

Supporting Information

Ladder-type Materials with D-A-D Architectures as Robust Gain Media for Organic Lasers

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Synthesis and characterization

Synthesis of (2,5-Dibromo-1,4-phenylene)bis((4-butylphenyl)methanone) (MA1): Under N₂ protection, 2,5- dibromoter phthalic acid (4.00 g, 12.3 mmol) was treated with 40 mL of thionyl chloride (SOCl₂) and refluxed for 12 h. The excess SOCl₂ was removed in vacuum. Subsequently, the previous products and 30 mL of dichloromethane (DCM) were added dropwise to a solution of *n*-butylbenzene (5.7 mL, 36.9 mmol) and aluminum trichloride (2.47g, 18.5 mmol). The organic layer was washed with 1 M NaOH and water, then dried over Na₂SO₄, and concentrated. The residue was chromatographically purified on silica gel eluting with CH₂Cl₂/ hexane (2:3) (by vol.) to afford MA1 4.92 g (72% yield) as a white crystal. ¹H NMR (400 MHz, CDCl₃): δ 7.76 (d, *J*=8.1 Hz, 4H), 7.58 (s, 2H), 7.32 (d, *J*=8.1 Hz, 4H), 2.72-2.68 (m, 4H), 1.47- 1.36 (m, 4H), 1.24 (t, *J*=5.8 Hz, 4H), 0.94 (t, *J*=5.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 193.39, 150.57, 143.36, 132.91, 130.50, 129.02, 118.44, 35.86, 33.10, 22.34, 13.90. MS (MALDI-TOF, *m/z*): [M]⁺ Calcd for C₂₈H₂₈Br₂O₂: 556.34; found: 556.60.

Synthesis of (4-Bromo-4'-(diphenylamino)-[1,1'-biphenyl]-2,5-diyl)bis((4-butylphenyl)methanone) (1). In the case of N₂ protection, a mixture of MA1 (556 mg, 1.0 mmol), *N,N*-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (446 mg, 1.2 mmol), Pd(PPh₃)₄ (69 mg, 0.06 mmol), 2M K₂CO₃ (15 mL), ethanol (15 mL) and toluene (30 mL) was heated to 85 °C for 24 h *via* magnetic stirring. By cooling to room temperature, the reaction mixture was poured into water and extracted with DCM. The combined organic layer was dried over anhydrous Na₂SO₄ and evaporated to dryness. The residue was purified through silica gel column chromatography with DCM/hexane (2:1) (by vol) affording **1** (0.56 g, 65% yield) of a yellow solid. ¹H NMR (400 MHz, CDCl₃, δ): 7.87 – 7.69 (m, 3H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.43 (s, 1H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.23 – 7.12 (m, 6H), 7.08 (d, *J* = 8.1 Hz, 2H), 7.00 (t, *J* = 6.2 Hz, 2H), 6.87 (d, *J* =

7.4 Hz, 6H), 2.75 – 2.59 (m, 4H), 1.60 (s, 4H), 1.36 (d, $J = 7.5$ Hz, 4H), 0.93 (d, $J = 7.4$ Hz, 8H); ^{13}C NMR (100 MHz, CDCl_3 , δ): 196.58, 195.03, 150.18, 149.08, 147.76, 147.28, 142.63, 141.27, 139.76, 134.39, 133.43, 133.13, 131.92, 130.55, 130.14, 129.75, 129.56, 129.22, 128.89, 128.28, 124.42, 123.17, 123.13, 117.91, 35.88, 35.76, 33.15, 22.37, 22.33, 13.90. MS (MALDI-TOF, m/z): $[\text{M}]^+$ Calcd for $\text{C}_{46}\text{H}_{42}\text{BrNO}_2$: 720.74; found: 719.963.

General procedures for the synthesis of precursors OBDT, OIDT and OIDTT: A mixture of the corresponding molecule (2, 3, or 4), (0.5 mmol), precursor **1** (1080 mg, 1.5 mmol), $\text{Pd}(\text{PPh}_3)_4$ (23.1 mg, 0.02 mmol), TBAB (161 mg, 0.5 mmol), was added into a solution of degassed toluene (30 mL) and K_2CO_3 (10 mL). The solution was heated as 100°C to reflux for 48 h under N_2 . When cooled to room temperature, the solution was extracted with DCM. After filtration and evaporation of the solvents, the resulting product was purified by flash chromatography on a silica gel column with hexane/DCM to yield OBDT, OIDT and OIDTT, respectively.

