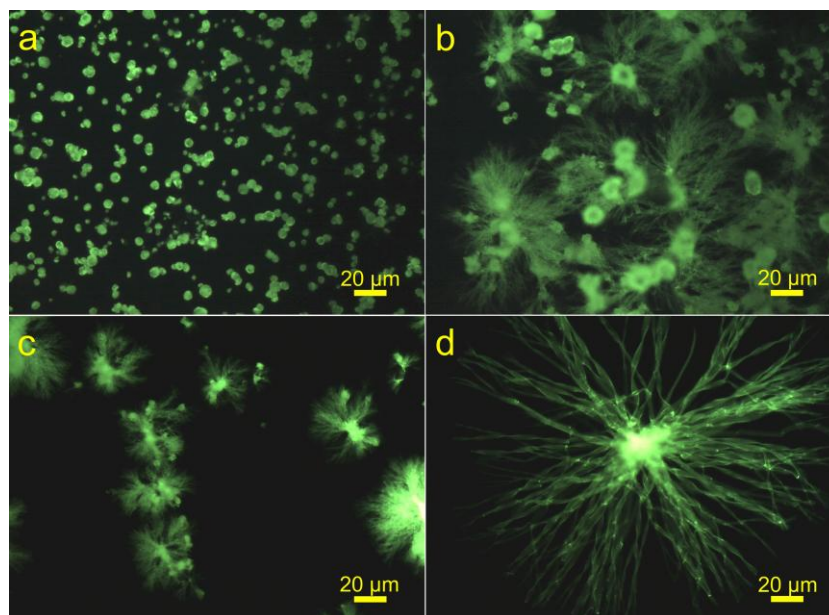


Figure S3. Fluorescence microscopy images of **DPAF-12** morphologies prepared by slow evaporation of the solutions in mixed solvents of chloroform and ethanol with different ratios: (a) 3:1; (b) 2:1; (c) 1:1; (d) 1:2.

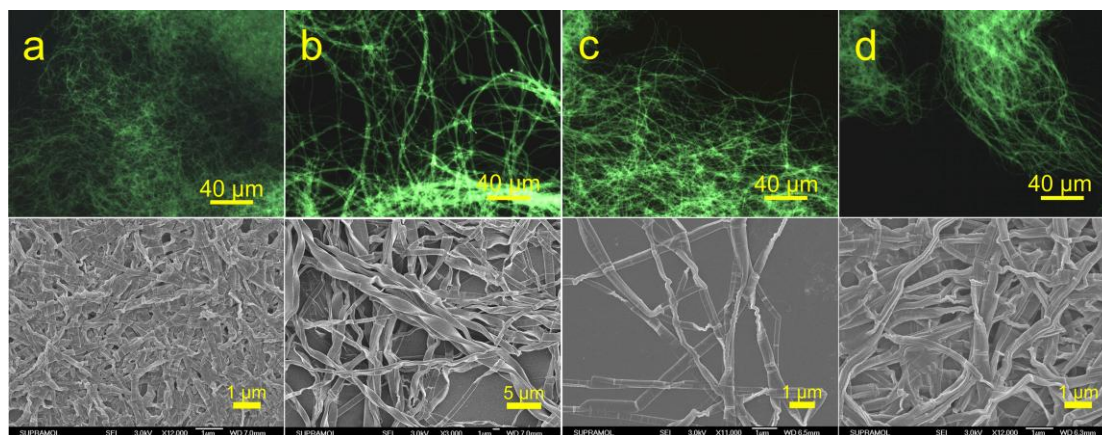


Figure S4. Fluorescence microscopy and FESEM images of **DPAF-12** microstructures prepared by phase transfer methods from methanol and dioxane solutions in different concentrations: (a) 1 mg mL^{-1} ; (b) 0.5 mg mL^{-1} ; (c) 0.1 mg mL^{-1} ; (d) 0.05 mg mL^{-1} .

