

## Supporting information

### **Spiro-Substitution Effect of Terfluorenes on Amplified Spontaneous Emission and Lasing Behaviors**

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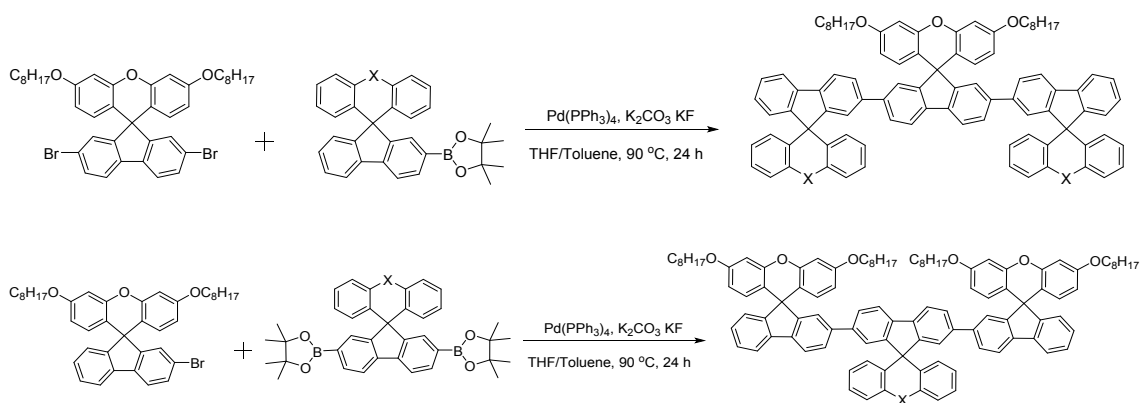


Fig. S1. Synthetic procedures.

## DSFX-OSFX

Under N<sub>2</sub> atmosphere, a mixture of 2,7-dibromo-3',6'-bis(octyloxy)spiro[fluorene-9,9'-xanthene] (0.75 g, 1.0 mmol), 4,4,5,5-tetramethyl-2-(spiro[fluorene-9,9'-xanthene]-2-yl)-1,3,2-dioxaborolane (1.15 g, 2.5 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.115 g, 0.1 mmol), 2M K<sub>2</sub>CO<sub>3</sub> solution (2.5 ml) and toluene/THF (30 ml, 1:1 v/v) was stirred and heated 90 °C for 18h. The mixture was abstracted with dichloromethane, and then the combined abstracts were dried by anhydrous MgSO<sub>4</sub>. The solvent was evaporated under vacuum condition. The crude product was purified by silica gel column chromatography to afford white solid (0.82 g) with 65.6% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.32 (s, 2H), 7.25 (s, 2H), 7.21 (d, *J* = 8.0 Hz, 4H), 7.19-7.12 (m, 8H), 6.76 (td, *J* = 7.6, 1.2 Hz, 2H), 6.70 (d, *J* = 2.0, 2H), 6.42 (d, *J* = 7.6, 4H), 6.32 (dd, *J* = 8.8, 2.0 Hz, 2H), 6.28 (d, *J* = 8.8 Hz, 2H), 3.91 (t, *J* = 6.8, 4H), 1.77-1.71 (m, 4H), 1.44-1.38 (m, 4H), 1.31-1.25 (m, 16H), 0.89 (t, *J* = 6.8 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.94, 156.55, 155.71, 155.31, 151.98, 151.35, 141.28, 141.08, 139.27, 138.81, 138.38, 128.92, 128.32, 128.08, 128.03, 127.76, 127.20, 126.96, 125.58, 124.81, 124.18, 124.00, 123.33, 120.04, 120.00, 119.95, 116.75, 116.38, 111.04, 101.71, 68.12, 54.31, 53.56, 31.81, 29.70, 29.33, 29.22, 26.05, 22.65, 14.09.

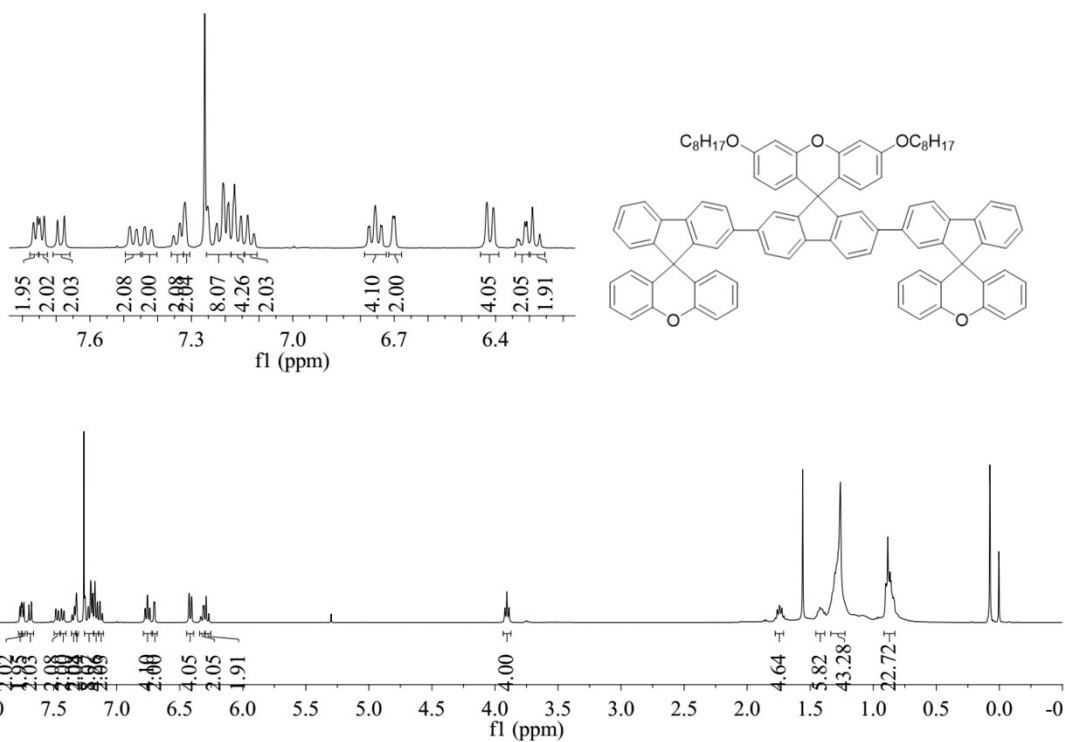


Fig. S2. <sup>1</sup>H-NMR spectrum of DSFX-OSFX.

