

Electronic Supplementary Information (ESI) for

**Ladder-type Poly(indenofluorene-co-benzothiadiazole)s as Efficient Gain
Media for Organic Lasers: Design, Synthesis, Optical Gain Properties, and
Stabilized Lasing Properties**

Si-Ju Chang,^{‡a} Xu Liu,^{‡a} Ting-Ting Lu,^a Yuan-Yuan Liu,^a Jin-Qiang Pan,^a Yi Jiang,^a Shuang-Quan
Chu,^a Wen-Yong Lai^{*ab} and Wei Huang^{ab}

^a Key Laboratory for Organic Electronics and Information Displays & Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts & Telecommunications, 9 Wenyuan Road, Nanjing 210023, China

^b Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing 211816, China

[‡]These authors contributed equally to this work.

*E-mail: iamwylai@njupt.edu.cn

General Methods: Commercial grade reagents were used without further purification unless otherwise stated. All the solvents for characterization were used after redistillation. THF was refluxed with sodium filament in the presence of benzophenone until a persistent violet-blue color appeared and then distilled. All reactions were monitored by thin layer chromatography (TLC) with silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (300-400 mesh). ¹H NMR and ¹³C NMR spectra were recorded on a Bruker 400 plus at 295 K. The MALDI-TOF mass spectroscopy measurements were carried out with a Bruker mass spectrometer use trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile as matrix. Elemental analysis was conducted with a Carlo Erba-1106 instrument. Differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA) were done on Shimadzu DSC-60A and DTG-60H equipment, respectively. AFM measurements of surface morphology were conducted on the Bruker ScanAsyst AFM in auto scan (AC) mode. UV-vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Fluorescence spectra were measured using a Shimadzu RF-5301PC spectrofluorimeter with a xenon lamp as a light source. The fluorescence quantum yields were determined by full-featured steady state/transient fluorescence spectrometer FLS-920 from Edinburgh Instruments. PL decays were measured with an Edinburgh FLS-920 spectrometer. All fluorescent lifetimes were determined from the data using the Edinburgh Instruments software package. Cyclic voltammetry (CV) was performed on an Eco Chemie's Autolab at room temperature under nitrogen with a scanning rate of 100 mV/s. Molecular weight was measured by gel permeation chromatography (GPC) on a Shimadzu LC-20A HPLC system equipped with 7911GP-502 and GP NXC columns. The calibration curves for GPC analysis were obtained by using polystyrene as standard with a low polydispersity.

Synthesis and characterization

Synthesis of Compound 2: To a solution of compound 1 (1 g, 2.27 mmol) and phenol (3.84 g, 40.82 mmol) under nitrogen atmosphere, carbon tetrachloride (100 mL) and methanesulfonic acid (0.7 mL) was slowly added. The reaction mixture was stirred at 80 °C for 42 h and evaporated under vacuum. To a solution of the crude solid product (4.16 g, 13.62 mmol), K₂CO₃ (3.13 g, 22.7 mmol) in ethanol (100 mL) was added 7-(bromomethyl)pentadecane (24.95 g, 18.72 mmol) at 90°C. The reaction mixture was refluxed for 14 h, and then poured into water. The organic layer was dried over MgSO₄ and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane as eluent) to yield 3.86 g (98%) colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.65 (s, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 1.5 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.8 Hz, 8H), 6.78 (d, *J* = 8.9 Hz, 8H), 3.78 (d, *J* = 5.5 Hz, 8H), 1.73 (d, *J* = 5.5 Hz, 4H), 1.41 – 1.26 (m, 96H), 0.88 (t, *J* = 6.7 Hz, 24H). ¹³C NMR (100 MHz, CDCl₃): δ 158.4, 154.4, 151.7, 139.3, 138.8, 137.0, 130.5, 129.2, 121.5, 121.3, 117.6, 114.3, 70.8, 64.0, 53.4, 38.0, 31.9, 31.4, 30.0, 29.6, 29.3, 26.9, 22.7, 14.1. MALDI-TOF MS (*m/z*): calcd for C₁₀₈H₁₅₆Br₂O₄; Exact Mass: 1675.04, Mol. Wt.: 1678.20; Found: 1677.88 (M⁺). Anal. Calcd. for C₁₀₈H₁₅₆Br₂O₄. C, 77.29; H, 9.37; Found: C, 77.19; H, 9.39.

Synthesis of Compound 4: A mixture of compound 3 (4.13 g, 3.93 mmol), methyl 2-bromobenzoate (3.38 g, 15.72 mmol), Pd(PPh₃)₄ (0.23 g, 0.2 mmol), 2M K₂CO₃ (10 mL), and toluene (20 mL) under nitrogen atmosphere were heated to 85 °C for 24 h with good magnetic stirring. After cooling to room temperature, the reaction mixture was poured into water and extracted with CH₂Cl₂. The organic layer was collected, dried over anhydrous Na₂SO₄ and evaporated under vacuum. The crude solid was purified by chromatography on silica gel, using hexanes : CH₂Cl₂ = 2 : 1 as the eluent to give compound 4 (3.65 g, 87%). ¹H NMR (400 MHz,

CDCl₃): δ 7.84 – 7.75 (m, 4H), 7.50 (d, J = 10.7, Hz, 2H), 7.40 – 7.34 (m, 6H), 7.28 (d, J = 1.1 Hz, 2H), 7.12 (d, J = 8.8 Hz, 4H), 6.73 (d, J = 8.8 Hz, 4H), 3.74 (d, J = 5.6 Hz, 4H), 3.37 (s, 6H), 1.71 (s, 2H), 1.26 (d, J = 14.2 Hz, 48H), 0.86 (t, J = 6.5 Hz, 12H). ¹³C NMR (100 MHz, CDCl₃): δ 169.2, 158.2, 152.1, 142.5, 140.8, 138.8, 137.8, 131.1, 130.7, 129.8, 129.2, 127.5, 127.1, 126.4, 120.0, 114.1, 70.8, 64.3, 51.8, 38.0, 31.9, 31.4, 30.0, 29.6, 29.3, 26.8, 22.7, 14.1. MALDI-TOF MS (m/z): calcd for C₇₃H₉₄O₆, Mol. Wt.: 1067.52; Found: 1067.50 (M⁺). Anal. Calcd. for C₁₀₈H₁₅₆Br₂O₄: C, 77.29; H, 9.37; Found: C, 77.19; H, 9.39.

Synthesis of Compound 5: To a solution of 1-bromo-4-butylbenzene (4.82 g, 20 mmol) in dry THF (40 mL) at -78°C was added *n*-BuLi (8 mL, 2.5 M in hexane) under nitrogen atmosphere. After stirring below -70 °C for 1.5 h, compound 4 (2.13 g, 2 mmol) in dry THF (10 mL) was added. The reaction was then required to warm up to room temperature and stirred overnight. The reaction mixture was quenched with ice water and extracted with CH₂Cl₂, and then dried over anhydrous Na₂SO₄. After the solvent had been removed, the residue was purified through silica gel column chromatography giving yellow oil directly used in the next step. The yellow oil mentioned above was dissolved into dichloromethane (20 mL) and then 0.2 mL of BF₃·Et₂O was added as catalyst. The mixture was stirred for 30 min at room temperature, and methanol (50 mL) was added to destroy the catalyst. The mixture was extracted with CH₂Cl₂. The organic layer was washed with water and brine, and the CH₂Cl₂ solvent was removed under reduced pressure. The residue was chromatographically purified on silica gel eluting with CH₂Cl₂/hexane (10:1) (by vol) to afford a white solid (2.23 g, 69% based on compound 4). ¹H NMR (400 MHz, CDCl₃): δ 7.71 – 7.60 (m, 6H), 7.31 (d, J = 20.7Hz, 4H), 7.25 – 7.11 (m, 14H), 7.08 – 6.99 (m, 8H), 6.78 (d, J = 8.9 Hz, 4H), 3.78 (d, J = 5.6 Hz, 4H), 2.58 – 2.48 (m, 8H), 1.73 (s, 2H), 1.56 (s, 8H), 1.55 – 1.16 (m, 72H), 0.87 (t, J = 6.6 Hz, 24H). ¹³C NMR (100 MHz, CDCl₃): δ 157.9, 152.1, 151.2, 143.3, 141.1, 140.2,

140.1,140.0, 138.2, 129.5, 128.2, 127.4, 127.2, 126.2,120.0, 117.7, 117.6, 114.1,67.9, 64.7, 63.5, 35.2, 33.5, 31.6, 31.5, 29.7, 29.3, 29.1, 25.8, 25.7, 22.6, 22.6, 22.5, 14.1, 14.0. MALDI-TOF MS (*m/z*): calcd for C₁₁₉H₁₅₄O₂; Exact Mass: 1066.71, Mol. Wt.: 1616.49; Found: 1615.40 (M⁺). Anal. Calcd. for C₁₁₉H₁₅₄O₂: C, 82.13; H, 8.88; Found: C, 82.01; H, 8.67.