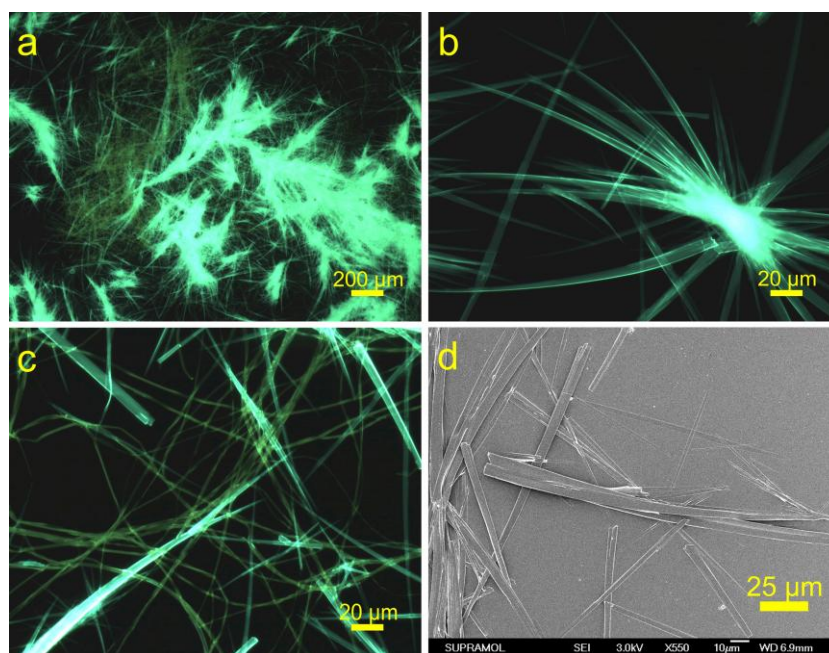


Figure S5. Fluorescence microscopy and FESEM images of **DPAF-12** microwires and straight needle-like crystalline ribbons prepared by phase transfer method from dioxane solution (1 mg mL^{-1})/isopropanol system.

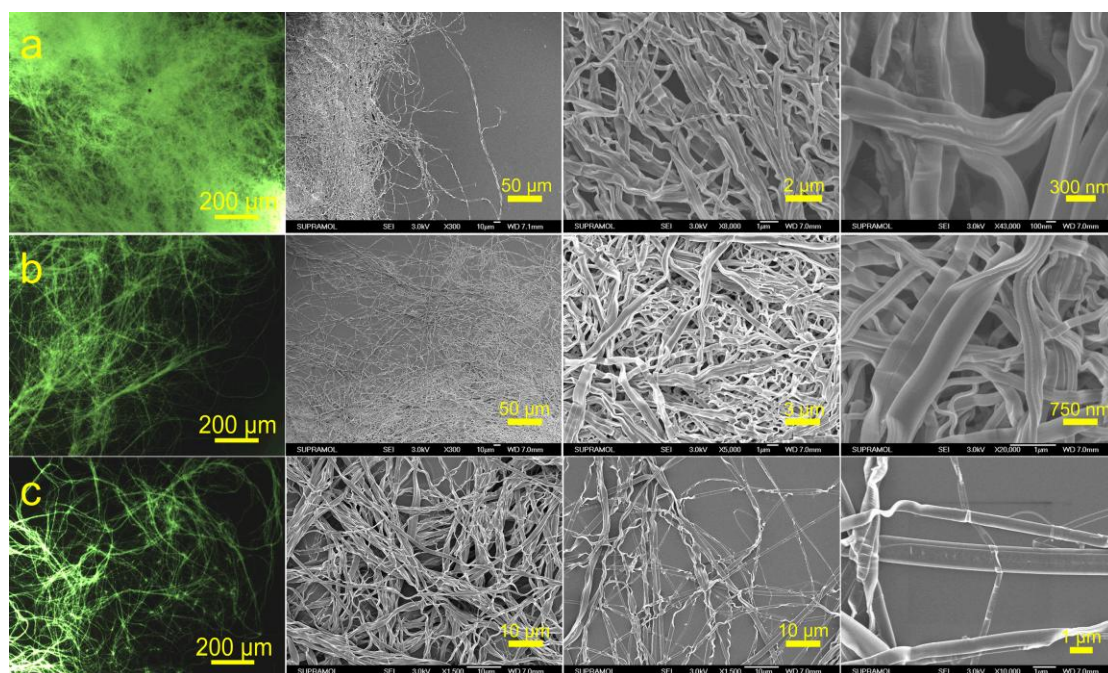


Figure S6. Fluorescence microscopy and FESEM images of **DPAF-16** microstructures prepared by phase transfer methods from methanol and chloroform solution in different concentrations: (a) 0.5 mg mL^{-1} ; (b) 0.1 mg mL^{-1} ; (c) 0.05 mg mL^{-1} .