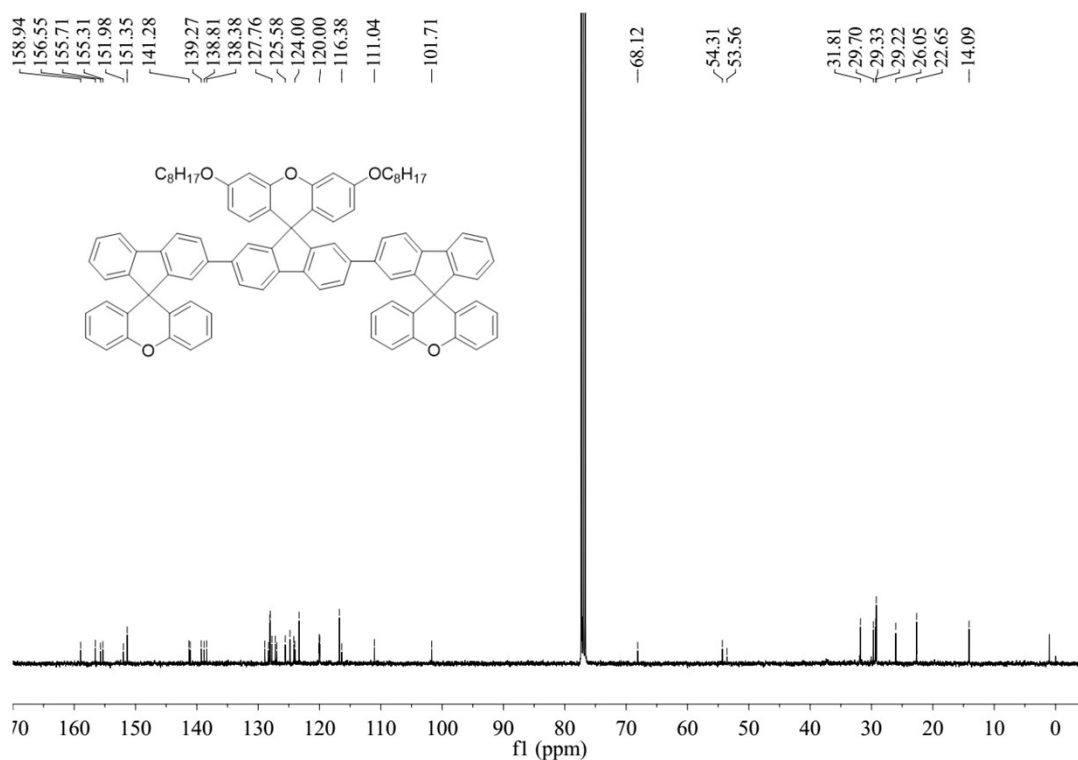


Fig. S3. <sup>13</sup>C-NMR spectrum of DSFX-OSFX.

## DSBF-OSFX

Under N<sub>2</sub> atmosphere, a mixture of 2,7-dibromo-3',6'-bis(octyloxy)spiro[fluorene-9,9'-xanthene] (0.75 g, 1.0 mmol), 4,4,5,5-tetramethyl-2-(spiro[fluorene-9,9'-xanthen]-2-yl)-1,3,2-dioxaborolane (1.10 g, 2.5 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.115 g, 0.1 mmol), 2M K<sub>2</sub>CO<sub>3</sub> solution (2.5 ml) and toluene/THF (30 ml, 1:1 v/v) was stirred and heated 90 °C for 18h. The mixture was abstracted with dichloromethane, and then the combined abstracts were dried by anhydrous MgSO<sub>4</sub>. 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 78.1% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.83 (d, *J* = 7.6 Hz, 4H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.37-7.30 (m, 8H), 7.18 (s, 2H), 7.10-7.05 (m, 6H), 6.87 (s, 2H), 6.73 (d, *J* = 7.6 Hz, 4H), 6.66 (d, *J* = 8.8 Hz, 4H), 6.28 (dd, *J* = 8.8, 2.4 Hz, 2H), 6.22 (d, *J* = 8.4 Hz, 2H), 3.89 (d, *J* = 6.4 Hz, 4H), 1.77-1.71 (m, 4H), 1.44-1.38 (m, 4H), 1.31-1.25 (m, 16H), 0.89 (t, *J* = 6.8 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.88, 156.48, 151.90, 149.26, 149.09, 148.69, 141.77, 141.23, 141.16, 141.06, 140.85, 138.25, 128.96, 127.85, 124.17, 122.54, 120.09, 116.34, 111.01, 101.61, 68.10, 66.01, 53.47, 31.85, 29.37, 26.08, 22.70, 14.16, 1.06.

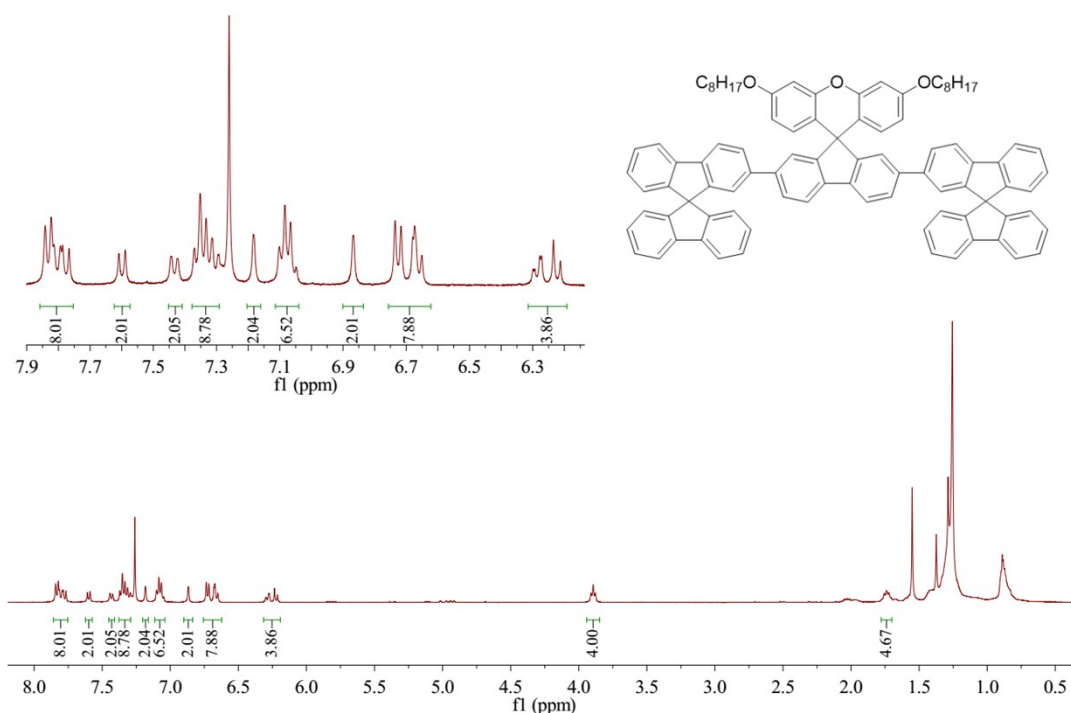


Fig. S4. <sup>1</sup>H-NMR spectrum of DSBF-OSFX.

