# **Supplementary Information for**

# Pyrene-Capped Starburst Emitters as Gain Media for Organic Lasers: Design, Synthesis, and Stabilized Lasing Properties

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#### 1. Experimental

#### 1.1 General methods

All samples for photophysical measurements including UV-vis absorption and photoluminescence, photoluminescence quantum yields (PLQY), PL decay, and ASE characterizations were prepared by spin-coating 66-180 nm thick films on precleaned quartz substrates from chloroform solutions (20 mg/mL and 30 mg/mL). UV-vis absorption and photoluminescence spectra were recorded by using Shimadzu UV-Vis-NIR spectrophotometer and Shimadzu Luminescence Spectrometer LS 50, respectively. PLQY of films were measured by using an integrating sphere. PL decay times were measured with Edinburgh FLSP920 lifetime spectrometer. Measurements of surface morphology were conducted by Bruker icon Dimension with scanAsyst atomic force microscopy (AFM). Determinations of film thicknesses were conducted on Bruker DektakXT Stylus Profiling System.

As for ASE characterizations, all samples were optically pumped by using a frequency-tripled pulsed Q-switched Nd<sup>3+</sup>:YAG laser system with 5 ns output pulses at a repetiton rate of 10 Hz. The raw pulsed beam from the laser passed through an adjustable slit to be spatially formed, and then was focused with acylindrical lens (with focal length f = 10 cm) to form a 4.1 mm×440 µm stripe-shaped excitation area on the sample. The pump energy incident on the sample was tuned by the insertion of a set of calibrated neutral density filters into the beam path. The edge emission from the slab waveguide was collected by a fiber-coupled spectrograph and recorded by a charge coupled device (CCD) detector.

For the investigation of the photostability, samples were annealed at each temperature (from 60 °C to 300 °C) for 5 min in ambient atmosphere and then cooled down fast to room temperature. The ASE actions were recorded including the threshold and the spectra.

As for the study of water-oxygen sensitivity of the materials, samples (active materials spin-coated on the quartz substrates) were first bathed in water (80°C) for 10 min, blew dry with

nitrogen and annealed at 160°C in ambient atmosphere for 5 min, and then cooled down fast to room temperature. Finally, standard ASE measurements were utilized to evaluate the ASE performance of the organic gain media.

The DFB gratings (50% fill factor, 30 nm modulation depth) were fabricated by nanoimprint lithography (NIL) method with periods of 280 nm, 290 nm, 300 nm. The DFB lasers were fabricated by spin-coating the active materials on the top of gratings.

Lasing characterizations were carried out by similar methods as the ASE measurements. The pump beam from the Nd<sup>3+</sup>:YAG laser was focused into a circular spot area of  $3.6 \times 10^{-3}$  cm<sup>2</sup> with a diameter of 681 µm.

For OLED devices, a 40 nm PEDOT:PSS was spin-coated on the ITO substrate after ultraviolet (UV)-ozone treating for 4 min and dried at 120°C in a vacuum oven for 15 min. The active area of the device is 13.5 mm<sup>2</sup>. SF-PyF or Py-PyF as the emitting layer (EML) was spin-coated from CHCl<sub>3</sub> solution.

#### 1.2. Materials

All reagents and solvents, unless otherwise specified, were obtained from Aldrich, Acros, and TCI Chemical Company and were used as received. All manipulations involving air sensitive reagents were performed in a dry argon atmosphere. PEDOT:PSS (Clevios TM AI4083) was used as purchased from Heraeus.

# 1.3. Synthesis

The synthetic procedures for monomer 4,4,5,5-tetramethyl-2-(pyren-1-yl)-1,3,2-dioxaborolane (1), (2,7-dibromo-9,9-bis(6-bromohexyl)-9H-fluorene) (2) and 1,3,6,8-tetrabromopyrene (5) are described in our previous work [*Macromol. Rapid Commun.* 2008, *29*, 659; *Adv. Funct. Mater.* 2015, *25*, 4617].