Synthesis of Compound 6: Compound 5 (1.62 g, 1 mmol) was dissolved in 50 mL of CCl₄ and cooled in an ice bath. Then Br₂ liquid (0.32 g, 2 mmol) was added and stirred for 14 h. The reaction was quenched with sodium sulfite solution and The crude solid was purified by chromatography on silica gel, using hexanes:CH₂Cl₂=10:1 as the eluent to give white solid (0.83 g, 47%). ¹H NMR (400 MHz, CDCl₃): δ 7.70 (s, 2H), 7.64 (s, 2H), 7.62 (d, *J* = 5.3 Hz, 2H), 7.34 (d, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.4 Hz, 2H), 7.22 (d, *J* = 2.0 Hz, 2H), 7.20 (s, 2H), 7.18 – 7.11 (m, 8H), 7.08 – 6.99 (m, 8H), 6.78 (d, *J* = 8.9 Hz, 4H), 3.78 (d, *J* = 5.6 Hz, 4H), 2.58 – 2.48 (m, 8H), 1.73 (s, 2H), 1.56 (s, 8H), 1.55 – 1.16 (m, 72H), 0.87 (t, *J* = 6.6 Hz, 24H). ¹³C NMR (100 MHz, CDCl₃): δ 158.1, 154.3, 152.2, 151.5, 143.2, 141.1, 140.1, 139.9,139.9, 137.5, 133.2, 129.4, 128.2, 127.5, 127.2, 126.2, 120.1, 117.8, 117.5, 114.3, 112.6, 112.1, 69.2, 68.0, 64.7, 63.2, 35.2, 33.5, 31.6, 31.5, 29.7, 29.3, 29.1, 25.8, 25.7, 22.6, 22.6, 22.5, 14.1, 14.0. MALDI-TOF MS (*m/z*): calcd for C₁₁₉H₁₅₂O₂Br₂; Exact Mass: 1771.02, Mol. Wt.: 1774.29; Found: 1774.11 (M⁺), 1695.33 [M-Br]⁺, 1615.40 [M-2Br]⁺. Anal. Calcd. for C₁₁₉H₁₅₂O₂Br₂: C, 80.55; H, 8.63; Found: C, 80.27; H, 8.78.

Synthesis of Compound 8: A mixture of compound 7 (6.75 g, 7.3 mmol), 2,5-dibromoterephthalic acid diethyl ester (0.69 g, 1.82 mmol), Pd(PPh₃)₄ (0.42 g, 0.36 mmol), 2M K₂CO₃ (5 mL), and toluene (12 mL) under nitrogen atmosphere were heated to 85 °C for 24 h with good magnetic stirring. After cooling to room temperature, the reaction mixture was poured into water and extracted with CH₂Cl₂. The organic layer was collected, dried over anhydrous Na₂SO₄ and evaporated under vacuum. The crude solid was purified by chromatography on silica gel, using

hexanes:CH₂Cl₂ = 1:2 as the eluent to give compound 8 (3.04 g, 92%). ¹H NMR (400 MHz, CDCl₃): δ 7.78 (dd, *J* = 15.3, 6.8 Hz, 6H), 7.41 – 7.27 (m, 10H), 7.09 (t, *J* = 6.0 Hz, 8H), 6.73 (d, *J* = 8.9 Hz, 8H), 3.78 – 3.68 (m, 12H), 1.71 (d, *J* = 5.5 Hz, 4H), 1.32 – 1.23 (m, 96H), 0.86 (t, *J* = 6.8 Hz, 24H), 0.73 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 168.2, 158.2, 152.3, 152.0, 141.1, 139.5, 137.6, 133.7, 131.5, 129.1, 127.9, 127.5, 127.3, 126.2, 126.1, 120.3, 120.0, 114.1, 70.8, 64.3, 61.2, 38.0, 31.9, 31.4, 30.0, 29.6, 29.4, 26.9, 22.7, 14.1, 13.6. MALDI-TOF MS (*m/z*): calcd. for C₁₂₆H₁₇₄O₈; Exact Mass: 1815.32, Mol. Wt.: 1816.72; Found: 1816.37 (M⁺). Anal. Calcd. for C₁₂₆H₁₇₄O₈: C, 83.30; H, 9.65; Found: C, 83.43; H, 9.49.

Synthesis of Compound 9: The synthesis of compound 9 was similar to the preparation of compound 5 through the nucleophilic addition and acid-catalyzed cyclization, using 1-bromo-4-butylbenzene (2.41 g, 10 mmol), *n*-BuLi (4 mL, 2.5 M in hexane), compound 8 (1.82 g, 1 mmol), and dry THF (40 mL) in the nucleophilic addition and 0.5 mL of BF₃·Et₂O in the cyclization step, respectively. The crude product was purified by silica gel column chromatography affording of a white solid (1.78 g, 76%) in two steps. ¹H NMR (400 MHz, CDCl₃): δ 7.67 (s, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 3.4 Hz, 2H), 7.30 (d, *J* = 7.5 Hz, 6H), 7.24 (s, 2H), 7.19 (d, *J* = 8.2 Hz, 8H), 7.13 (d, *J* = 8.8 Hz, 8H), 7.05 (d, *J* = 8.3 Hz, 8H), 6.75 (d, *J* = 8.8 Hz, 8H), 3.75 (d, *J* = 5.4 Hz, 8H), 2.64 – 2.45 (m, 8H), 1.71 (s, 4H), 1.63 – 1.57 (m, 8H), 1.40 – 1.22 (m, 120H), 0.90 – 0.82 (m, 36H). ¹³C NMR (100 MHz, CDCl₃): δ 158.1, 154.4, 152.1, 151.8, 151.4, 143.3, 141.2, 140.7, 140.1, 139.0, 138.6, 137.2, 133.2, 130.4, 129.2, 128.3, 121.4, 121.0, 117.8, 117.4, 114.3, 67.9, 64.3, 64.0, 31.9, 31.9, 31.7, 31.4, 31.3, 30.1, 29.7, 29.6, 29.4, 29.2, 26.8, 22.7, 22.6, 14.2, 14.2. MALDI-TOF MS (*m/z*): calcd for C₁₇₀H₂₃₀O₄; Exact Mass: 2335.78, Mol. Wt.: 2337.64; Found: 2337.57 (M⁺). Anal. Calcd. for C₁₇₀H₂₃₀O₄: C, 87.35; H, 9.92; Found: C, 87.63; H, 9.84.

