Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Hydrogen-Bonded-Assisted Supramolecular Microwires for Pure Violet Lasers: Benefits of Preventing Intermolecular π-π Stacking and Aggregation in Single Crystals

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EXPERIMENTAL SECTION

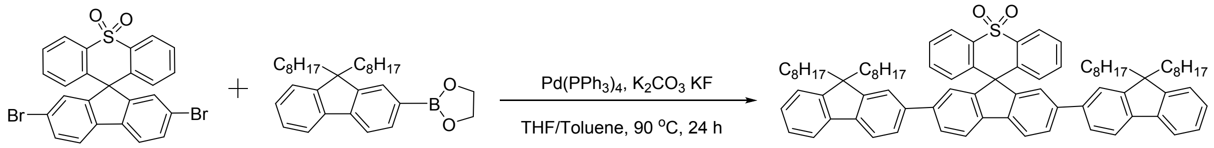
Materials: All solvents were purchased from Aldrich or J&K Chemicals without further purification. Anhydrous THF (HPLC grade) was obtained from Solvent Purification Systems (Innovative Technology, Inc.). Anhydrous chloroform was pre-dried over molecular sieves. DMF was dried over calcium hydride (CaH) and distilled under a dry nitrogen atmosphere immediately prior to use. The other solvents were distilled under a dry nitrogen atmosphere immediately prior to use.

Characterizations: ^{1}H NMR and ^{13}C NMR spectra were obtained using a Varian Mercury Plus 400 spectrometer with tetramethylsilane as the internal standard. Absorption and photoluminescence (PL) emission spectra were acquired in toluene solution using a PerkinElmer Lambda 35 spectrophotometer and a PerkinElmer LS55 spectrophotometer, respectively. The thin films of the DOF-SFSO were prepared via spin-coating on a quartz plate at the spin-coating speed of 800 rpm from toluene solution with a concentration of 8 mg mL^{-1}. Thermogravimetric analysis (TGA) was conducted via a Shimadzu thermogravimetry and differential thermal analysis DTG-60H at a heating rate of 10 ℃ min^{-1} under N_2. Differential scanning calorimetry (DSC) measurements were performed under a N_2 atmosphere at both the heating and cooling rates of 10 ℃ min^{-1} using Shimadzu DSC-60A. The absolute fluorescence quantum efficiency of DOF-SFSO was measured via Edinburgh Instruments FLS-920 in the integrating sphere. The single crystal data collection was performed at around 100 or 298 K via a Bruker 2000 CCD area detector using graphite-monochromated Mo Ka radiation (λ= 0.71073 Å). All structures were solved via direct methods using SHELXS-2015 and refined against F2 using SHELXL-2015. Hydrogen atoms were geometrically fixed and isotropically refined. The samples were examined with a field emission SEM (Hitachi, S-4800) at an accelerating voltage of 3 kV.

The experimental parameters of fluorescence lifetime measurements are show as follows. The incident 390-nm, 150-fs laser pulses were generated from a Coherent TOPAS-C optical parametric amplifier; pumped by a 1 kHz Coherent Legend regenerative amplifier that is seeded by a Coherent Vitesse oscillator. These input laser pulses were focused by a lens (*f* = 20 cm) on the sample solutions in a 1-mm-thick quartz cell (beam spot ~1 mm inside the cell). The emission from the samples was collected at a back scattering angle of 150° by a pair of lenses and directed to an Optronis Optoscope^{TM} streak camera system which has an ultimate temporal resolution of 6 ps.

ASE and microlaser characterization. For the film ASE study, the samples were optically pumped at 355 nm (match the maximum absorption wavelength) using a Q-switched, neodymium ion-doped yttrium aluminium garnet [Nd3+:YAG] laser (Continum Surelite II-10) pumped type-II b-BaB204[BBO] optical parametric oscillator (Panther EX) that delivered 5 ns pulses at the repetition rate of 1000 Hz. The pump beam was focused using a cylindrical lens to create a narrow stripe of 4 mm × 550 μm size on the sample surface in the perpendicular direction. Output signals were obtained using a fiber-coupled grating spectrometer (Andor Co.) equipped with a charge-coupled device (CCD) detector (Newton Co.). The pump source was a liquid-nitrogen-cooled cryostat (Janis ST-500, Microscope Cryostat) with 325 nm femtosecond pulse laser at a repetition of 1000 Hz. The lasing spectra of the microcrystals were excited by a focused 325 nm laser through a confocal m-PL system (OLYMPUS BX53). The size of the light spot was about 20 mm in diameter. The luminescent light was obtained through an optical multichannel analyzer (Princeton, Acton SP2500i), and the spectral resolution of the spectrometer was 0.167 nm. All the measurements were performed under an ambient atmosphere.