OBDT: yellow powder; yield 75%. ^1H NMR (400 MHz, CDCl_3): δ 7.83 (s, 2H), 7.74 (d, $J = 8.2$ Hz, 4H), 7.62 (d, $J = 8.0$ Hz, 4H), 7.58 (s, 2H), 7.22 – 7.11 (m, 22H), 7.02 (t, $J = 7.1$ Hz, 4H), 6.91 (d, $J = 18.6$ Hz, 12H), 3.94 – 3.85 (m, 4H), 2.70 – 2.63 (m, 4H), 2.56 (t, $J = 7.8$ Hz, 4H), 1.71 – 1.60 (m, 6H), 1.53 – 1.47 (m, 6H), 1.42 – 1.33 (m, 24H), 0.95 (d, $J = 13.2, 7.4$ Hz, 18H), 0.83 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 197.75, 197.37, 149.52, 148.92, 147.68, 147.34, 144.08, 141.00, 140.39, 140.27, 140.09, 134.64, 134.19, 132.46, 131.87, 131.30, 130.32, 130.28, 130.20, 130.02, 129.86, 129.21, 128.62, 128.24, 124.41, 123.19, 123.11, 121.03, 35.76, 35.68, 33.17, 32.96, 31.91, 30.44, 29.47, 29.31, 25.96, 22.71, 22.33, 22.17, 14.15, 13.90, 13.76. MS (MALDI-TOF, m/z): $[\text{M}]^+$ Calcd for $\text{C}_{118}\text{H}_{120}\text{N}_2\text{O}_6\text{S}_2$: 1724.86; found: 1724.47.

OIDT: orange-yellow powder; yield 81%. ^1H NMR (400 MHz, Acetone): δ 7.76 (d, $J = 13.3, 7.0$ Hz, 4H), 7.66 – 7.46 (m, 16H), 7.33 – 7.16 (m, 18H), 7.10 – 6.97 (m, 10H), 6.96 – 6.74 (m,

20H), 2.75 – 2.39 (m, 16H), 1.71 – 1.37 (m, 34H), 1.03 – 0.66 (m, 38H). ^{13}C NMR (100 MHz, CDCl_3): δ 198.00, 156.46, 152.96, 148.90, 147.62, 147.41, 147.17, 142.91, 142.34, 141.69, 141.36, 140.50, 140.47, 139.82, 138.63, 138.54, 135.19, 134.77, 133.99, 133.46, 132.68, 132.62, 132.40, 132.29, 131.84, 131.60, 130.27, 130.20, 129.89, 129.27, 128.64, 128.52, 128.38, 128.30, 127.80, 124.73, 124.55, 124.43, 124.09, 123.29, 123.15, 68.20, 62.93, 35.83, 35.68, 34.97, 34.61, 33.25, 32.96, 32.03, 31.86, 31.55, 31.43, 30.30, 29.81, 29.48, 29.26, 22.81, 22.73, 22.40, 22.35, 14.26, 14.02, 13.92. MS (MALDI-TOF, m/z): $[\text{M}]^+$ Calcd for $\text{C}_{156}\text{H}_{156}\text{N}_2\text{O}_4\text{S}_2$: 2185.15; found 2183.89.