Synthesis of Compound 10: Compound 9 (2.34 g, 1 mmol) was dissolved in 50 mL of CCl₄ and

cooled in an ice bath. Then Br₂ liquid (0.32 g, 2 mmol) was added and stirred for 14 h. The reaction was quenched with sodium sulfite solution and The crude solid was purified by chromatography on silica gel, using hexanes:CH₂Cl₂=10:1 as the eluent to give a yellow solid (1.42g, 57%). ¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, *J* = 17.1 Hz, 2H), 7.54 (m, 6H), 7.40 (d, *J* = 1.5 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 8H), 7.10 (d, *J* = 8.8 Hz, 8H), 7.05 (d, *J* = 8.2 Hz, 8H), 6.76 (d, *J* = 8.9 Hz, 8H), 3.76 (d, *J* = 5.5 Hz, 8H), 2.59 – 2.47 (m, 8H), 1.72 (s, 4H), 1.58 (s, 8H), 1.41 – 1.21 (m, 120H), 0.87 (t, *J* = 6.6 Hz, 36H). ¹³C NMR (100 MHz, CDCl₃): δ 158.3, 154.5, 152.1, 151.8, 151.4, 143.3, 141.3, 140.7, 140.1, 139.0, 138.6, 137.1, 130.3, 129.3, 128.3, 121.5, 121.0, 117.8, 117.8, 117.4, 114.2, 70.7, 64.3, 64.0, 31.9, 31.9, 31.7, 31.4, 31.3, 30.1, 29.7, 29.6, 29.4, 29.2, 26.8, 22.7, 22.6, 14.2, 14.1. MALDI-TOF MS (*m/z*): calcd for C₁₇₀H₂₂₈Br₂O₄; Exact Mass: 2491.60, Mol. Wt.: 2495.43; Found: 2495.57 (M⁺), 2416.55 [M-Br]⁺, 2337.12 [M-2Br]⁺. Anal. Calcd. for C₁₇₀H₂₂₈Br₂O₄: C, 81.82; H, 9.21 Found: C, 81.97; H, 9.06.

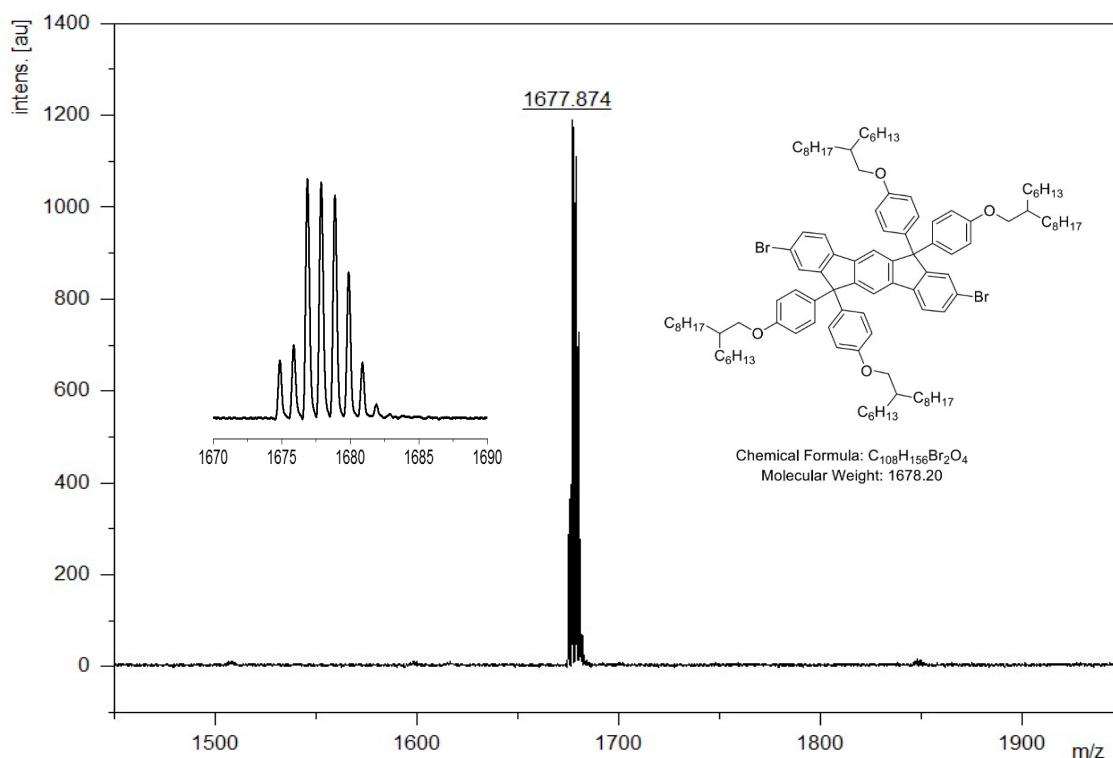


Fig. S1 MADIL-TOF spectra of compound 2.

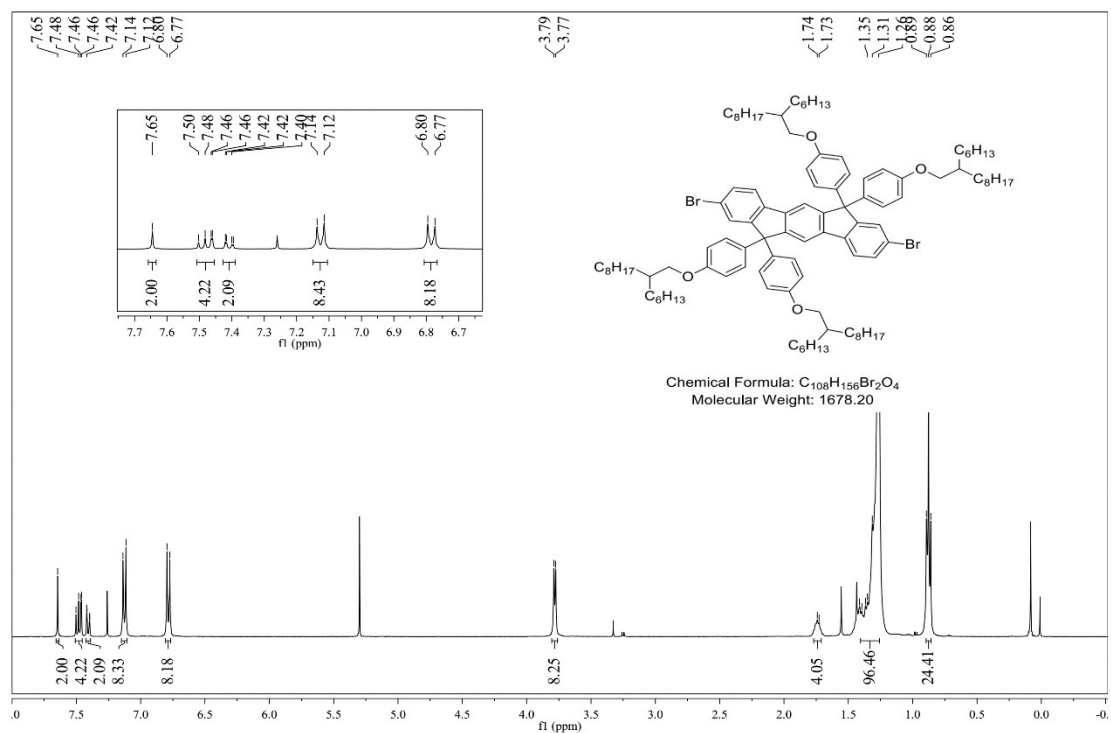


Fig. S2 1H NMR spectra of compound 2.