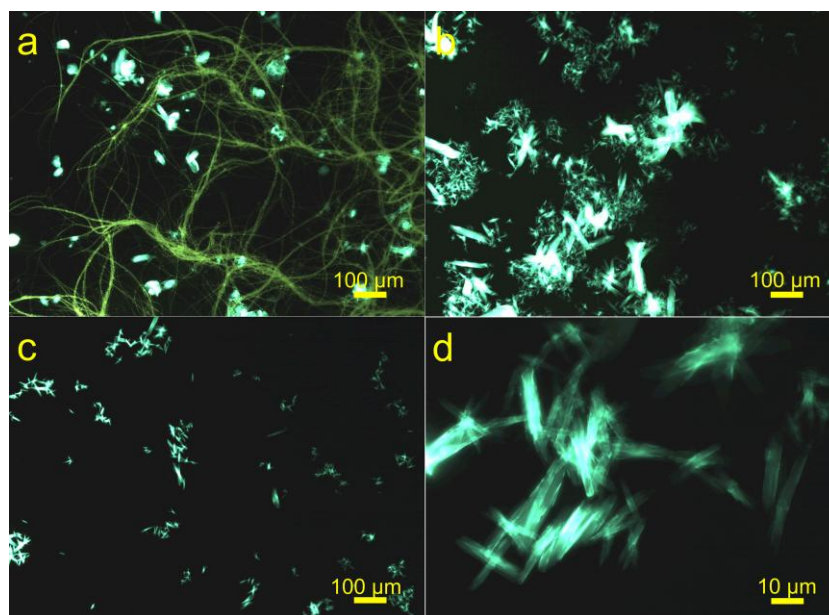


Figure S7. Fluorescence microscopy images of **DPAF-16** microstructures prepared by phase transfer methods from ethanol and chloroform solution in different concentrations: (a) 0.5 mg mL^{-1} ; (b) 0.1 mg mL^{-1} ; (c) (d) 0.05 mg mL^{-1} .

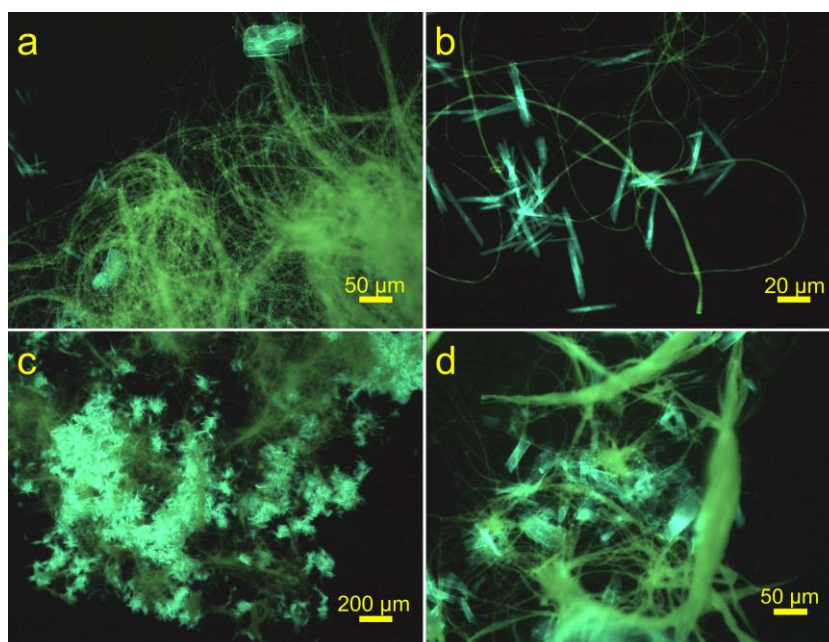


Figure S8. Fluorescence microscopy and FESEM images of **DPAF-16** mixed microstructures prepared by phase transfer methods from: (a) (b) chloroform solution (1 mg mL^{-1})/ethanol system; (c) THF solution (1 mg mL^{-1})/methanol system; (d) toluene solution (1 mg mL^{-1})/methanol system.

