**Supporting information**

**Low, threshold amplified spontaneous emission and ambipolar charge transport in non-volatile liquid fluorene derivatives**

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**Experimental Procedure**

**Synthesis of the fluorene derivatives**

![Synthesis diagram]

Scheme.S1 Synthetic route for the preparation of the fluorene-based compounds 1 to 4.

All reagents and chemicals were purchased from commercial sources (Aldrich, Across, Fluka) and used without further purification. All reactions were carried out in an argon
atmosphere, except for the hydrosilylation reactions where oxygen atmosphere was used. Toluene and THF solvents were distilled over appropriate drying agent(s) prior to use and were purged with nitrogen.

**Compound a.** To a mixture of fluorene (3 g, 18.0 mmol) and a catalytic amount of triethylbenzylammonium chloride in DMSO (200 mL) and NaOH 50% (10 mL) was added allyl bromide (5 g, 41.3 mmol) in one portion. The reaction mixture was stirred at room temperature for 5h and then quenched with AcOEt. The organic layer was washed with dilute HCl (2×), water (3×), dried over MgSO$_4$ and finally concentrated. The residue was purified by column chromatography on silica gel with petroleum ether:CH$_2$Cl$_2$ 10:1 as eluent providing the desired product a as a yellow oil (3.6 g, 81 %).

$^1$H NMR (CDCl$_3$-300 MHz): $\delta$ (ppm) = 7.89-7.70 (m, 2H), 7.54-7.23 (m, 4H), 5.40-5.20 (m, 2H), 5.00-4.72 (m, 4H), 2.76 (d, 4H, J = 7.3 Hz); $^{13}$C NMR (CDCl$_3$-75 MHz): $\delta$ (ppm) = 149.3 / 140.7 / 133.7 / 127.1 / 127.0 / 123.6 / 119.8 / 117.5 / 54.2 / 43.5.

**Compound 1.** Compound a (400 mg, 1.6 mmol), 1,1,1,3,3,5,5-heptamethyltrisiloxane (1.1 mL, 4.1 mmol), toluene (20 mL) and the Karstedt catalyst (300 ppm/SiH of platinum-divinyltetramethylsiloxane complex, 3-3.5% Pt content) were combined in a flask under oxygen atmosphere. The mixture was stirred overnight at 60°C. Then, after removing the solvent, the crude product was purified by column chromatography on silica gel with petroleum ether:CH$_2$Cl$_2$ 10:1 as eluent providing the desired product 1 as a colorless liquid (1.1 g, 94 %). $^1$H NMR (CDCl$_3$-300 MHz): $\delta$ (ppm) = 7.77-7.61 (m, 2H), 7.41-7.16 (m, 6H), 2.12-1.85 (m, 4H), 0.86-0.58 (m, 4H), 0.43-0.20 (m, 4H), 0.14 to -0.27 (m, 42H); $^{13}$C NMR (CDCl$_3$-75 MHz): $\delta$ (ppm) = 150.5 / 141.0 / 126.9 / 126.6 / 122.7 / 119.6 / 55.3 / 44.0 / 18.6 / 17.4 / 1.8 / 1.0 / 0.2. Purity > 99.5% as measured by GC-MS (EI), with m/z 690.33 (M$^+$) and 221.08 (Me$_3$SiOSiMe$_2$O$^+$). Anal. Calcd. (found) for C$_{33}$H$_{62}$O$_4$Si$_6$: C, 57.33 (56.92), H, 9.04 (8.97). UV-Vis absorption peaks in CH$_2$Cl$_2$, $\lambda$/nm ($\varepsilon$/L.mol$^{-1}$.cm$^{-1}$): 266 (15800), 293 (6800), 304 (10000).