OIDTT: orange-yellow powder; yield 76%. ^1H NMR (400 MHz, CDCl_3): δ 7.73 (s, 2H), 7.68 (d, $J = 8.2$ Hz, 4H), 7.62 – 7.52 (m, 6H), 7.44 (d, $J = 7.3$ Hz, 2H), 7.36 (d, $J = 16.7$ Hz, 2H), 7.22 (t, $J = 7.8$ Hz, 8H), 7.18 – 7.12 (m, 10H), 7.12 – 6.97 (m, 24H), 6.90 (d, $J = 8.1$ Hz, 11H), 2.60 (d, $J = 14.1$ Hz, 16H), 1.59 (s, 28H), 0.99 – 0.77 (m, 44H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.85, 197.70, 153.34, 149.31, 148.87, 147.62, 147.38, 147.31, 147.12, 145.98, 143.30, 142.00, 141.75, 141.22, 140.61, 140.37, 140.13, 139.65, 135.97, 134.71, 134.40, 134.26, 132.57, 131.81, 130.59, 130.19, 130.09, 129.87, 129.78, 129.57, 129.23, 128.92, 128.48, 128.30, 128.25, 127.97, 124.51, 124.44, 124.39, 124.03, 123.26, 123.20, 123.17, 123.11, 120.96, 119.16, 117.00, 114.13, 62.86, 35.80, 35.66, 34.92, 34.57, 33.20, 33.10, 31.98, 31.76, 31.56, 31.49, 31.32, 30.25, 30.09, 29.76, 29.57, 29.42, 29.26, 29.01, 22.75, 22.64, 22.41, 22.36, 22.29, 14.17, 14.14, 13.95, 13.91. MS (MALDI-TOF, m/z) $[\text{M}]^+$ Calcd for $\text{C}_{160}\text{H}_{156}\text{N}_2\text{O}_4\text{S}_4$: 2297.09; found 2296.78.

General procedures for the synthesis of target products LBDT, LIDT and LIDTT: Under the protection of N_2 , $n\text{-BuLi}$ (0.6 mL, 2.5 M in hexane) was slowly added to a solution of 1-bromo-4-butylbenzene (20 equiv.) in dry THF (25 mL) at the temperature of -78 °C. After stirring at -78 °C for 1 h, the corresponding compound OBDT, Oidt or Oidtt (1 equiv.) in dry THF (5 mL) was added, respectively. Subsequently, the reaction was warmed up to room temperature and stirred

for 12 hours. The reaction mixture was quenched with ice water, extracted with DCM, dried over anhydrous MgSO_4 , and evaporated to dryness. After the solvent was removed, the residue was purified *via* silica gel column chromatography, yielding a yellow oil. The yellow oil was dissolved into dry DCM (20 mL) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.2 mL) was added dropwise as the catalyst. After 1 hour, methanol (50 mL) was added to quench the reaction. The mixture was extracted with CH_2Cl_2 . The target product was purified by flash chromatography on a silica gel column with hexane/DCM to yield LBDT, LIDT and LIDTT, respectively.

LBDT: yellow powder; yield 47%. ^1H NMR (400 MHz, CDCl_3): δ 7.45 (d, $J = 10.0$ Hz, 4H), 7.39 (d, $J = 8.4$ Hz, 10H), 7.22 – 7.16 (m, 10H), 7.11 (d, $J = 8.0$ Hz, 8H), 7.08 – 6.99 (m, 26H), 6.98 (s, 2H), 6.96 (s, 2H), 3.57 (s, 4H), 2.63 – 2.51 (m, 16H), 1.57 (d, $J = 11.9$ Hz, 26H), 1.34 (d, $J = 7.3$ Hz, 24H), 0.93 (d, $J = 7.6$ Hz, 36H). ^{13}C NMR (100 MHz, CDCl_3): δ 153.32, 150.63, 147.65, 147.04, 143.07, 142.61, 141.09, 139.64, 138.93, 134.93, 129.08, 129.03, 128.20, 128.15, 127.84, 126.99, 123.95, 123.29, 122.59, 121.99, 120.59, 119.14, 117.00, 116.83, 64.79, 64.55, 35.26, 35.22, 33.56, 31.95, 31.47, 30.23, 29.73, 29.41, 28.77, 25.81, 23.48, 22.78, 22.73, 22.65, 22.57, 22.49, 14.29, 14.19, 14.00, 10.96. MS (MALDI-TOF, m/z): $[\text{M}]^+$ Calcd for $\text{C}_{158}\text{H}_{168}\text{N}_2\text{O}_2\text{S}_2$: 2189.25; found 2188.15. Melting point: 310°C .