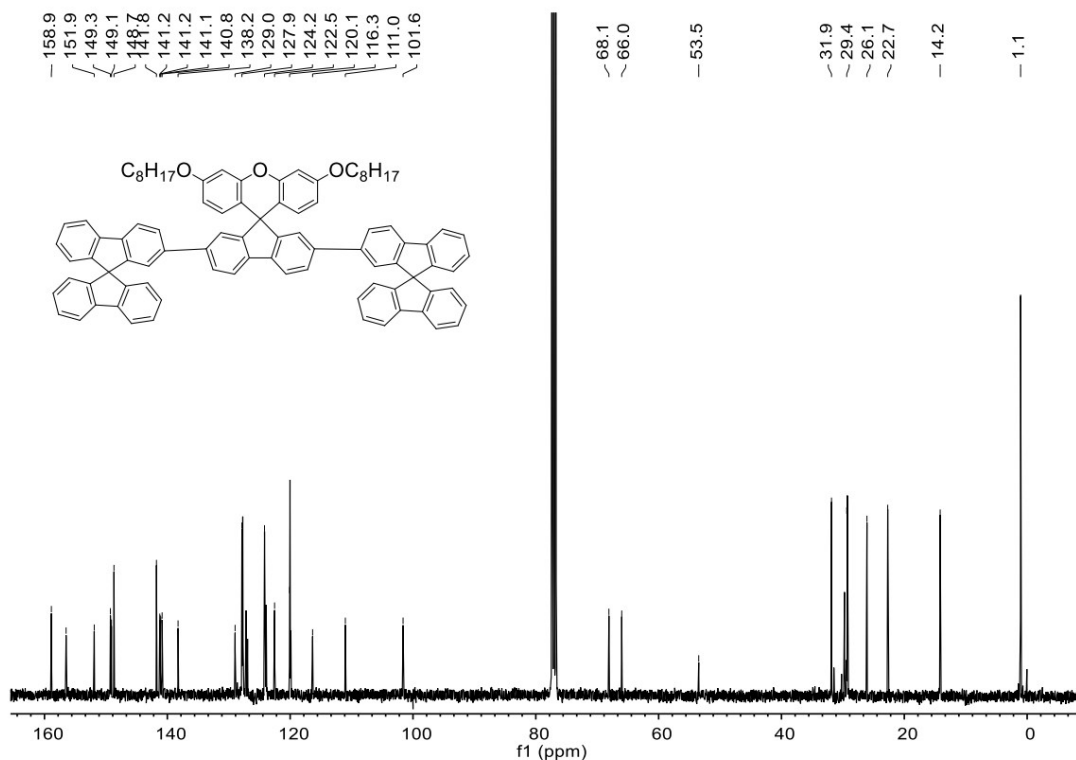


Fig. S5.  $^{13}C$ -NMR spectrum of DSBF-OSFX.

## DOSFX-SFX

Under  $N_2$  atmosphere, a mixture of 2,7-dibromospiro[fluorene-9,9'-xanthene] (0.49 g, 1.0 mmol), 2-(3',6'-bis(octyloxy)spiro[fluorene-9,9'-xanthene]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.57g, 2.2 mmol),  $Pd(PPh_3)_4$  (0.115 g, 0.1 mmol), 2M  $K_2CO_3$  solution (2.0 ml) and toluene/THF (20 ml, 1:1 v/v) was stirred and heated  $90^\circ C$  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 (0.98 g) with 65.1% yield.  $^1H$ -NMR(400 Mz,  $CDCl_3$ )  $\delta$  7.74-7.71(m, 6H), 7.47(dd,  $J = 8.0, 1.6$  Hz, 2H), 7.43(dd,  $J = 8.0, 1.6$  Hz, 2H), 7.31(t,  $J = 7.6$  Hz, 2H), 7.29(d,  $J = 4.0$  Hz, 4H), 7.23(dd,  $J = 8.0, 1.6$  Hz, 2H), 7.19(dd,  $J = 7.6$  Hz, 2H), 7.17-7.15(m, 2H), 7.09(d,  $J = 7.6$  Hz, 2H), 6.76(dd,  $J = 7.6, 1.6$  Hz, 2H), 6.71(d,  $J = 1.6$  Hz, 4H), 6.44(dd,  $J = 8.0, 2.4$  Hz, 2H), 6.33(dd,  $J = 8.4, 2.4$  Hz, 4H), 6.27(d,  $J = 8.4$  Hz, 4H), 3.91(t,  $J = 6.8$  Hz, 8H), 1.78-1.71(m, 8H), 1.46-1.39(m, 8H), 1.34-1.27(m,

32H), 0.89(t,  $J = 2.8$  Hz, 12H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.95, 156.11, 156.06, 155.93, 152.03, 151.31, 141.25, 141.09, 139.14, 138.79, 138.44, 128.79, 128.30, 128.19, 128.11, 127.57, 127.20, 126.96, 125.52, 124.71, 123.10, 124.08, 123.41, 120.10, 119.97, 119.85, 116.82, 116.51, 111.02, 101.68, 68.12, 54.38, 53.48, 31.82, 29.34, 29.23, 29.21, 26.06, 22.66, 14.10.