**Compound b.** The same procedure was used as for compound a, starting from 2-bromofluorene (6 g, 24.4 mmol), DMSO (250 mL), NaOH 50% (15 mL) and allyl bromide (6.5 g, 53.8 mmol). The column chromatography was performed with petroleum ether as eluent providing the desired product b as a white solid (6.3 g, 79 %). $^1$H NMR (CDCl$_3$-300 MHz): $\delta$ (ppm) = 7.73-7.66 (m, 1H), 7.60-7.54 (m, 2H), 7.52-7.47 (m, 2H), 7.45-7.40 (m, 1H), 7.39-7.35 (m, 2H), 6.37-5.18 (m, 2H), 4.95-4.74 (m, 4H), 2.72 (d, 4H, J = 7.2 Hz); $^{13}$C NMR (CDCl$_3$-75 MHz): $\delta$ (ppm) = 151.5 / 148.9 / 139.8 / 139.6 / 133.1 / 130.2 / 127.4 / 126.9 / 123.6 / 121.1 / 120.8 / 119.8 / 118.0 / 54.4 / 43.3.

**Compound c.** A 30 mL microwave tube was placed into a glove box and filled with compound b (820 mg, 2.52 mmol), 2,2'-bipyridine (510 mg, 3.27 mmol), Ni(COD)$_2$ (900 mg, 3.27 mmol). Then, degassed COD (400 µL, 3.27 mmol) and dry toluene (15 mL) were introduced under argon and the tube was placed into a microwave oven (Anton Paar, Monowave 300). The resulting mixture was irradiated for 20 min at 130°C (power monitored by the temperature). The reactional mixture was cooled down to room temperature and was passed through a celite pad, rinsed with chloroform and the filtrate was washed with water (3
× 100 mL). The organic phase was dried over MgSO₄ and the solvent was removed under reduced pressure. The residue was finally chromatographed on silica gel with petroleum ether:CH₂Cl₂ 5:1 as eluent to provide the pure compound e (475 mg, 77%). ¹H NMR (CDCl₃-300 MHz): δ (ppm) = 7.85-7.60 (m, 8H), 7.50-7.30 (m, 6H), 5.55-5.30 (m, 4H), 5.00-4.75 (m, 8H), 2.84 (m, 8H); ¹³C NMR (CDCl₃-75 MHz): δ (ppm) = 149.3 / 140.7 / 133.7 / 127.1 / 127.0 / 123.6 / 119.8 / 117.5 / 54.2 / 43.5. MS (Maldi-TOF): m/z 490.16 (M+).

**Compound 2.** The same procedure was used as for compound 1, starting from compound e (400 mg, 0.816 mmol), 1,1,1,3,3,5,5-heptamethyltrisiloxane (1.11 mL, 4.1 mmol), toluene (20 mL) and the Karstedt catalyst (300 ppm/SiH). Purification by column chromatography provided the desired compound 2 as a colorless liquid (1.08 g, 96%). ¹H NMR (CDCl₃-300 MHz): δ (ppm) = 7.85-7.25 (m, 14H), 2.18-2.05 (m, 8H), 0.95-0.80 (m, 8H), 0.45-0.35 (m, 8H), 0.10 to -0.20 (m, 84H); ¹³C NMR (CDCl₃-75 MHz): δ (ppm) = 151.4 / 150.9 / 141.0 / 140.4 / 127.1 / 127.0 / 126.4 / 123.01 / 121.6 / 120.0 / 119.9 / 55.7 / 44.4 / 18.8 / 17.7 / 2.0 / 1.4 / 0.4. MS (Maldi-TOF): m/z 1379.19 (M+).

**Compound d.** The same procedure was used as for compound 1, starting from compound b (500 mg, 1.5 mmol), 1,1,1,3,3,5,5-heptamethyltrisiloxane (1 mL, 4.1 mmol), toluene (20 mL) and the Karstedt catalyst (300 ppm/SiH). Purification by column chromatography provided the desired compound c as a colorless liquid (0.9 g, 77%). ¹H NMR (CDCl₃-300 MHz): δ (ppm) = 7.70-7.62 (m, 1H), 7.57-7.51 (m, 1H), 7.49-7.40 (m, 2H), 7.35-7.28 (m, 1H), 2.08-1.88 (m, 4H), 0.77-0.60 (m, 4H), 0.39-0.25 (m, 4H), 0.11 to -0.26 (m, 42H); ¹³C NMR (CDCl₃-75 MHz): δ (ppm) = 150.1 / 149.6 / 140.4 / 140.3 / 139.9 / 133.8 / 127.2 / 126.9 / 126.4 / 123.7 / 122.4 / 120.0 / 119.8 / 54.2 / 43.5.