LIDT: orange-yellow powder; yield 53%. ^1H NMR (400 MHz, CDCl_3): δ 7.37 (d, $J = 8.2$ Hz, 2H), 7.30 (s, 2H), 7.28 (s, 2H), 7.27 (s, 2H), 7.20 – 7.13 (m, 10H), 7.08 (d, $J = 8.3$ Hz, 8H), 7.05 – 6.93 (m, 22H), 6.92 – 6.88 (m, 2H), 6.81 (d, $J = 7.8$ Hz, 14H), 6.63 (t, $J = 8.7$ Hz, 16H), 2.61 – 2.53 (m, 8H), 2.51 – 2.38 (m, 16H), 1.63 – 1.48 (m, 42H), 0.98 – 0.83 (m, 58H). ^{13}C NMR (100 MHz, CDCl_3): δ 157.43, 156.80, 153.20, 151.00, 150.76, 150.56, 149.39, 147.79, 146.88, 145.62, 145.32, 144.90, 143.32, 141.15, 140.54, 140.44, 139.35, 139.09, 138.89, 138.84, 138.21, 135.84, 135.32, 134.95, 129.19, 128.32, 128.28, 127.80, 127.44, 124.53, 123.98, 123.66, 123.47, 122.64, 122.27,

120.45, 119.22, 119.04, 116.66, 115.64, 115.01, 114.30, 64.62, 63.98, 35.77, 35.43, 35.36, 35.16, 34.61, 34.01, 33.69, 33.46, 32.11, 31.99, 31.81, 31.69, 31.21, 30.33, 29.88, 29.69, 29.55, 29.34, 29.13, 22.95, 22.85, 22.62, 14.31, 14.19, 14.16. MS (MALDI-TOF, m/z): [M]⁺ Calcd for C₁₉₆H₂₀₄N₂S₂: 2649.55; found: 2650.43. Melting point: 243°C.

LIDTT: orange-yellow powder; yield 41%. ¹H NMR (400 MHz, CDCl₃): δ 7.67 (s, 2H), 7.50 (d, $J = 8.2$ Hz, 2H), 7.37 (s, 2H), 7.31 (s, 2H), 7.22 – 7.13 (m, 26H), 7.10 – 7.04 (m, 28H), 7.03 – 6.95 (m, 18H), 2.56 (d, $J = 7.5$ Hz, 24H), 1.68 – 1.52 (m, 46H), 0.97 – 0.82 (m, 50H). ¹³C NMR (100 MHz, CDCl₃): δ 153.29, 153.22, 153.03, 147.66, 147.00, 146.80, 146.77, 142.94, 142.82, 141.73, 141.61, 141.08, 140.57, 140.32, 137.85, 136.92, 135.79, 134.96, 129.09, 128.41, 128.16, 128.13, 128.09, 128.04, 123.96, 122.60, 64.57, 62.92, 62.89, 35.61, 35.27, 35.21, 33.56, 33.45, 31.72, 31.26, 29.73, 29.18, 22.59, 22.54, 22.46, 14.10, 13.98. MS (MALDI-TOF, m/z): [M]⁺ Calcd for C₂₀₀H₂₀₄N₂S₄: 2761.49; found 2763.31. Melting point: 257°C.