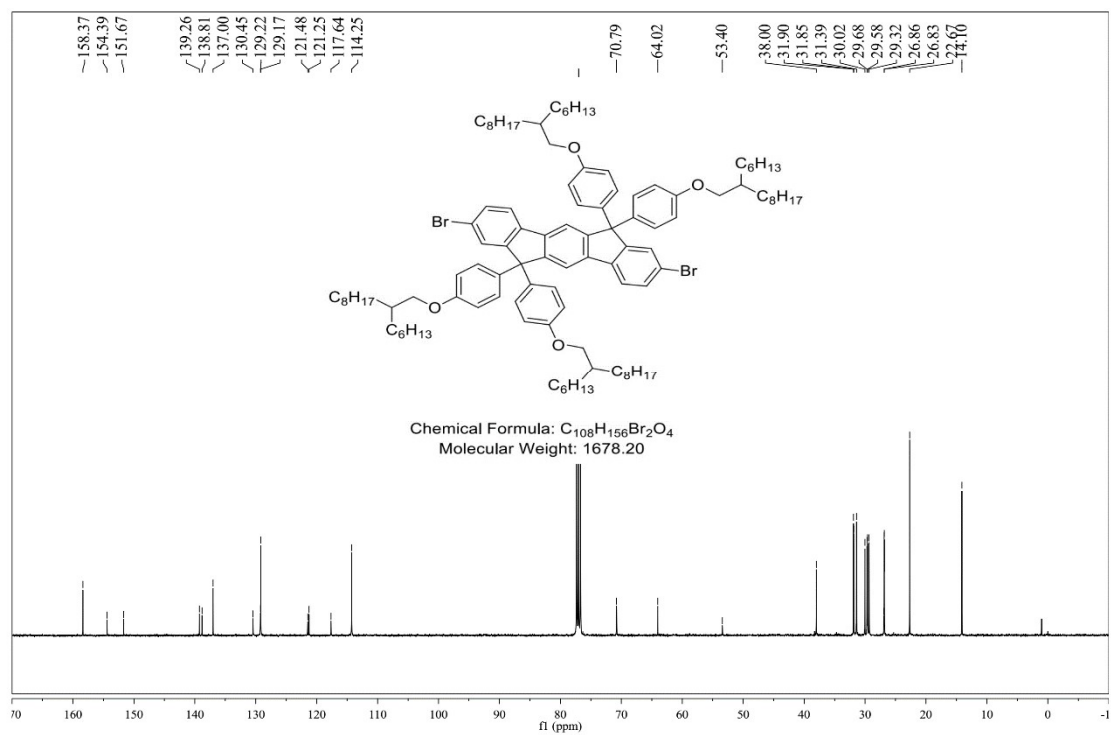


Fig. S3 ^{13}C NMR spectra of compound 2.

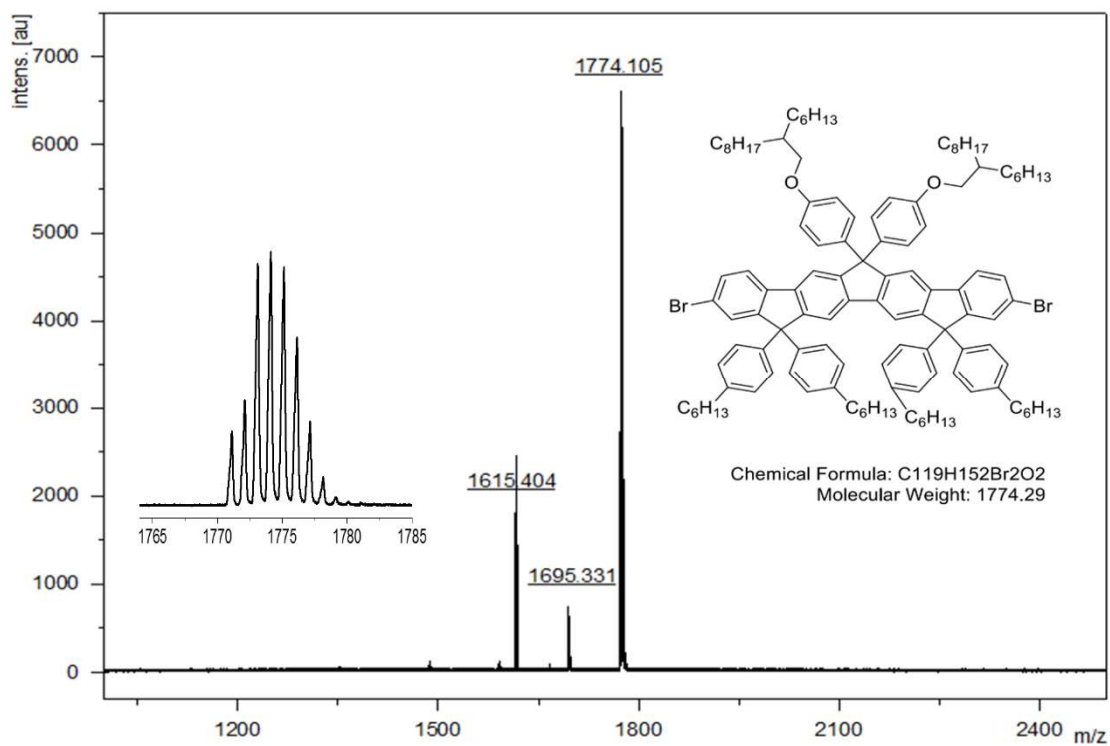


Fig. S4 MADIL-TOF spectra of compound 6.

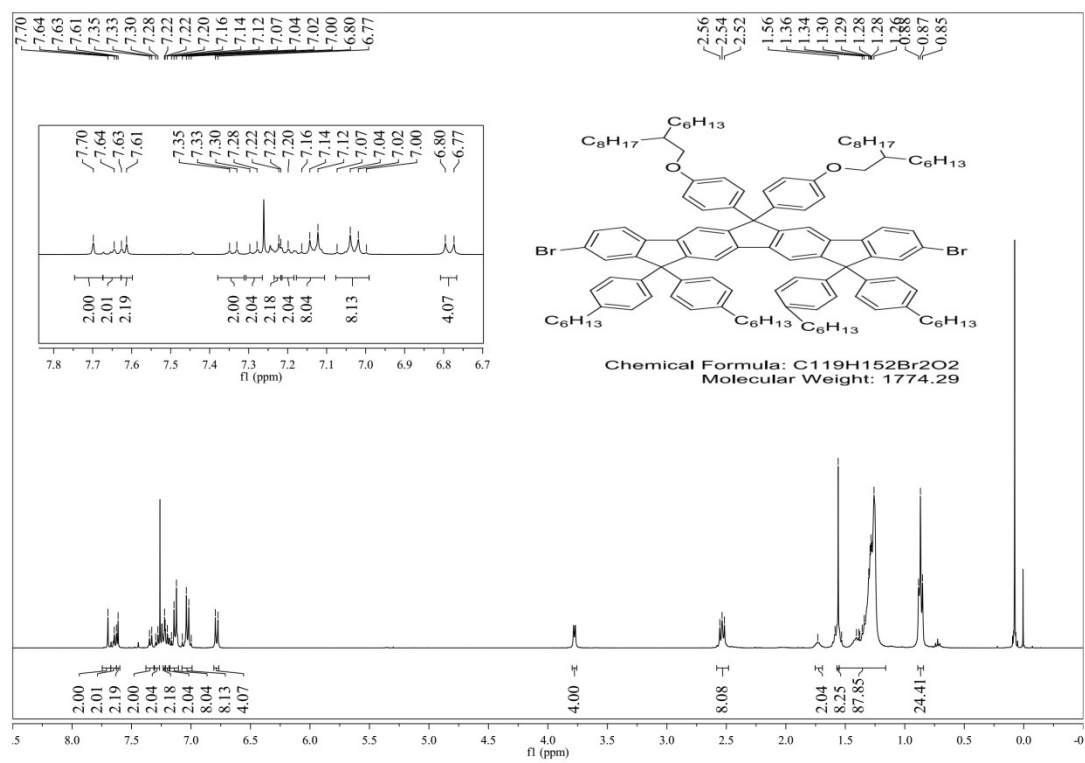


Fig. S5 ¹H NMR spectra of compound 6.