**Compound e.** Under an argon atmosphere, a solution of 9,9-dioctyl-2,7-dibromofluorene (2 g, 3.6 mmol) in THF (10 mL) was cooled to -78°C. Then n-BuLi 2.5 M in hexane (3.2 mL, 8 mmol) was added dropwise. The solution was kept at -40°C during 10min, warmed up to room temperature during 15 min and then cooled back at -78°C before being quenched by trimethyltin chloride 1 M in THF (9.1 mL, 9.1 mmol). The cooling bath was removed and the mixture was stirred under argon overnight at room temperature. Water was then added under vigorous stirring. The mixture was extracted with CH₂Cl₂, washed with water (∗3) and dried over MgSO₄. The solvent was removed under reduced pressure and was further dried under high vacuum providing the desired compound e as a yellow oil (1.8 g, 70 %). Although slightly contaminated with the started material, this monostannylated compound was used without further purification in the next step. ¹H NMR (CDCl₃-300 MHz): δ (ppm) = 7.74-7.61 (m, 2H), 7.53-7.29 (m, 4H), 2.04-1.80 (m, 4H), 1.30-0.99 (m, 20H), 0.82 (t, 6H, J = 6.7 Hz), 0.75-0.58 (m, 4H), 0.33 (s, 18H).

**Compound 3.** (9,9-dioctyl-9H-fluorene-2,7-diyl)bis(trimethylstannane) e (265 mg, 0.4 mmol) and compound d (600 mg, 0.8 mmol) were dissolved in dry toluene (25 mL). Then, Pd₂dba₃ (10 mg, 10.9 µmol) and P-(o-tolyl)₃ (13 mg, 42.7 µmol) were added and the reaction mixture was stirred at 120°C for 3 days under argon atmosphere. The reaction mixture was filtered through a pad of celite and the solution was concentrated under high vacuum. The
crude product was purified by column chromatography on silica gel with petroleum ether:CH₂Cl₂ 6:1, providing the desired compound 3 as a colorless oil (352 mg, 54 %). ¹H NMR (CDCl₃-300 MHz): δ (ppm) = 7.94-7.76 (m, 6H), 7.51-7.61 (m, 8H), 7.49-7.31 (m, 6H), 2.29-2.06 (m, 12H), 1.37-1.19 (m, 20H), 0.99-0.77 (m, 18H), 0.51-0.16 (m, 8H), 0.16 to -0.16 (m, 84H); ¹³C NMR (CDCl₃-75 MHz): δ (ppm) = 151.7 / 151.3 / 150.8 / 140.8 / 140.7 / 140.6 / 140.3 / 139.9 / 126.9 / 126.8 / 126.1 / 122.9 / 121.4 / 119.9 / 119.8 / 119.7 / 55.5 / 55.3 / 44.1 / 40.5 / 31.9 / 30.1 / 29.2 / 23.9 / 22.6 / 18.6 / 17.6 / 14.0 / 1.8 / 1.6 / 0.3. MS (Maldi-TOF): m/z 1768.90 [M⁺]. Anal. Calcd. (found) for C₇₀H₁₆₂O₈Si₁₂: C, 64.49 (64.58), H, 9.23 (9.13). UV-Vis absorption peaks in CH₂Cl₂, λ/nm (ε/L.mol⁻¹.cm⁻¹) : 352 (86000).