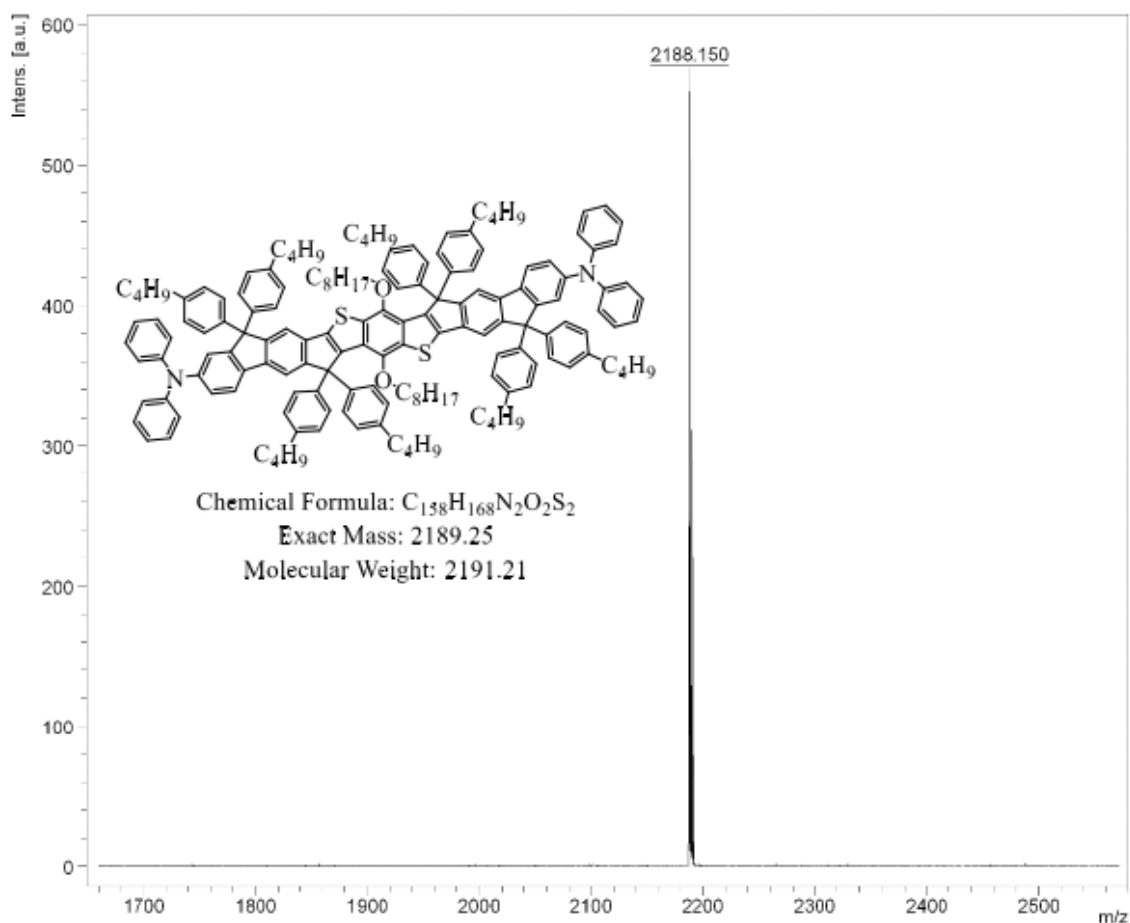


Figure S1. MALDI-TOF of LBDT.