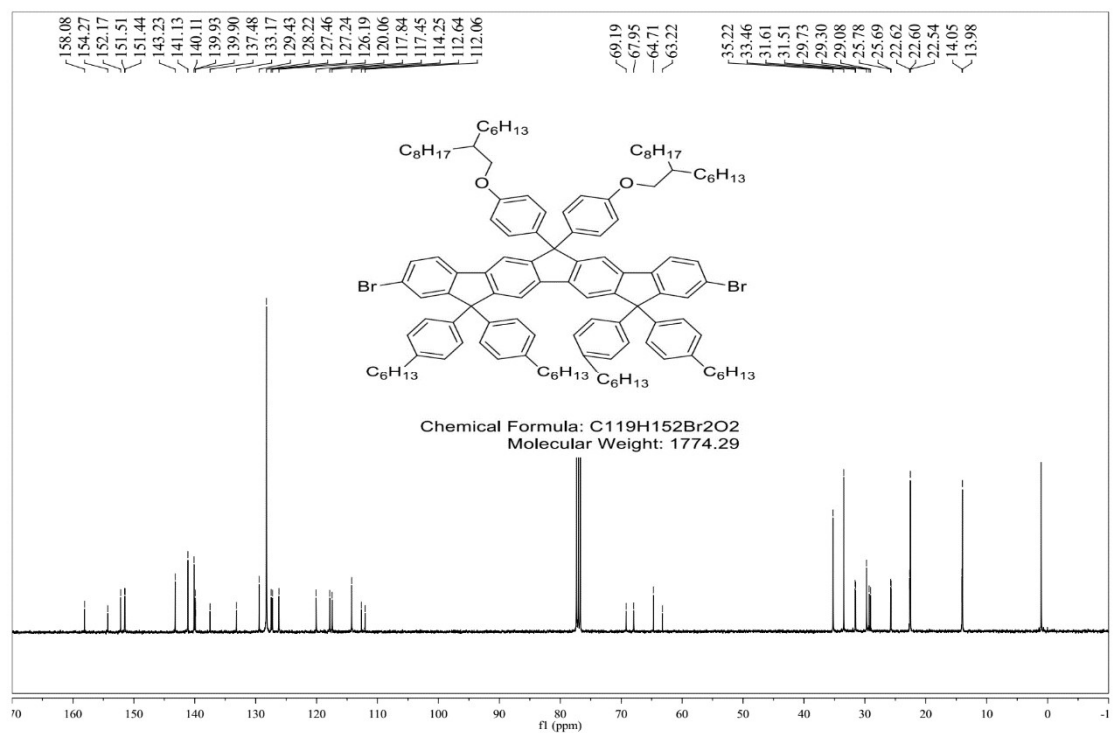


Fig. S6 ¹³C NMR spectra of compound 6.

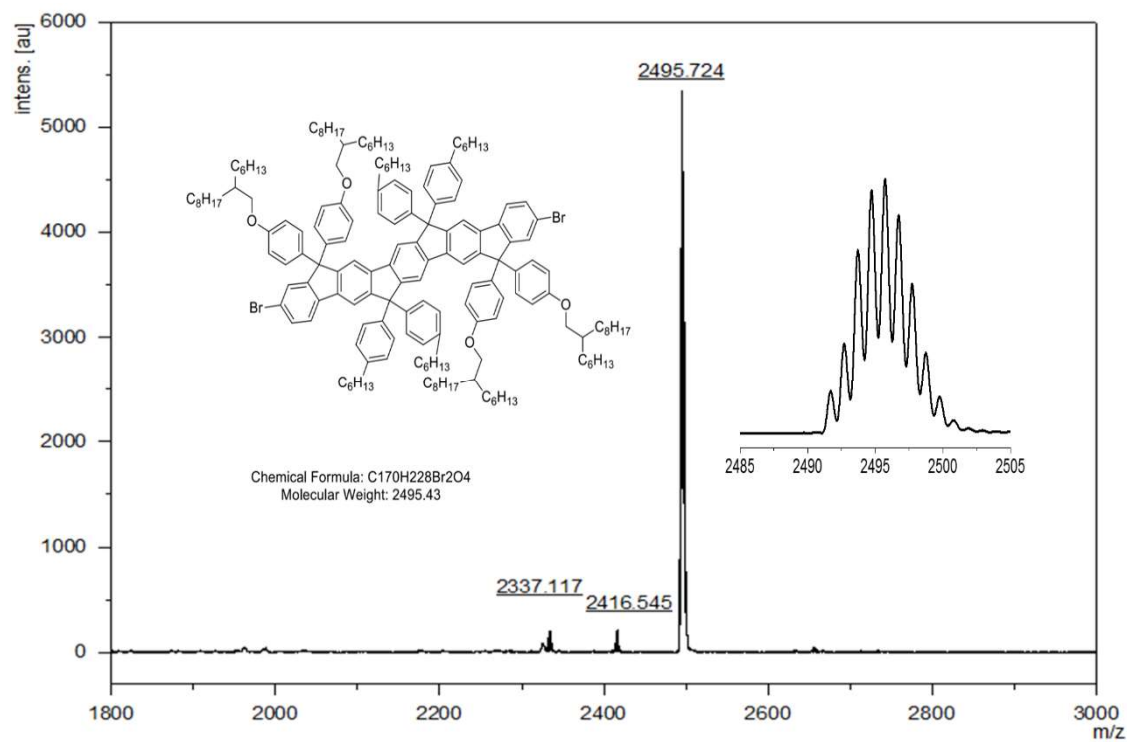


Fig. S7 MADIL-TOF spectra of compound 10.

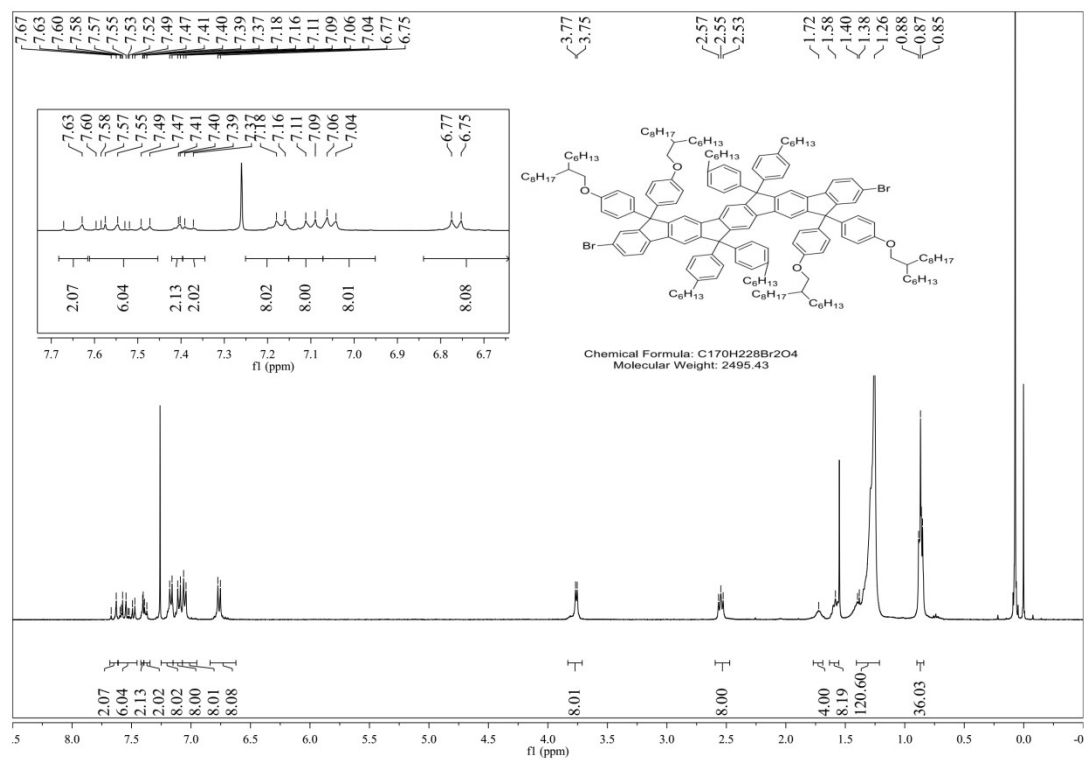


Fig. S8 ¹H NMR spectra of compound 10.