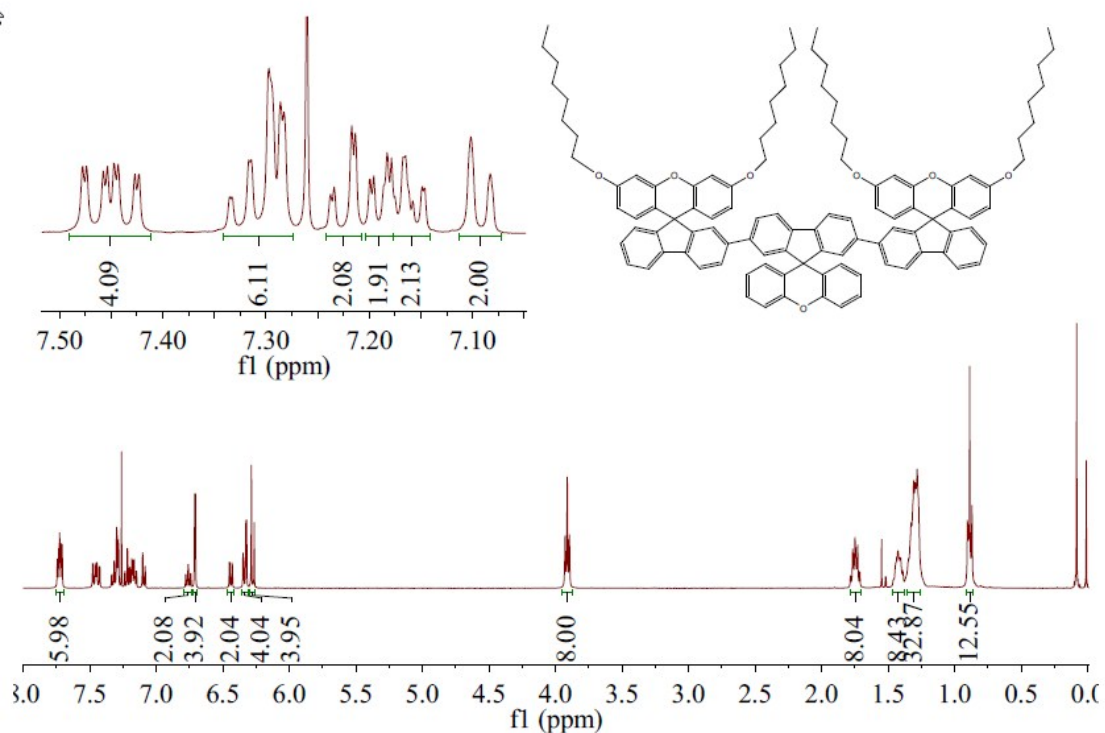


Fig. S6.  $^1\text{H}$ -NMR spectrum of DOSFX-SFX.

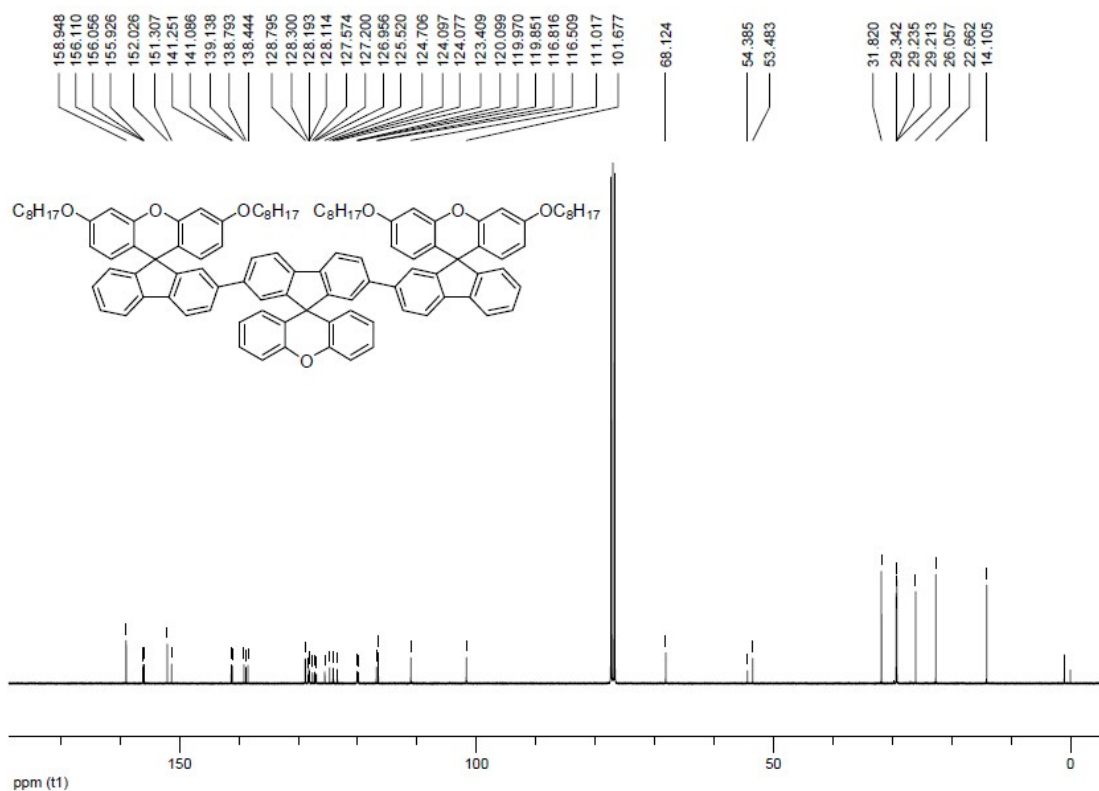


Fig. S7.  $^{13}\text{C}$ -NMR spectrum of DOSFX-SFX.

## DOSFX-SBF

Under  $\text{N}_2$  atmosphere, a mixture of 2,7-dibromo-9,9'-spirobifluorene (0.47 g, 1.0 mmol), 2-(3',6'-bis(octyloxy)spiro[fluorene-9,9'-xanthen]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.57 g, 2.2 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.115 g, 0.1 mmol), 2M  $\text{K}_2\text{CO}_3$  solution (2.0 ml) and toluene/THF (20 ml, 1:1 v/v) was stirred and heated  $90^\circ\text{C}$  for 24h. The mixture was abstracted with dichloromethane, and then the combined abstracts were dried by anhydrous  $\text{MgSO}_4$ . The solvent was evaporated under vacuum condition. The crude product was purified by silica gel column chromatography to afford white solid (1.1 g) with 73.4% yield.  $^1\text{H}$ -NMR(400 Mz,  $\text{CDCl}_3$ )  $\delta$  7.84(d,  $J = 7.6$  Hz, 2H), 7.76(d,  $J = 8.0$  Hz, 2H), 7.70(d,  $J = 7.6$  Hz, 2H), 7.65(d,  $J = 8.0$  Hz, 2H), 7.44(dd,  $J = 8.0, 1.6$  Hz, 2H), 7.36(t,  $J = 8.0$  Hz, 2H), 7.33(d,  $J = 8.0$  Hz, 2H), 7.29(t,  $J = 7.6$  Hz, 2H), 7.23(s, 2H), 7.14(t,  $J = 7.6$  Hz, 2H), 7.09(t,  $J = 7.6$  Hz, 2H), 7.09(d,  $J = 7.6$  Hz, 2H), 6.84(s, 2H), 6.75(d,  $J = 7.2$  Hz, 2H), 6.69(sd,  $J = 2.4$  Hz, 4H), 6.31(d,  $J = 8.4, 2.4$  Hz, 4H), 6.24(d,  $J = 8.4$  Hz, 4H), 3.90(t,  $J = 6.4$  Hz, 8H), 1.78-1.71(m, 8H), 1.45-1.38(m, 8H), 1.34-1.27(m, 32H), 0.88(t,  $J = 6.8$  Hz, 12H).  $^{13}\text{C}$ -NMR(100 Mz,  $\text{CDCl}_3$ )