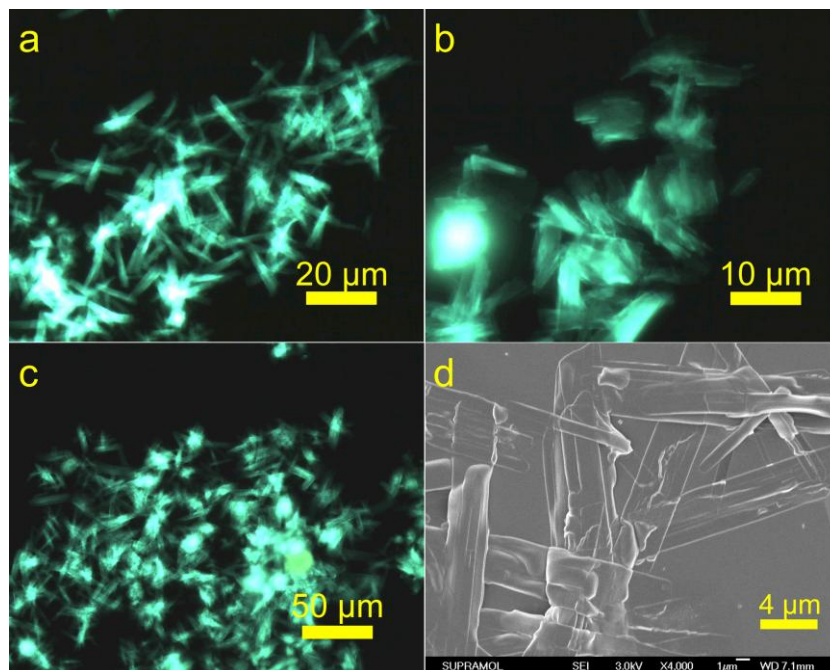


Figure S9. Fluorescence microscopy and FESEM images of **DPAF-16** microsheets prepared by phase transfer methods from: (a) THF solution (1 mg mL^{-1})/ethanol system; (b) THF solution (1 mg mL^{-1})/isopropanol system; (c) (d) toluene solution (1 mg mL^{-1})/ethanol system.

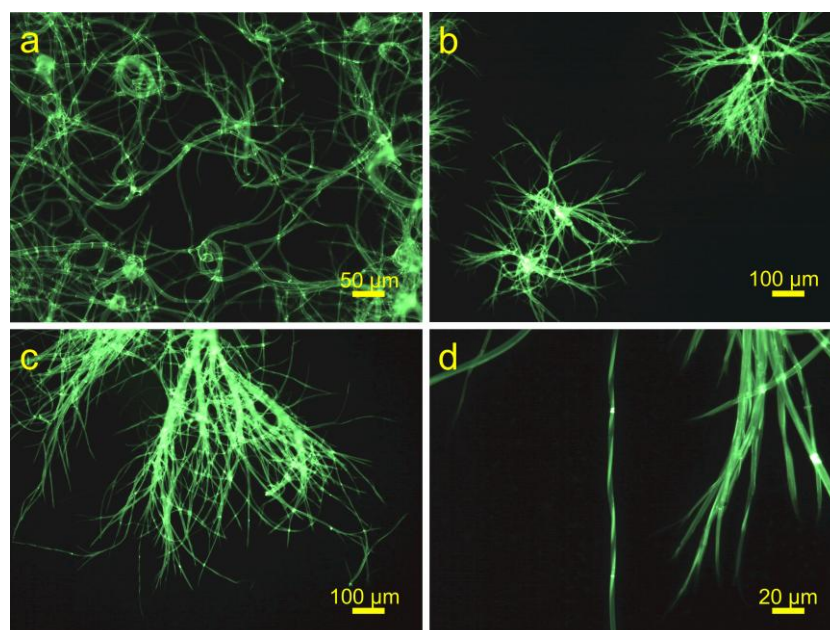


Figure S10. Fluorescence microscopy images of **DPAF-8** flexible microribbons prepared by phase transfer methods from methanol and dioxane solution in different concentrations: (a) 0.5 mg mL^{-1} ; (b) 0.1 mg mL^{-1} ; (c) (d) 0.05 mg mL^{-1} .