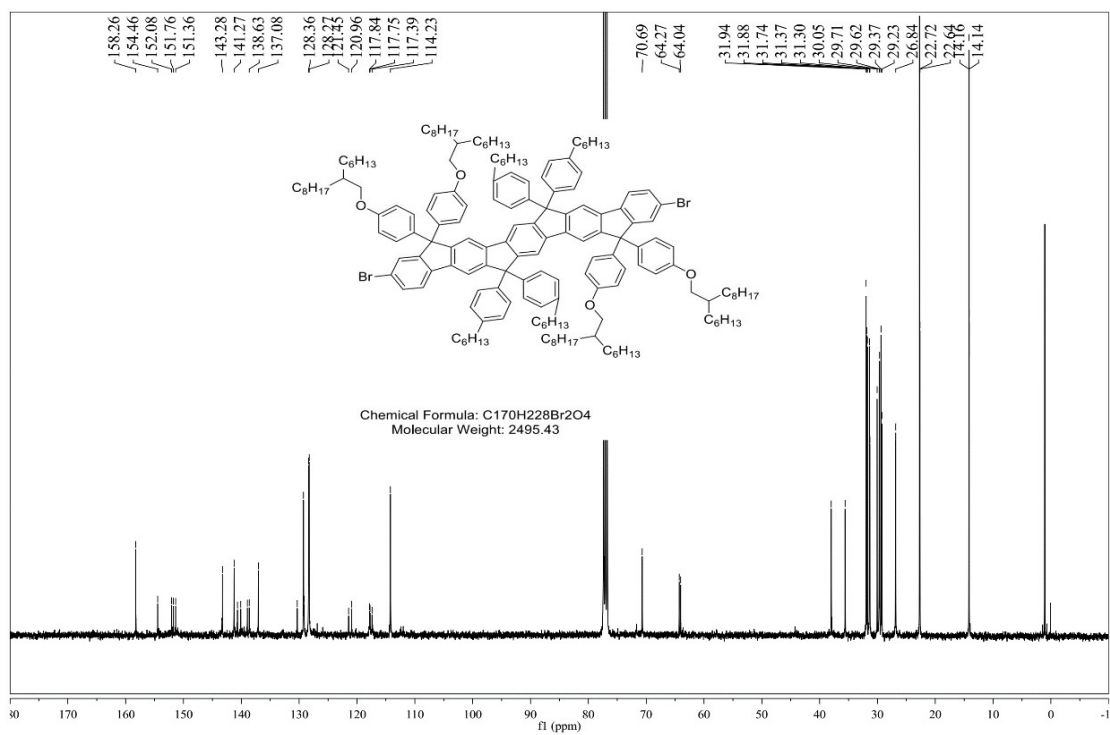


Fig. S9 ¹³C NMR spectra of compound 10.

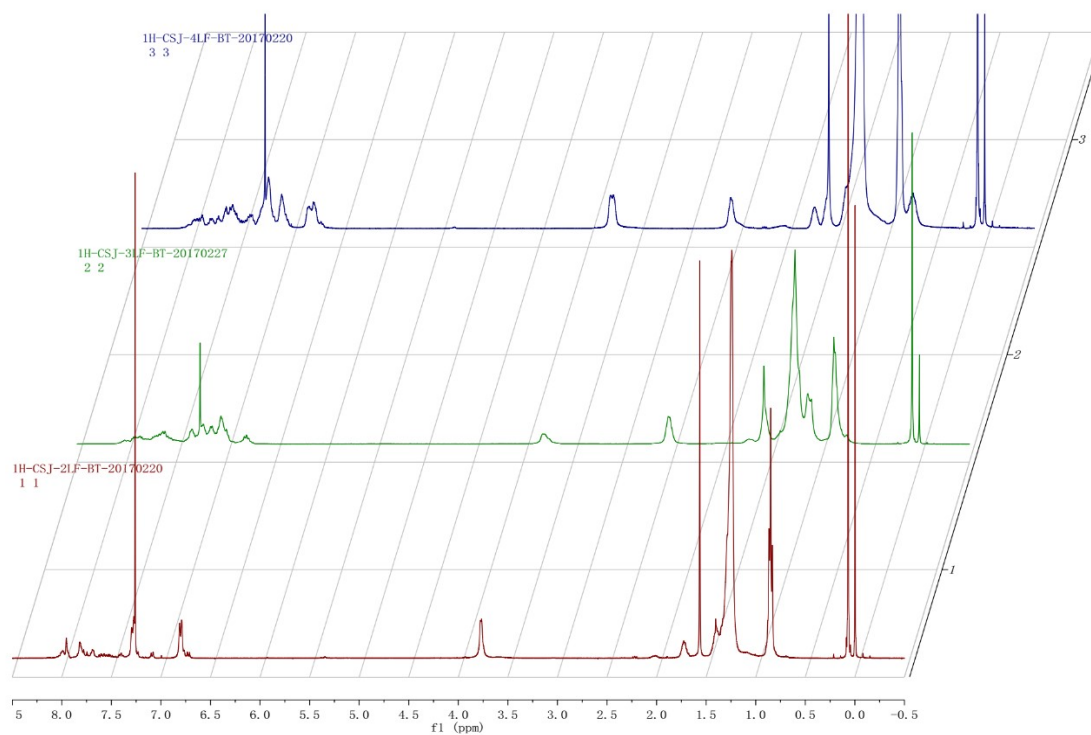


Fig. S10 ^1H NMR spectra of $n\text{LF-BT}$ ($n = 2-4$).

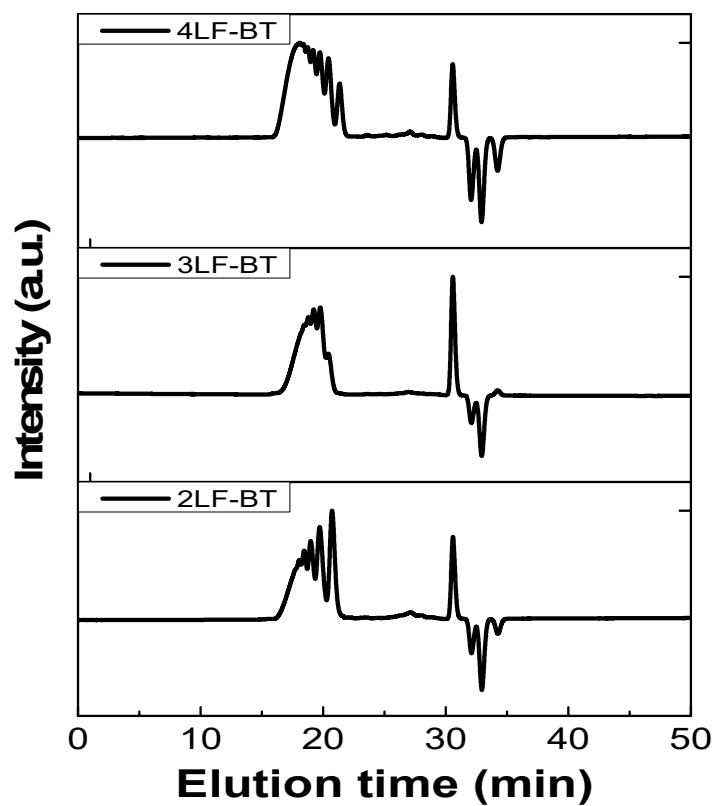


Fig. S11 The GPC elution curves of $n\text{LF-BT}$ ($n = 2-4$).

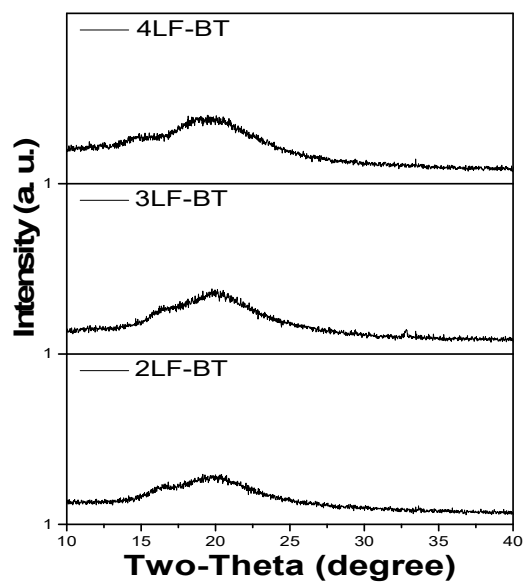


Fig. S12 Powder WAXD patterns of n LF-BT ($n = 2-4$).