Preparation of the DOF-SFSO microcrystals. First, DOF-SFSO (2 mg) was dissolved in dichloromethane (2 ml) at room temperature. Then, hexane (6 ml) was quickly added to the DOF-SFSO solution under stirring. After being stirred for 15 min, the solution was left undisturbed overnight, and a large amount of wire-type microcrystals were formed.



Scheme S1. Synthetic route of DOF-SFSO.

Preparations of DOF-SFSO. Under N_2 atmosphere, a mixture of 2-(9,9-dioctylfluoren-2-yl)-1,3,2-dioxaborolane (1.15 g, 2.5 mmol), 2,7-DBrSFSO (0.54 g, 1.0 mmol), $Pd(PPh_3)_4$ (0.12 g, 0.1 mmol), 2 M K_2CO_3 solution (1.8 ml) and toluene/THF (20 ml, 1:1 v/v) was stirred and heated 90 °C for 24h. The mixture was abstracted with dichloromethane, and then the combined abstracts were dried by anhydrous $MgSO_4$. The solvent was evaporated under vacuum condition. The crude product was purified by silica gel column chromatography to afford white solid (0.95 g) with 82.1% yield. ^{1}H-NMR (400 Mz, $CDCl_3$) δ 8.31 (dd, J = 8.0, 0.8 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H), 7.81 (dd, J = 8.0, 1.6 Hz, 2H), 7.77 (s, 2H), 7.69-7.66 (m, 4H), 7.54-7.45 (m, 6H), 7.35-7.28 (m, 8H), 6.80 (d, J = 8.0 Hz, 2H), 1.96 (t, J = 8.0 Hz, 8H), 1.20-.1.13 (m, 8H), 1.12-1.02 (m, 32H), 0.80 (t, J = 6.8 Hz, 12H), 0.64-0.56 (m, 8H). ^{13}C-NMR (100 Mz, $CDCl_3$) δ 153.22, 151.54, 151.02, 142.12, 140.81, 140.59, 140.16, 139.17, 138.75, 137.03, 132.95, 129.03, 128.47, 127.46, 127.09, 126.75, 125.75, 124.13, 123.59, 122.90, 120.91, 120.69, 120.00, 119.78, 58.36, 55.18, 40.31, 31.76, 29.99, 29.19, 23.76, 22.58, 14.07.

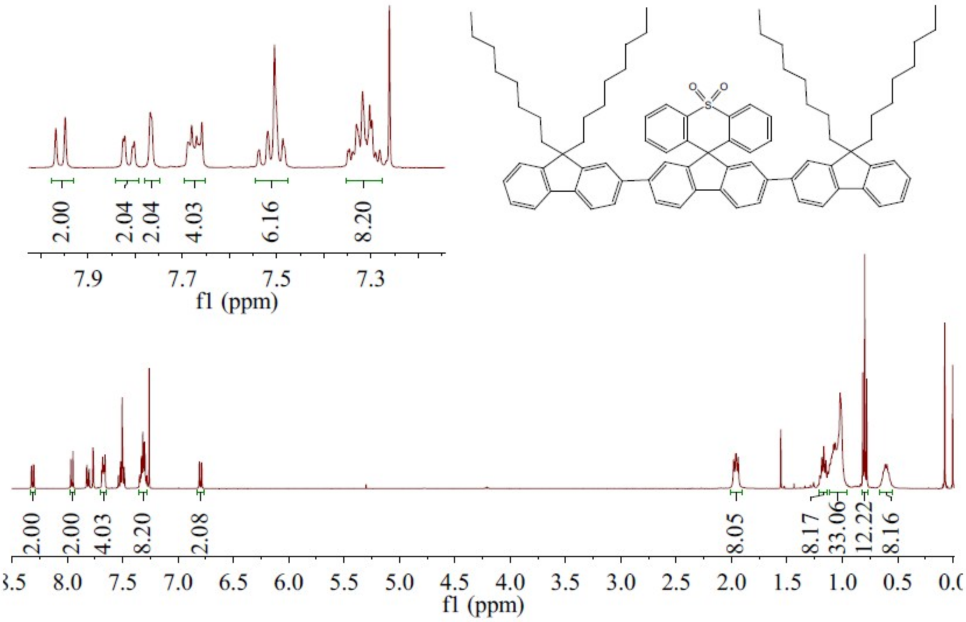


Figure S1. ^{1}H spectra of DOF-SFSO in CHCl$_3$.