**Compound f.** Under an argon atmosphere, a solution of 2,2'-bithiophene (1.2 g, 7.2 mmol) in THF (8 mL) was cooled to -78°C. Then n-BuLi 2.5 M in hexane (6.1 mL, 15.4 mmol) was added dropwise. The solution was kept at -40°C during 10 min, warmed up to room temperature during 15 min and then cooled back at -78°C before to be quenched by trimethyltin chloride 1 M in THF (16.0 mL, 16.0 mmol). The cooling bath was removed and the mixture was stirred under argon overnight at room temperature. Water was then added under vigorous stirring. The mixture was extracted with CH₂Cl₂, washed with water (×3) and dried over MgSO₄. The solvent was removed under reduced pressure and was further dried under high vacuum providing the desired compound f as a blue solid (3.2 g, 93 %). It should be noted that, although slightly contaminated with the started material, this monostannylated compound was used without further purification in the next step. ¹H NMR (CDCl₃-300 MHz): δ (ppm) = 7.50 (d, 2H, J = 3.4 Hz), 7.30 (d, 2H, J = 3.4 Hz), 0.62 (s, 18H); ¹³C NMR (CDCl₃-75 MHz): δ (ppm) = 143.2 / 137.0 / 136.1 / 125.1 / -7.9.

**Compound 4.** 5,5'-trimethylstannyl-2,2'-bithiophene (150 mg, 0.3 mmol) and compound d (500 mg, 0.6 mmol) were dissolved in dry toluene (7 mL). Then, Pd₂dba₃ (13 mg, 14.6 μmol) and P-(o-tolyl)₃ (17 mg, 58.4 μmol) were added and the reaction mixture was stirred at 120°C for 3 days under argon atmosphere. The reaction mixture was filtered through a pad of celite and the solution was concentrated under high vacuum. The crude product was purified by column chromatography on silica gel with petroleum ether:CH₂Cl₂ 5:1, providing the desired compound 3 as a lightly yellow wax (0.3 g, 62 %). ¹H NMR (CDCl₃-300 MHz): δ (ppm) = 7.74-7.67 (m, 4H), 7.62-7.58 (m, 4H), 7.42-7.28 (m, 8H), 7.23 (d, 2H, J = 3.3 Hz), 2.20-1.95 (m, 8H), 0.94-0.67 (m, 8H), 0.37 (t, 8H, J = 8 Hz), 0.12 to -0.23 (m, 84H); ¹³C NMR (CDCl₃-75 MHz): δ (ppm) = 151.4 / 150.6 / 143.9 / 140.8 / 140.5 / 136.4 / 132.8 / 127.1 / 126.8 / 124.5 / 124.3 / 123.4 / 122.8 / 120.1 / 119.8 / 119.7 / 55.5 / 44.1 / 18.6 / 17.5 / 1.8 / 1.3 / 0.2. MS (Maldi-TOF): m/z 1542.61 [M⁺]. Anal. Calcd. (found) for C₇₄H₁₂₈O₈S₂Si₁₂: C, 57.53 (57.07), H, 8.22 (8.24). UV-Vis absorption peaks in CH₂Cl₂, λ/nm (ε/L.mol⁻¹.cm⁻¹) : 404 (55000).

**Characterization of the chemical properties**

¹H and ¹³C NMR spectra were recorded on a Bruker Avance 300 and a Bruker 400 Ultrashield™ NMR spectrometers, with an internal lock on the ²H-signal of the solvent (CDCl₃). UV-visible absorption spectroscopy measurements were performed using a Hitachi U-3000 spectrophotometer. Mass spectra analyses were performed by using a Maldi-TOF or
an electron ionization technique. The former were carried out on a time-of-flight mass spectrometer (MALDI-TOF-TOF Autoflex II TOF-TOF, Bruker Daltonics, Bremen, Germany) equipped with a nitrogen laser ($\lambda = 337$ nm) at the Laboratory of Bio-Organic Mass Spectrometry (LMSBO) from the University of Strasbourg. An external multi-point calibration was carried out before each measurement. Scan accumulation and data processing were performed with FlexAnalysis 3.0 software. The latter mass spectra measurements were carried out on a gas chromatograph coupled with an electron ionization mass spectrometer (GC-MS) 7090-5975C from Agilent Technologies. Differential Scanning Calorimetry (DSC) measurements were performed on a Q2000 equipment from TA instrument equipped with a LNCS (liquid nitrogen cool system) cooling system in the temperature range of -80 to +150°C, at a heating and cooling rates of 5°C.min$^{-1}$. Measurements were performed on samples (3-5 mg) placed into 10 mL aluminum pans under nitrogen.