$\delta$  158.93, 156.15, 155.80, 152.00, 149.65, 148.65, 141.81, 141.22, 140.83, 140.55, 139.06, 138.74, 128.80, 128.25, 127.90, 127.74, 127.53, 127.20, 126.95, 125.48, 124.30, 124.18, 122.40, 120.11, 120.08, 119.86, 119.81, 116.51, 111.00, 101.65, 68.12, 53.45, 53.43, 31.83, 29.35, 29.24, 29.21, 26.06, 22.67, 14.12.

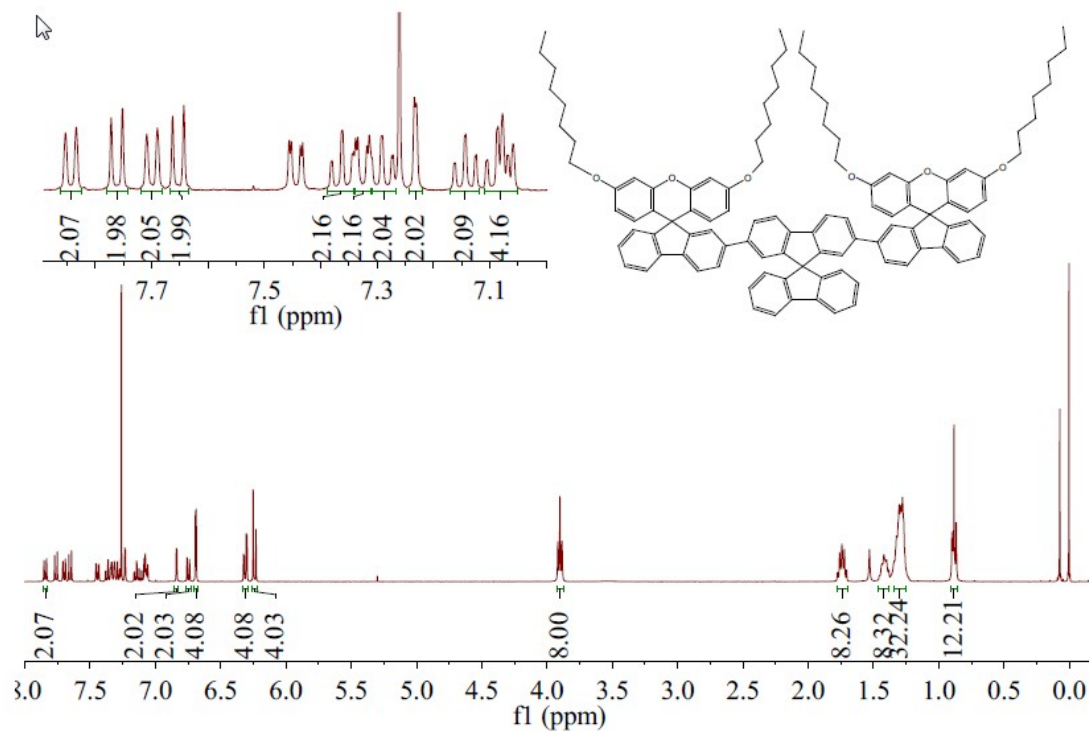


Fig. S8. <sup>1</sup>H-NMR spectrum of DOSFX-SBF.



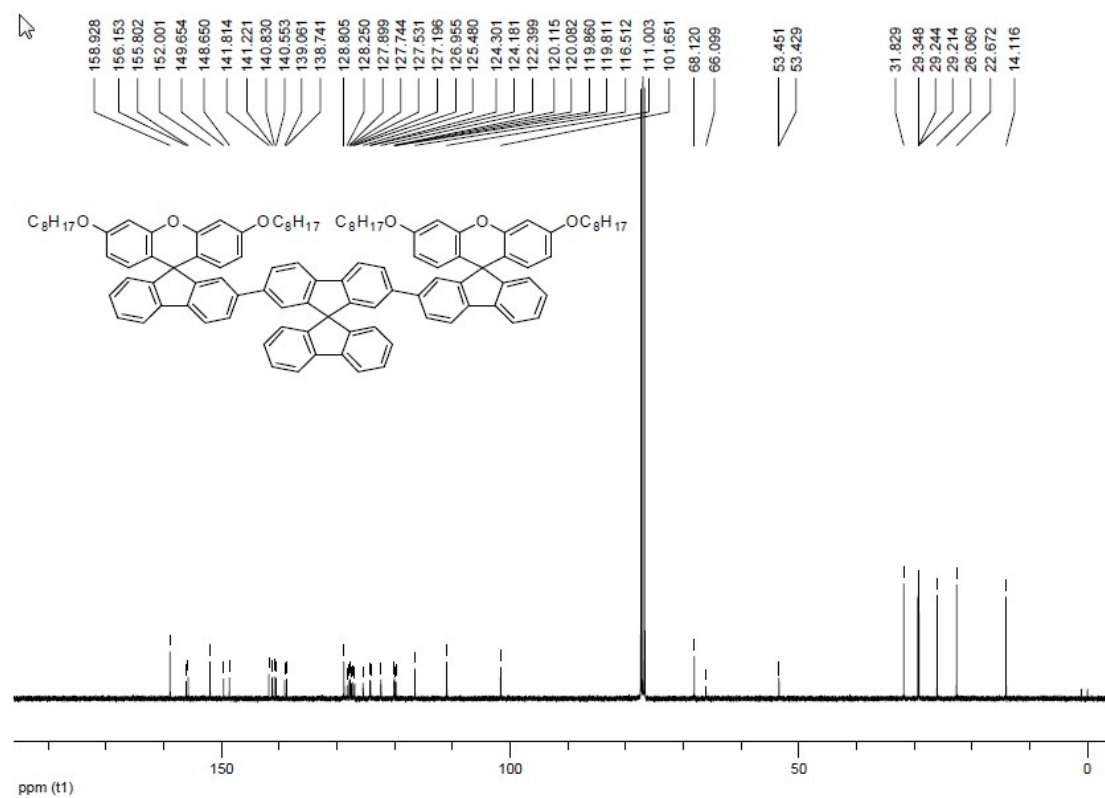


Fig. S9.  $^{13}\text{C}$ -NMR spectrum of DOSFX-SBF.