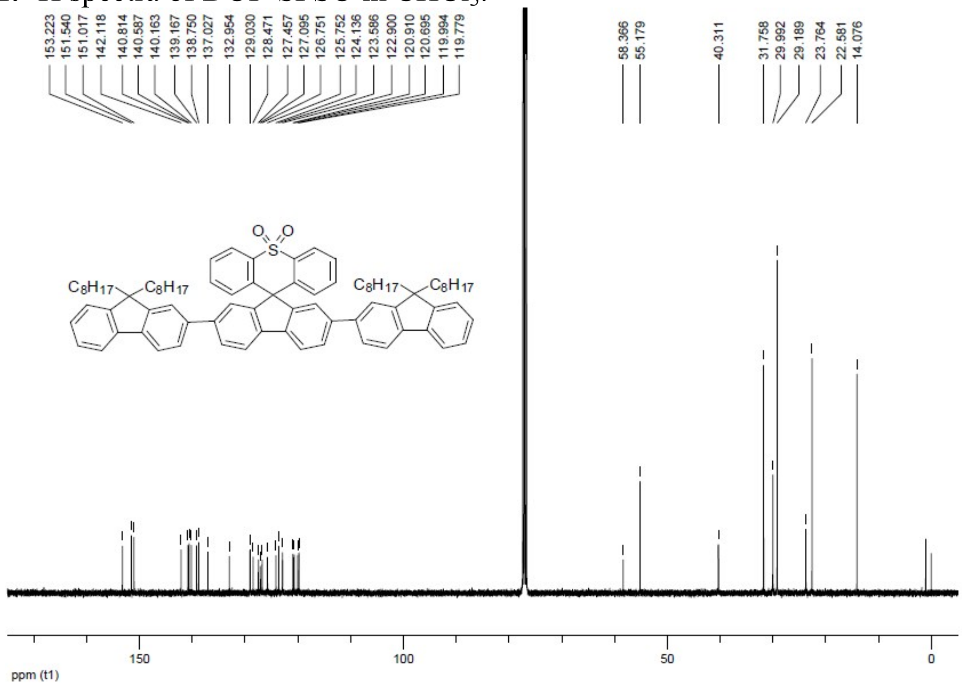


Figure S2. ^{13}C spectra of DOF-SFSO in CHCl$_3$.

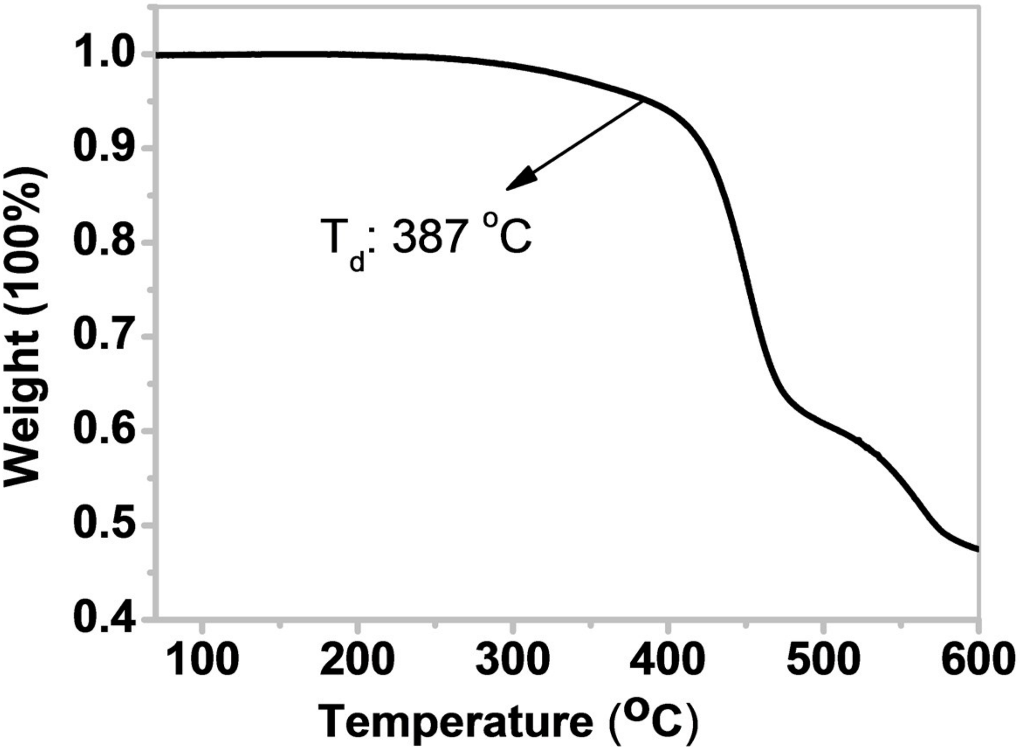


Figure S3. TGA curve of DOF-SFSO.