Characterization of the photophysical properties

For the steady-state absorption spectra and PL measurements in solution, the molecules 1 to 4 were dissolved at low concentration in degased chloroform. The solutions were then placed in a 1 cm quartz cuvette. The photophysical measurements in solvent-free liquid materials were carried out in two different systems; the neat film of 3 and the blend 1:4 (50:50 wt.%). For this latter composite system, the molecules 1 and 4 were mixed in chloroform solution and the blend was used after the full evaporation of the residual solvent. The liquid organic layers were obtained by capillarity between two identical flat pre-cleaned fused silica substrates. Thickness of the liquid films was controlled by using silica microspheres with a diameter of 1 $\mu$m.

The absorption and steady-state PL spectra of both solutions and liquid films were recorded using an UV-vis spectrophotometer (Perkin-Elmer Lambda 950-PKA) and a spectrofluorometer (Jasco FP-6500), respectively. The PLQYs were measured using a xenon lamp with an excitation wavelength of 340 nm and an integrating sphere (C11347-11 Quantaurus QY, Hamamatsu Photonics). Regarding the characterization of the ASE properties, the liquid films were optically-pumped using a pulsed nitrogen laser at 337 nm. Pulse duration and repetition rate of this laser source were 800 ps and 8 Hz, respectively. About the size of the excitation spot onto the samples, the excitation beam was focused into a stripe of 0.5 cm x 0.08 cm. The pump intensity was varied by using a set neutral density filters. An optical fiber coupled to a CCD spectrometer was used to collect the emission spectra and intensities from the edge of the liquid organic layers.

Fabrication and characterization of the solvent-free liquid organic DFB laser

An ultra-violet (UV) curable polyurethaneacrylate (PUA) mixture was synthesized in accordance with previous reports.$^{3,4}$ The PUA mixture was drop-dispensed onto a master-pattern silicon (Si) mold which consists of one-dimensional (1D) grating structure with a period (height) of 140 nm (100 nm), and it was brought into contact with a polyethyleneterephthalate (PET) film. Then the PUA mixture was exposed to UV light ($\lambda \sim 365$ nm) for several minutes through the UV transparent PET film. After the UV curing, the
PET film was easily peeled off from the Si mold, and the PUA replica of the master pattern was prepared on the PET film as shown in Scheme S2a. The prepared PUA replica with the corrugated pattern was subsequently covered with a flat pre-cleaned fused silica substrate. Silica microsphere spacers (of ~1 µm diameter) were used for a fixed gap distance between the PUA replica and the fused silica cover. The gap between the PUA replica and the cover was then filled with the liquid terfluorene derivative 3 by capillary action to complete the device structure as shown in Scheme S2b.

Scheme S2 (a) SEM image of the PUA replica with 1D grating structure. Length between the two red lines (~140.6 nm) indicates a period of the structure. (b) Schematic illustration of the solvent-free liquid organic DFB laser prepared by capillary action of the liquid terfluorene derivative 3.

Characterization of the charge transport properties

The samples for the TOF measurements are prepared by capillary-filling the liquid semiconductors into commercial liquid crystal cells based on two ITO coated glass substrates. Thickness between the two ITO electrodes is 10 µm. Regarding the setup used for the TOF measurements, the samples were irradiated by a pulsed nitrogen laser emitting 800 ps pulses at 337 nm with a repetition rate of 8 Hz. The penetration depth estimated from the absorption coefficient at 337 nm was found to be around 200-250 nm in 2 and 3 neat films. The thickness of the liquid layers is thus large enough by respect to the penetration depth of the light in the materials to ensure a proper estimation of the charge carrier mobilities. The photogeneration of a photocarrier sheet leads to a transient photocurrent signal, which is amplified and monitored using a digital storage oscilloscope (Agilent Technologies DSO5034A). The resistance-capacitance RC time constant of our setup is evaluated to be around 5 µs which is fast enough to properly determine the charge carrier mobilities in the liquid materials. Note that both hole and electron mobilities were probed by changing the polarity of the applied electric field.