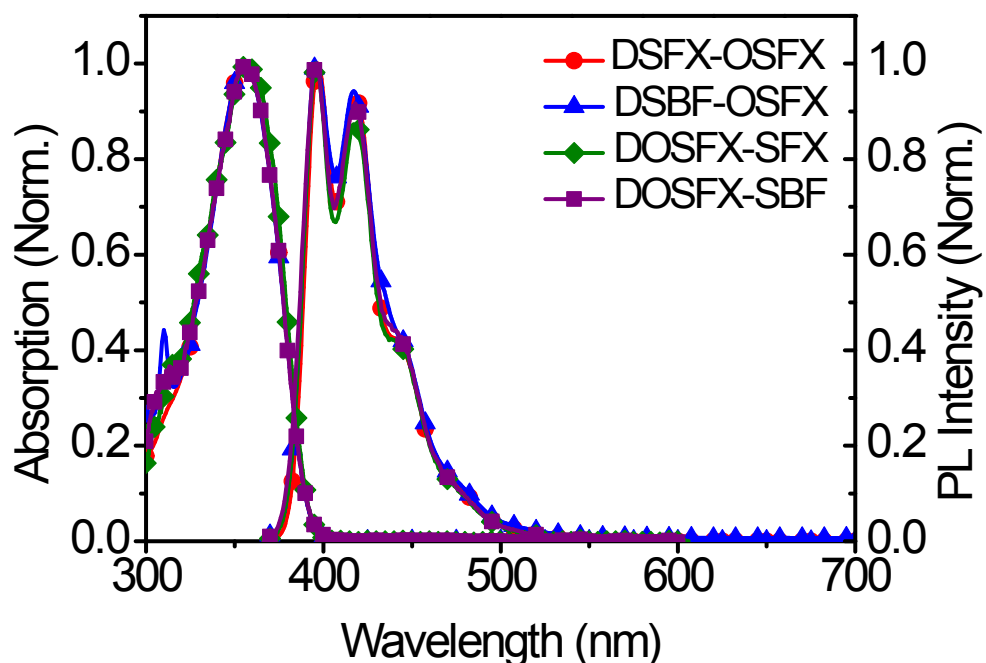


Fig. S10. Absorption and emission spectra of DSFX-OSFX, DSBF-OSFX, DOSFX-SFX and DOSFX-SBF in toluene solution.

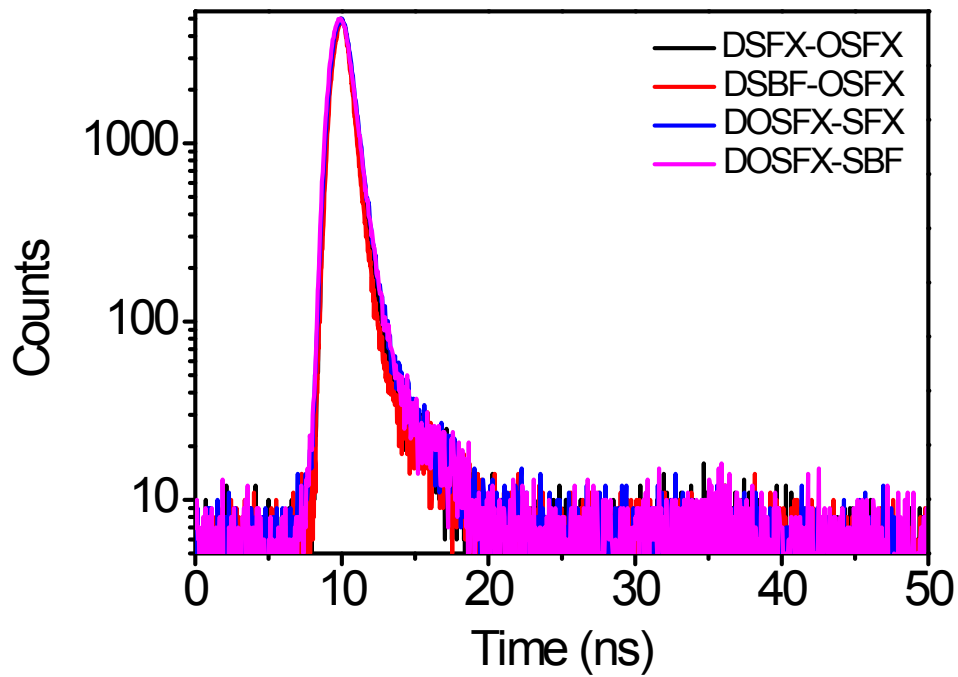


Fig. S11. Fluorescence decay of DSFX-OSFX, DSBF-OSFX, DOSFX-SFX and DOSFX-SBF film samples.

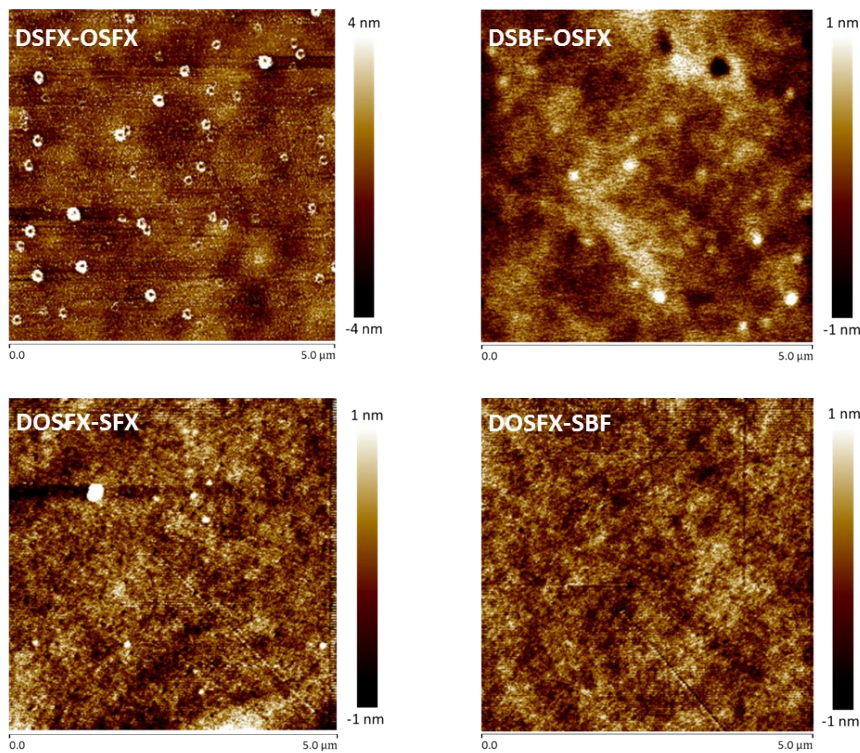


Fig. S12. AFM topography images of DSFX-OSFX, DSBF-OSFX, DOSFX-SFX and DOSFX-SBF film. The root mean square roughness is 1.54, 0.329, 0.462, and 0.297 nm for DSFX-OSFX, DSBF-

OSFX, DOSFX-SFX and DOSFX-SBF, respectively.