1.3.1. Synthesis of 1-(7-bromo-9,9-dihexyl-9H-fluoren-2-yl)pyrene (3)

Monomer **1** (0.60 g, 0.18 mmol), monomer **2** (2.69 g, 0.54 mmol), Aliquat 336 (3 drops) and Pd(PPh<sub>3</sub>)<sub>4</sub> (70 mg) were placed into a 150 mL vessel. A mixture of 2M K<sub>2</sub>CO<sub>3</sub> aqueous solution (7 mL) and toluene (21 mL) were added to the vessel and then refluxed at 95°C for 12 h under nitrogen. After the mixture was cooled to room temperature, water and DCM were added. The organic portions were dried over anhydrous magnesium sulfate, and then filtered. The residue was purified by column chromatography over silica using ethyl acetate/petroleum mixtures (1:6 ~ 1:2) as eluent. A white powder was obtained (0.50 g, 45%). mp 85 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.29 – 8.17 (m, 4H), 8.16 – 8.10 (m, 2H), 8.09 – 8.01 (m, 3H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.68 – 7.60 (m, 3H), 7.57 – 7.51 (m, 2H), 2.13 – 1.94 (m, 4H), 1.24 – 1.05 (m, 12H), 0.83 (t, *J* = 7.0 Hz, 10H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 153.3, 150.5, 140.4, 139.9, 139.2, 138.1, 131.5, 131.0, 130.6, 130.1, 129.5, 128.6, 127.7, 127.3, 126.2, 126.0, 125.4, 124.5, 121.2, 119.7, 55.6, 40.3, 31.5, 29.7, 23.9, 22.6.

*1.3.2.* Synthesis of 2-(9,9-dihexyl-7-(pyren–1-yl)-9H-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4)

A 250 mL two-neck flask was injected with compound **3** (2.0 g, 3.26 mmol), 4,4,5,5tetramethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolane (10.0 g, 35.56 mmol), potassium acetate (4.15 g, 71.12 mmol), Pd (dppf)<sub>2</sub>Cl<sub>2</sub> (120 mg) and 1,4-dioxane (60 mL). The mixture was deoxygenated (by placing under vacuum and backfilling with argon) and then heated at 100°C under argon for 24 h. The resulting solution was extracted with DCM, and the combined organic layers were dried over anhydrous MgSO<sub>4</sub>. After the solvent was evaporated, the residue was purified by chromatography using silica gel (light petroleum:ethyl acetate = 5:1) to afford compound **4** (1.05 g, 51%) as a white solid. mp 162 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.29 – 8.17 (m, 4H), 8.11 (dd, *J* = 14.4, 5.0 Hz, 3H), 8.04 (dd, *J* = 8.5, 4.5 Hz, 2H), 7.91 (dd, *J* = 12.4, 4.4 Hz, 2H), 7.84 (d, *J* = 2.8 Hz, 2H), 7.66 – 7.60 (m, 2H), 2.07 (d, *J* = 7.3 Hz, 4H), 1.44 (s, 12H), 1.12 (s, 12H), 0.81 (t, *J* = 6.9 Hz, 10H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 151.4, 150.2, 143.9, 140.4, 140.1, 138.3, 133.9, 131.5, 131.0, 130.5, 129.3, 128.9, 128.6, 127.6, 127.5, 127.2, 126.0, 125.4, 125.2, 124.5, 120.1, 119.2, 83.7, 77.0, 76.7, 55.3, 40.2, 31.5, 29.7, 25.0, 23.8, 22.6.

# 1.3.3. Synthesis of SF-PyF

Monomer **4** (1.04 g, 1.58 mmol), 2,2',7,7'-tetrabro-9,9'-spirodifluorene (200 mg, 0.32 mmol) and Aliquat 336 (3 drops) and Pd(PPh<sub>3</sub>)<sub>4</sub> (62 mg) were placed into a 150 mL vessel. A mixture of 2M K<sub>2</sub>CO<sub>3</sub> aqueous solution (7 mL) and toluene (21 mL) was added to the vessel. The mixture was then heated at 95°C under argon for 12 h. After the mixture was cooled to room temperature and then water (10 mL) and dichloromethane (10 mL) were added. The organic layer was separated and the aqueous layer was extracted with dichloromethane ( $3\times10$  mL). The organic portions were dried and filtered. The filtrate was collected and the residue was purified by column chromatography over silica using ethyl acetate/petroleum mixtures ( $1:6 \sim 1:2$ ) as eluent to give compound SF-PyF as a white solid (0.17 g, 21.7%). mp 290 °C; TGA<sub>(5%)</sub> 393 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.26 – 7.99 (m, 40H), 7.86 (d, J = 8.2 Hz, 8H), 7.75 (d, J = 7.9 Hz, 4H), 7.64 – 7.49 (m, 16H), 7.29 (s, 4H), 2.13 – 1.97 (m, 16H), 1.25 (d, J = 3.9 Hz, 16H), 1.16 – 1.06 (m, 48H), 0.76 (t, J = 6.9 Hz, 24H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 151.8, 151.1, 150.0, 141.5, 140.8, 140.2, 139.8, 138.3, 131.5, 131.0, 130.5, 129.3, 128.6, 127.6, 127.4, 126.3, 126.0, 125.3, 124.8, 122.7, 121.3, 120.5, 119.9, 119.7, 77.3, 77.0, 76.7, 55.4, 40.3, 31.4, 29.6, 23.9, 22.5.