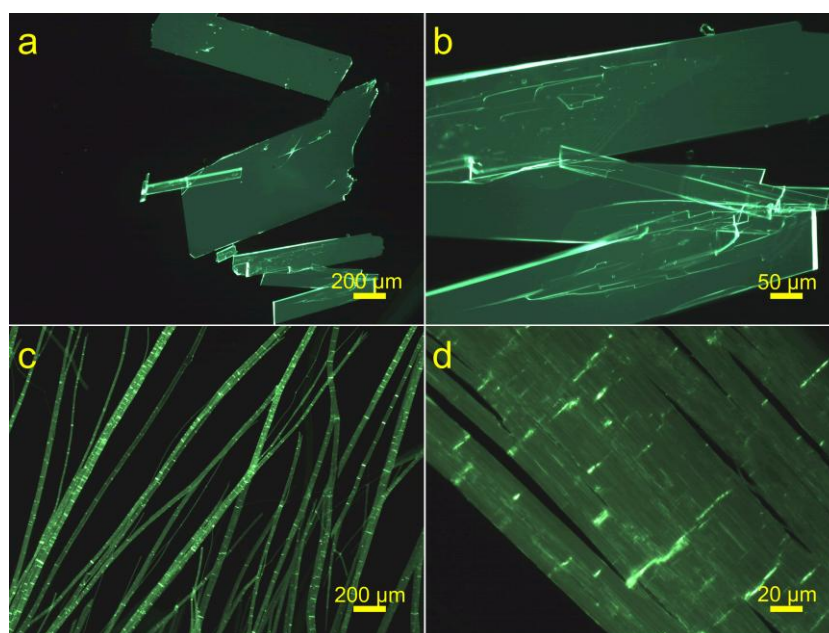


Figure S11. Fluorescence microscopy images of **DPAF-8** flat thin emissive crystals: (a) (b) prepared by phase transfer method from chloroform solution (1 mg mL^{-1})/methanol; (c) (d) prepared by slow evaporation of dioxane solution (1 mg mL^{-1}).

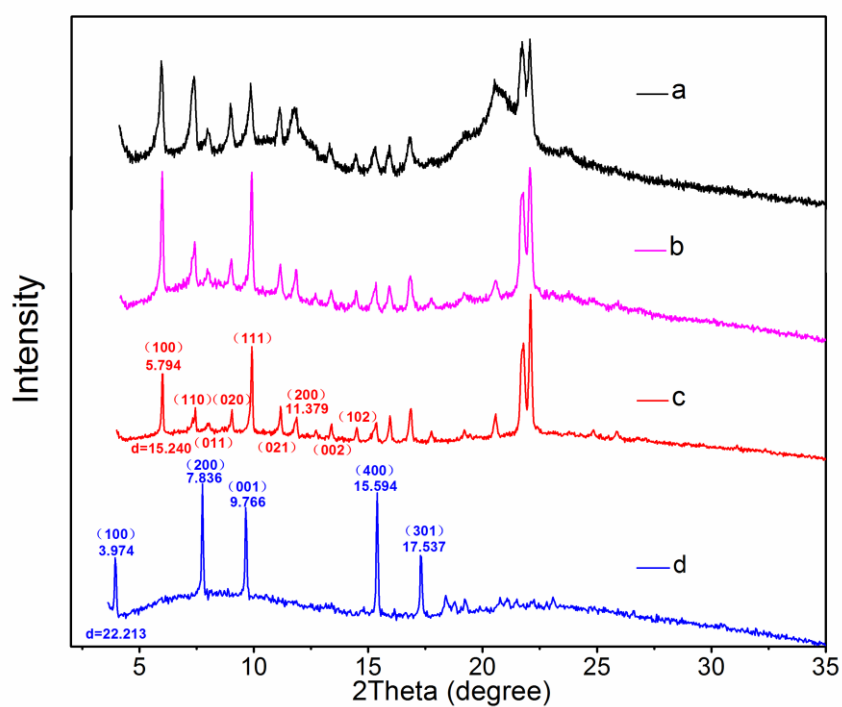


Figure S12. XRD patterns of **DPAF-12** based samples: (a) solids in powder states; (b) microwires prepared from dioxane solution (1 mg mL^{-1})/methanol system by phase transfer method; (c) twisted microwires prepared from dioxane solution (1 mg mL^{-1})/ethanol system by phase transfer method; (d) needle-like crystalline ribbons prepared from dioxane solution (1 mg mL^{-1})/isopropanol by phase transfer method.

4. Single Crystal Structure of DPAF-8

By slow vaporization of **DPAF-8** solution in mixed solvent of chloroform and ethanol, the single crystals were obtained for X-ray structural analysis. Single crystal X-ray diffraction data were collected on a Rigaku RAXIS-PRID diffractometer using the ω -scan mode with graphite-monochromator Mo K α radiation. The structures were solved with direct methods using the SHELXTL programs and refined with full-matrix least squares on F^2 . Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined isotropically.