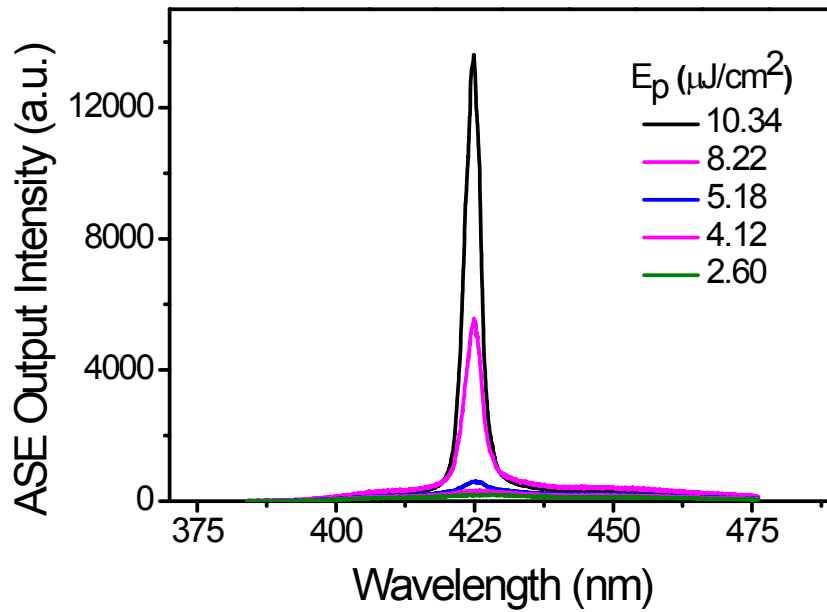


Fig. S13. The ASE emission intensity of the DSFX-OSFX waveguide as a function of the wavelength at various pump energy densities.

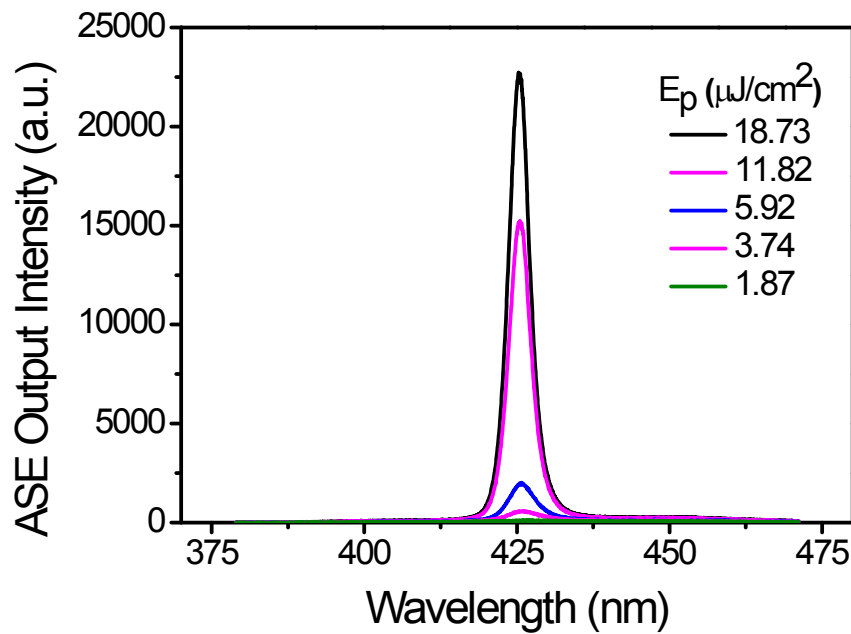


Fig. S14. The ASE emission intensity of the DSBF-OSFX waveguide as a function of the wavelength at various pump energy densities.

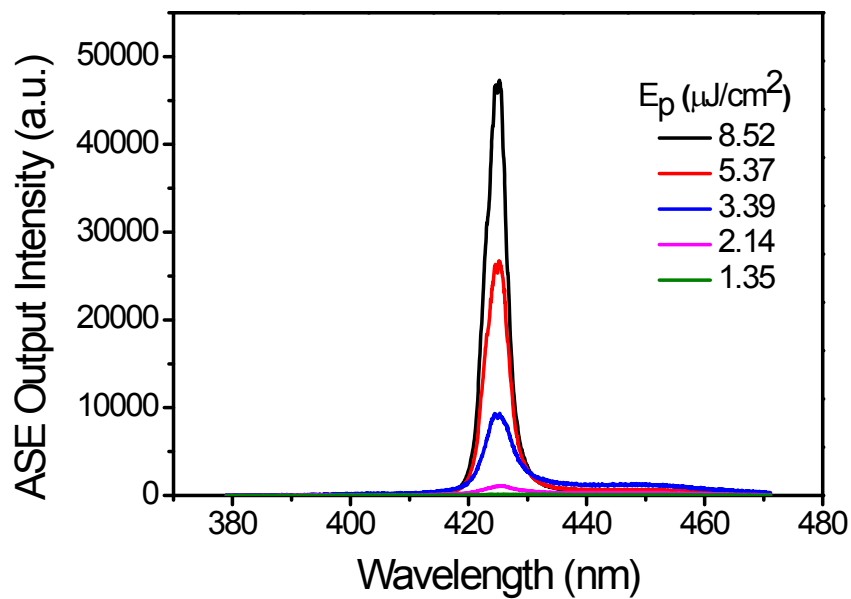


Fig. S15. The ASE emission intensity of the DOSFX-SFX waveguide as a function of the wavelength at various pump energy densities.