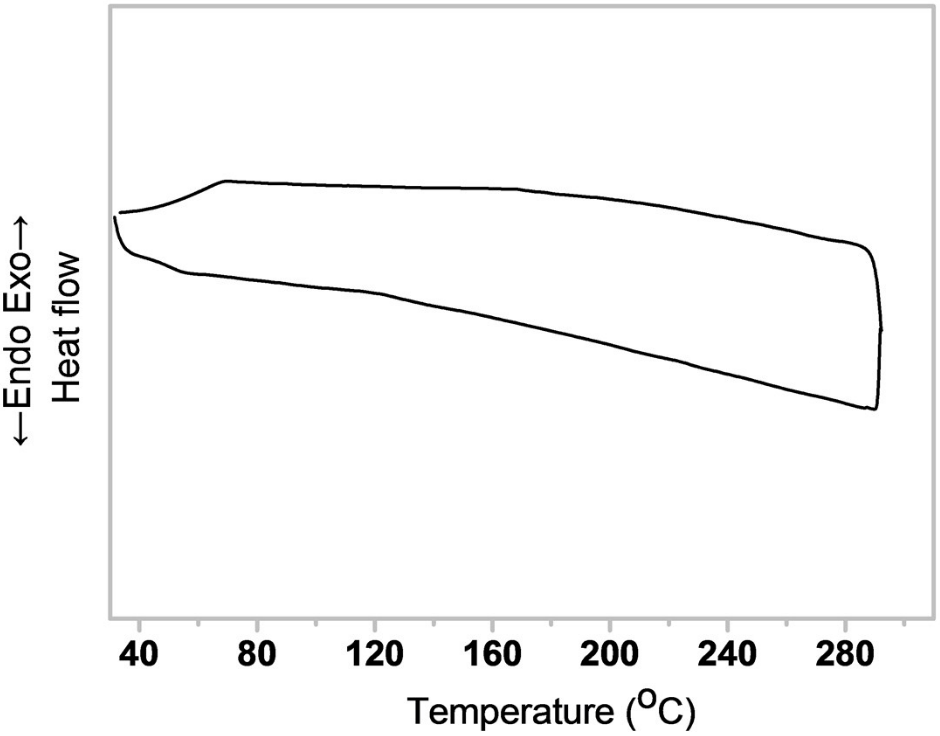


Figure S4. DSC curve of DOF-SFSO.

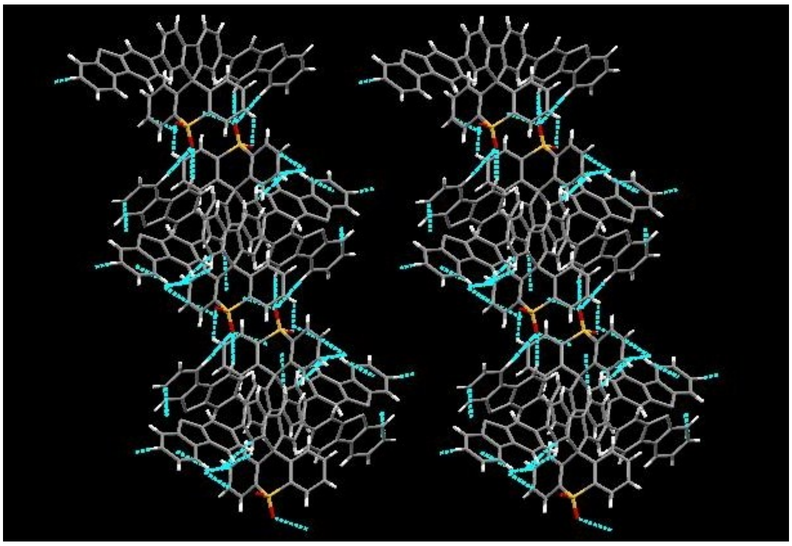


Figure S5. Molecular packing mode of DOF-SFSO in single crystals.