#### 1.3.4. Synthesis of Py-PyF

Monomer 4 (1.04 g, 1.58 mmol), 1,3,6,8-tetrabromopyrene (165 mg, 0.32 mmol), and Aliquat 336 (3 drops) and Pd(PPh<sub>3</sub>)<sub>4</sub> (62 mg) were placed into a 150 mL vessel. A mixture of 2M K<sub>2</sub>CO<sub>3</sub> aqueous solution (7 mL) and toluene (21 mL) was added to the vessel. The mixture was then heated at 95°C under argon for 12 h. After the mixture was cooled to room temperature and then water (10 mL) and dichloromethane (10 mL) were added. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3×10 mL). The organic portions were dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent was removed.

The residue was purified by column chromatography over silica using ethyl acetate/petroleum mixtures (1:6 ~ 1:2) as eluent to give compound Py-PyF as a white solid (0.18 g, 23.7%). mp >330 °C; TGA<sub>(5%)</sub> 402 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.45 – 7.90 (m, 50H), 7.81 (s, 8H), 7.69 (s, 8H), 2.14 (s, 16H), 1.17 (s, 48H), 0.99 (s, 16H), 0.77 (s, 24H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 151.5, 151.2, 140.1, 138.3, 137.9, 131.5, 131.0, 130.5, 129.6, 129.4, 129.2, 128.5, 127.7, 127.4, 126.0, 125.4, 124.9, 119.8, 77.3, 77.0, 76.1, 55.5, 40.3, 31.5, 29.7, 24.1, 22.6.

# 2. <sup>1</sup>H NMR and MALDI-TOF spectra



Fig. S1a<sup>1</sup>H NMR spectra of SF-PyF in CDCl<sub>3</sub>.



**Fig. S1b** <sup>1</sup>H NMR spectra of Py-PyF in CDCl<sub>3</sub>.



Fig. S1c MALDI-TOF mass spectra for SF-PyF.



Fig. S1d MALDI-TOF mass spectra for Py-PyF.



Fig. S2 (a) TGA and (b) DSC curves of SF-PyF and Py-PyF.



**Fig. S3** Configurations and the corresponding HOMO and LUMO electron cloud distributions of SF-PyF and Py-PyF.



Fig. S4 CV curves for (a) SF-PyF and (b) Py-PyF in films.

Table S1. Electrochemical Properties of SF-PyF and Py-PyF.<sup>a</sup>

Compound	$E_{\mathrm{ox}},$	$E_{\rm red}$ ,	$E_{\mathrm{HOMO}}$ ,	$E_{\text{LUMO}},$	$E_{g}^{CV}$ ,	$E_{g}^{opt}$ ,	$E_{\rm g}^{\rm \ cal},$
	$\mathbf{V}^b$	$\mathrm{V}^b$	$eV^c$	$eV^{c}$	$eV^d$	eV <sup>e</sup>	eV <sup>f</sup>
SF-PyF	1.06	-2.47	-5.86	-2.33	3.53	2.96	3.14
Py-PyF	0.94	-2.48	-5.74	-2.32	3.42	2.73	3.07

<sup>*a*</sup>CV curves of the drop-coated film were measured in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> acetonitrile solution at a scan rate of 50 mV s<sup>-1</sup> at room temperature (*versus* Ag/Ag<sup>+</sup>). <sup>*b*</sup>Onset oxidation (*p*-doping) and reduction (*n*-doping) potentials *versus* Ag/Ag<sup>+</sup>. <sup>*c*</sup>Estimated from the onset oxidation and reduction potential by using  $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.80)$  eV and  $E_{\text{LUMO}} = -(E_{\text{red}} + 4.80)$  eV. <sup>*d*</sup>Electrochemical band gaps ( $E_{g}^{\text{CV}}$ ) determined by using  $E_{g} = E_{\text{LUMO}} - E_{\text{HOMO}}$ . <sup>*e*</sup>Optical band gaps ( $E_{g}^{\text{opt}}$ ) obtained from the absorption onsets in film states. <sup>*f*</sup>Calculated band gaps ( $E_{g}^{\text{cal}}$ ) obtained from Gaussian simulation.

# 3. Electroluminescent properties



Fig. S5 The device configuration and the corresponding energy diagram.



**Fig. S6** (a) Current density–voltage curves, (b) Brightness–voltage curves, (c) Efficiency–current density characteristics, (d) Electroluminescence spectra of the devices obtained from CBP host doped with various concentrations of Py-PyF.

4. ASE stability with increasing the annealing temperatures in ambient atmosphere.



**Fig. S7** The normalized emission spectra well above thresholds for (a) SF-PyF, (b) Py-PyF, and (c) PFO with increasing the annealing temperatures in ambient atmosphere. RT means room temperature.

5. ASE stability with increasing the treatment cycles.



**Fig. S8** The ASE spectra well above thresholds for (a) SF-PyF, (b) Py-PyF and (c) PFO with increasing the treatment times up to 7 cycles in boiling water and annealing in air conditions. RT means room temperature.