The transit time (t_tr) of the charge carrier packet is determined from the inflection point found in the photocurrent transients. The charge carrier mobilities can then be calculated using the standard equation \( \mu = d / (t_{tr} \times E) \), where d is the liquid film thickness and E is the magnitude of the applied electric field.
Fig. S1a. $^1$H-NMR spectrum of molecule 1 in CDCl$_3$
Fig. S1b. $^{13}$C-NMR spectrum of molecule 1 in CDCl$_3$
Fig. S1c. GC chromatogram of molecule 1.
Fig. S1d. $^1$H-NMR spectrum of molecule 2 in CDCl$_3$
Fig. S1e. $^{13}$C-NMR spectrum of molecule 2 in CDCl$_3$
Fig. S1f. Maldi-TOF mass spectrum of molecule 2.
Fig. S1g. $^1$H-NMR spectrum of molecule 3 in CDCl$_3$
Fig. S1h. $^{13}$C-NMR spectrum of molecule 3 in CDCl$_3$
Fig. S1i. Maldi-TOF mass spectrum of molecule 3
Fig. S1j. $^1$H-NMR spectrum of molecule 4 in CDCl$_3$
Fig. S1k. $^{13}$C-NMR spectrum of molecule 4 in CDCl$_3$
Fig. S11. Maldi-TOF mass spectrum of molecule 4.
Fig. S1m Heating and cooling traces of differential scanning calorimetry (DSC) thermograms measured in compounds 1 to 4. Photographs of 1 and 2 show that these two compounds are in the liquid state at room temperature.
Fig. S2 Absorption and steady-state PL spectra of 1, 2, 3 and 4 in diluted dichloromethane solution. For the emission spectra, excitation wavelengths were 270, 328, 350 and 400 nm for 1, 2, 3 and 4, respectively. PLQYs of 2, 3 and 4 in solution were measured to be 85, 90 and 23%, respectively.
Fig. S3 Steady-state PL spectra of solvent-free 1:4 (50:50 wt.%), 2 and 3 liquid films sandwiched between two flat fused silica substrates. Excitation wavelength was 337 nm. PLQYs of 1:4, 2 and 3 in neat liquid films were measured to be 28, 55 and 80%, respectively.
**Liquid bisfluorene (2)**

**Hole**

0.21 MV/cm

**Electron**

0.20 MV/cm

**Liquid terfluorene (3)**

**Hole**

0.21 MV/cm

**Electron**

0.32 MV/cm

**Fig. S4** Photocurrent transients measured in 2 and 3 liquid neat films at room temperature using a conventional TOF technique.
Fig. S5 (a) Temporal decay of the emission intensity above the ASE threshold from 3. The incident pumping intensity was about 33 μJ/cm². (b) Temporal decay of the emission intensity above the ASE threshold from 2. The incident pumping intensity was 2.7 μJ/cm². In these experiments, the excitation wavelength is 337 nm and the repetition rate of the nitrogen laser used for the photo-excitation is 8 Hz. It should be noted that the liquid materials were not degassed and the devices were not encapsulated in inert atmosphere before the measurements carried out in air. The results show that the emission intensity from 3 is decreased by only 25 % after 4500 s (for an incident pumping intensity of about 33 μJ/cm²). However, the emission intensity from 2 is decreased by 50 % after about 700 s (for an incident pumping intensity of 2.7 μJ/cm²). The photostability of 2 under high excitation densities is thus significantly lower than that of 3, which might be related to the lower PLQY value measured in 2.
Motivated by the excellent ASE properties of the liquid fluorene derivatives, an organic DFB laser was fabricated using 3 as the active gain material and a polyurethaneacrylate (PUA) one dimensional corrugated pattern with a grating period of about 140 nm. The preparation method of the polymer grating has been published elsewhere. Fig. S6a shows the emission spectra of this liquid DFB laser at different pumping intensities. A blue laser emission peak with a FWHM of about 2 nm is observed at 432 nm at high excitation densities. The output intensity from the liquid organic laser is plotted in Fig. S6b as a function of the incident excitation intensity. From these data, the lasing threshold was determined to be around 1 \mu J/pulse. This achievement corresponds to the first realization of an organic laser based on a monolithic solvent-free liquid molecular semiconductor.

References