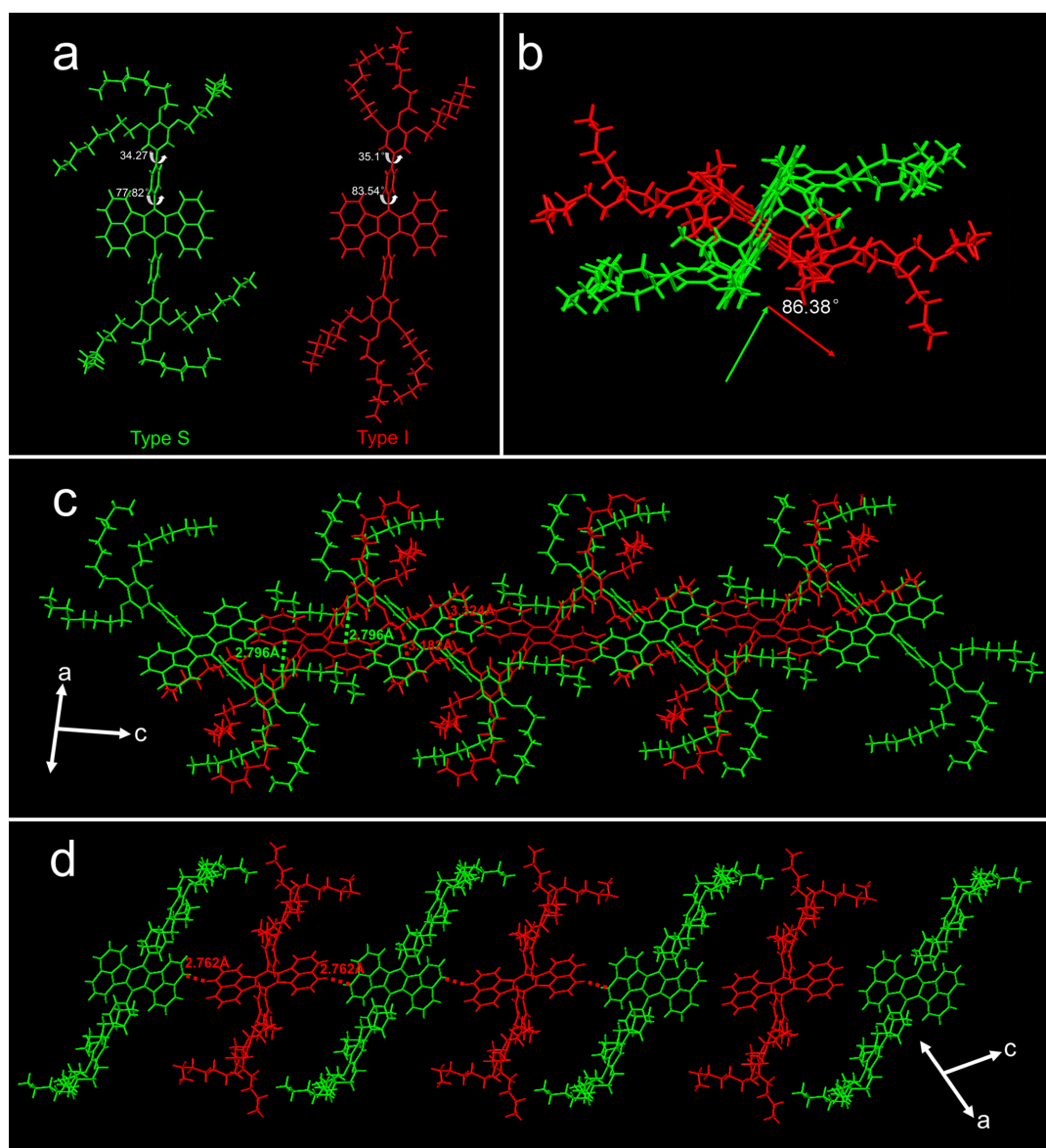


Figure S13. (a) The two conformations of **DPAF-8** molecules in the crystal structures; (b) view of the molecules arrangement in layer form along the ac axial plane; (c) Molecular packing along $[10\bar{1}]$ direction; (d) Molecular packing along $[101]$ direction.

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