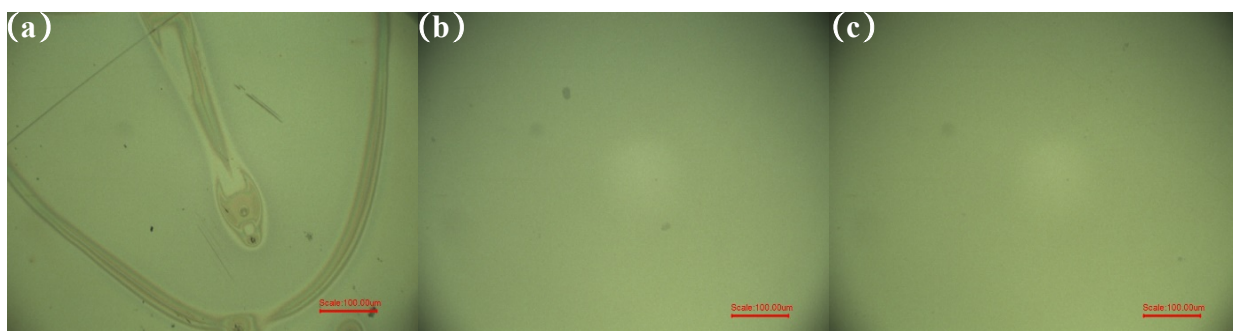


Fig. S13 The metallographic microscope images of (a) 2LF-BT, (b) 3LF-BT, (c) 4LF-BT.

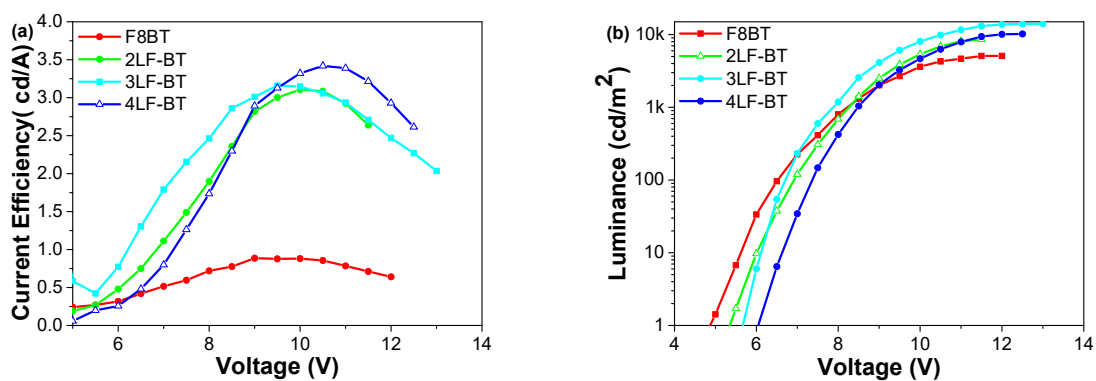


Fig. S14 (a) Current efficiency-voltage characteristics of Devices A-D; (b) brightness-voltage characteristics for Devices A-D.

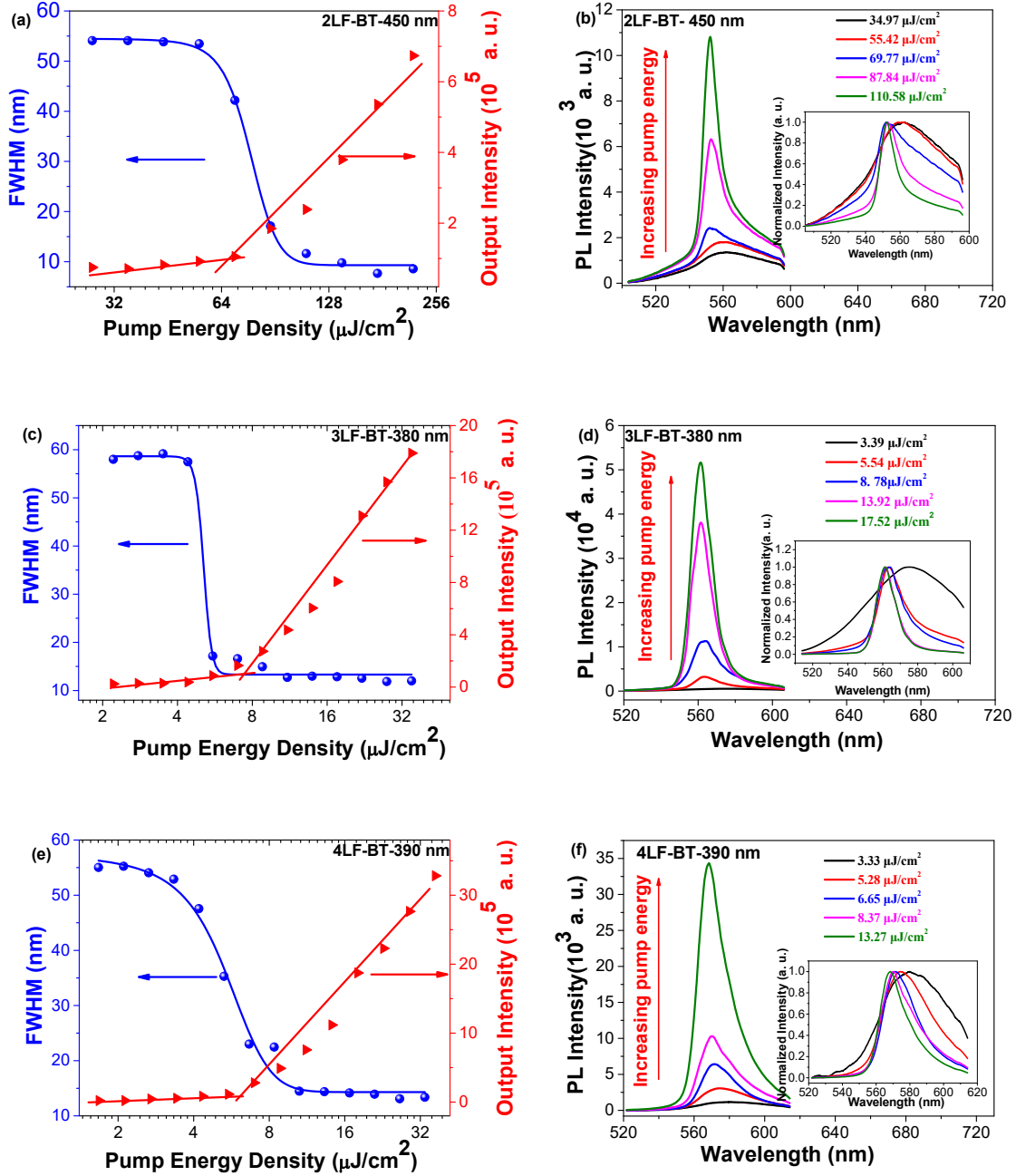


Fig. S15 Full width at half-maximum (FWHM) of the emission spectrum (left, solid spheres) and the corresponding output intensity (right, solid triangles) for (a) 2LF-BT, (c) 3LF-BT, (e) 4LF-BT as a function of the pump energy density, indicating its pump threshold. The emission spectra for the planar waveguide of (b) 2LF-BT, (d) 3LF-BT, (f) 4LF-BT with various pump fluences and the corresponding normalized spectra shown in the inset.