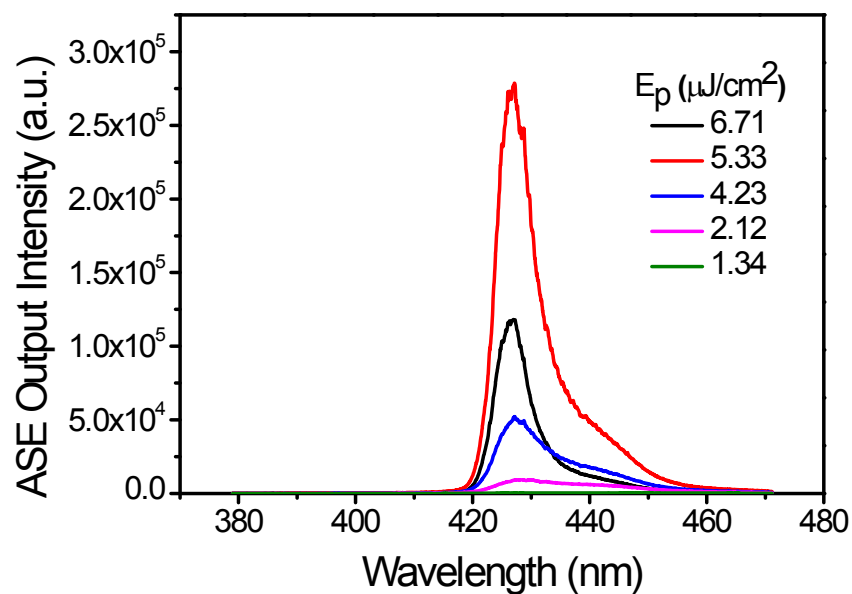


Fig. S16. The ASE emission intensity of the DOSFX-SBF waveguide as a function of the wavelength at various pump energy densities.

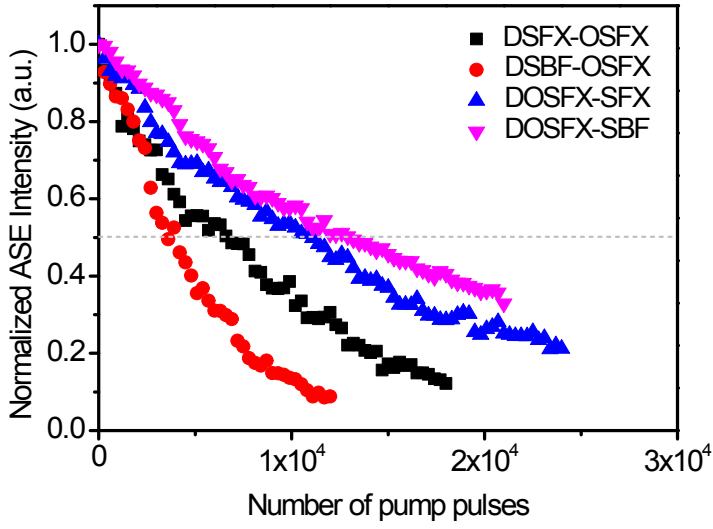


Fig. S17. Normalized ASE intensity as a function of the number of pump pulses in ambient atmosphere for DSFX-OSFX, DSBF-OSFX, DOSFX-SFX and DOSFX-SBF films.

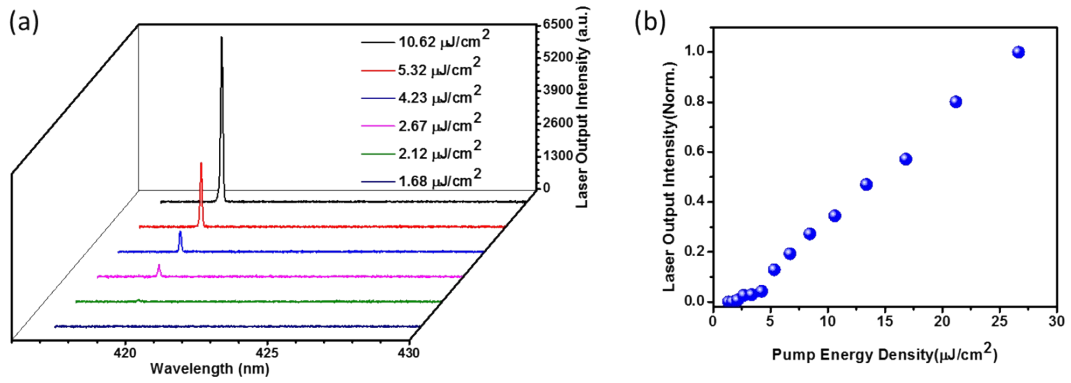


Fig. S18. (a) The laser emission spectra of DOSFX-SFX as a function of the pump energy density. (b) Laser output as a function of the pump energy density for DOSFX-SFX.

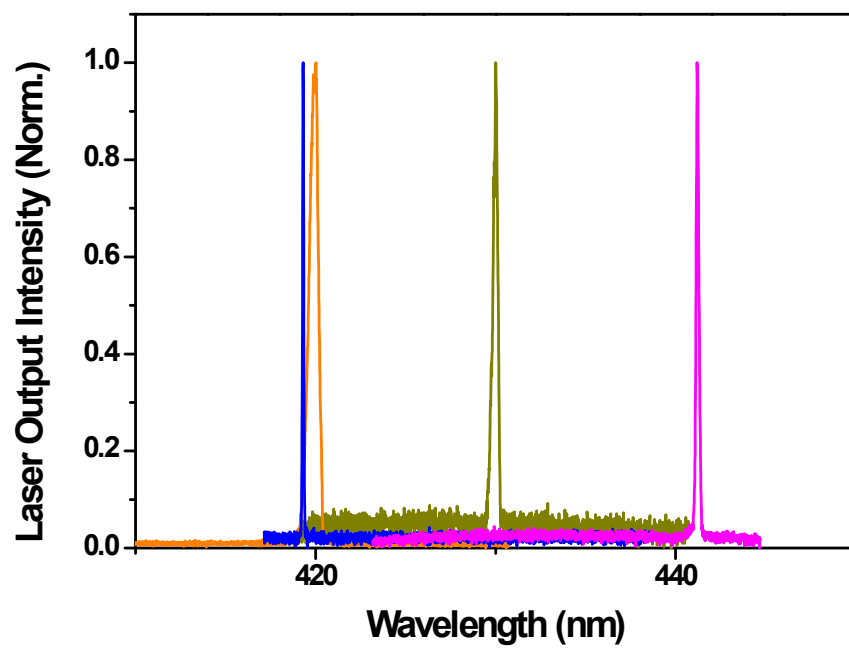


Fig. S19. Laser emission spectra of 1-D DFB laser from DOSFX-SFX and DOSFX-SBF. The emission peaks: 419 nm and 441 nm (DOSFX-SFX); 420 nm and 430 nm (DOSFX-SBF).