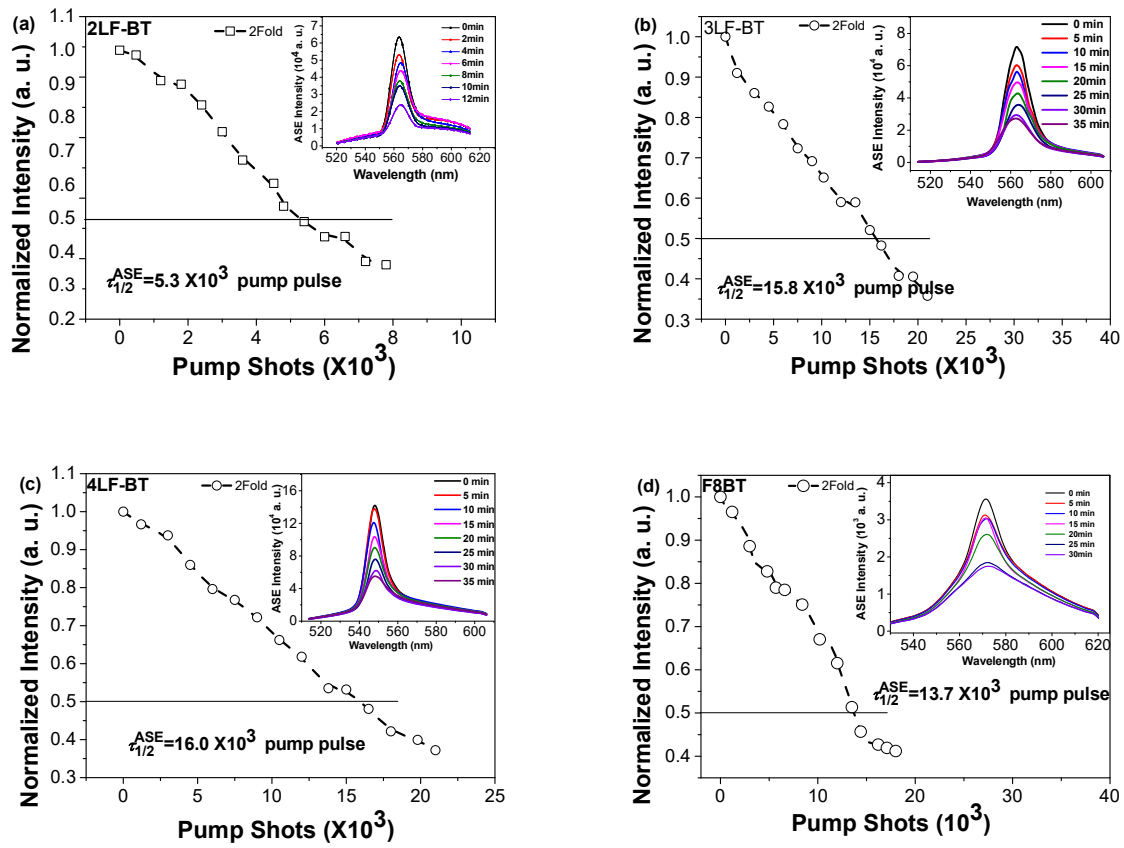


Fig. S16 The ASE photostability half-life ($\tau_{1/2}^{ASE}$) for (a) 2LF-BT; (b) 3LF-BT; (c) 4LF-BT; and (d) F8BT. The ASE photostability half-life ($\tau_{1/2}^{ASE}$) is defined as the time at which the ASE intensity decays to half of its initial value.

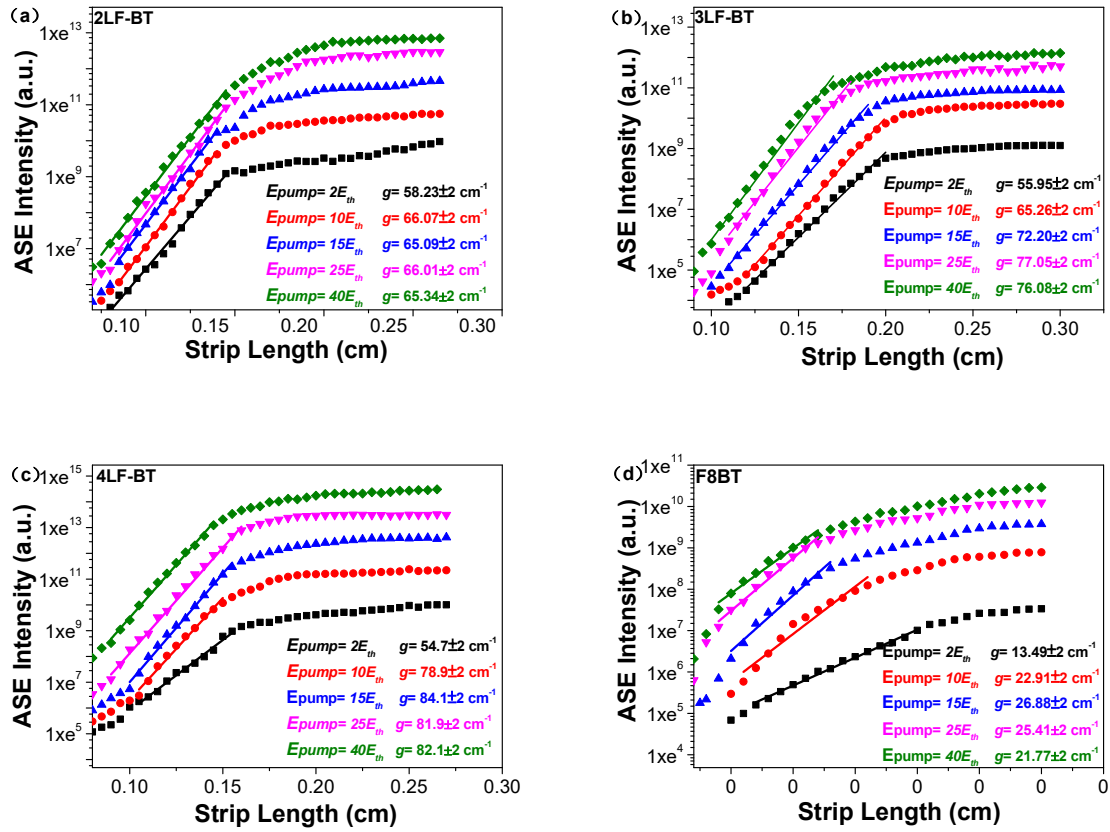


Fig. S17 The dependence of ASE emission intensity on the stripe length at different pump intensities for (a) 2LF-BT, (b) 3LF-BT, (c) 4LF-BT, and (d) F8BT.

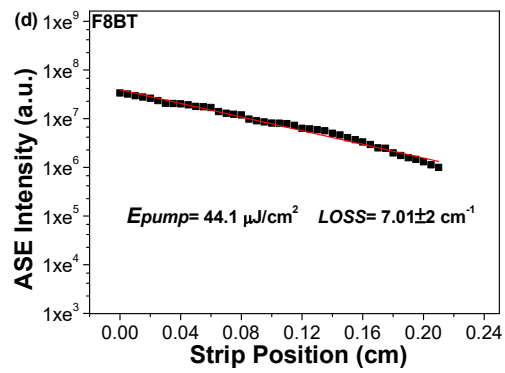
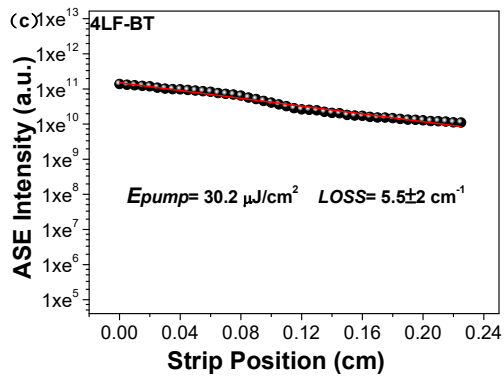
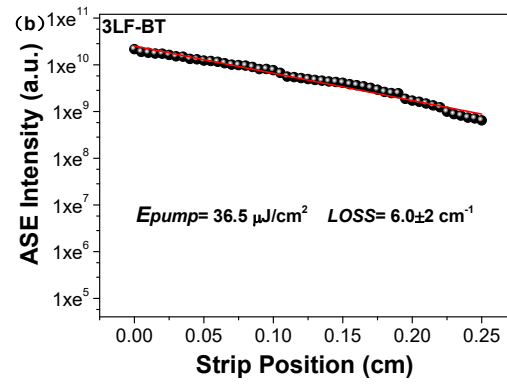
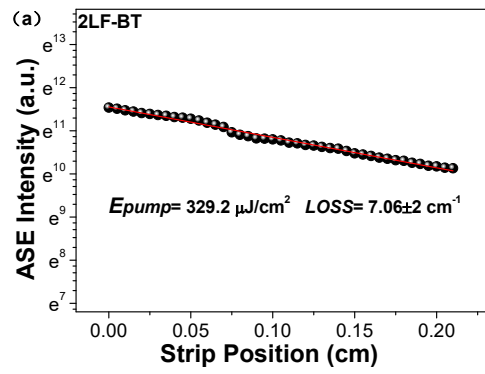


Fig. S18 The ASE loss coefficients of the waveguides for (a) 2LF-BT; (b) 3LF-BT; (c) 4LF-BT; and (d) F8BT.