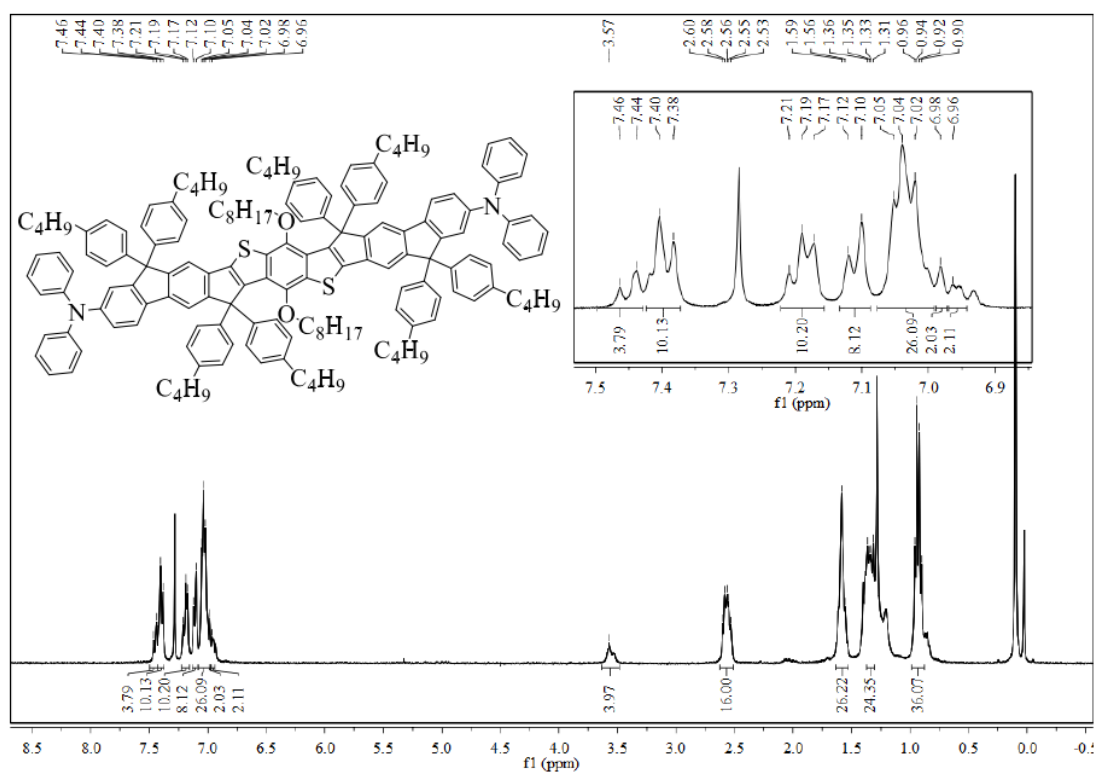


Figure S2. ^1H NMR of LBDT.

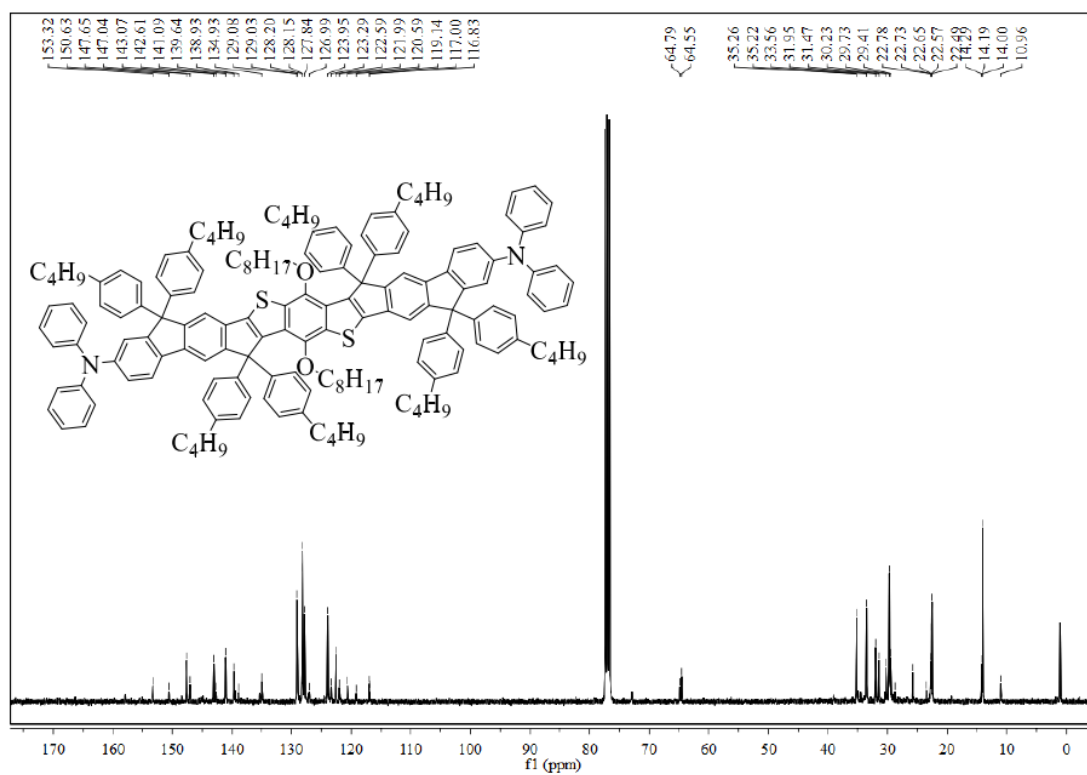


Figure S3. ^{13}C NMR of LBDT.

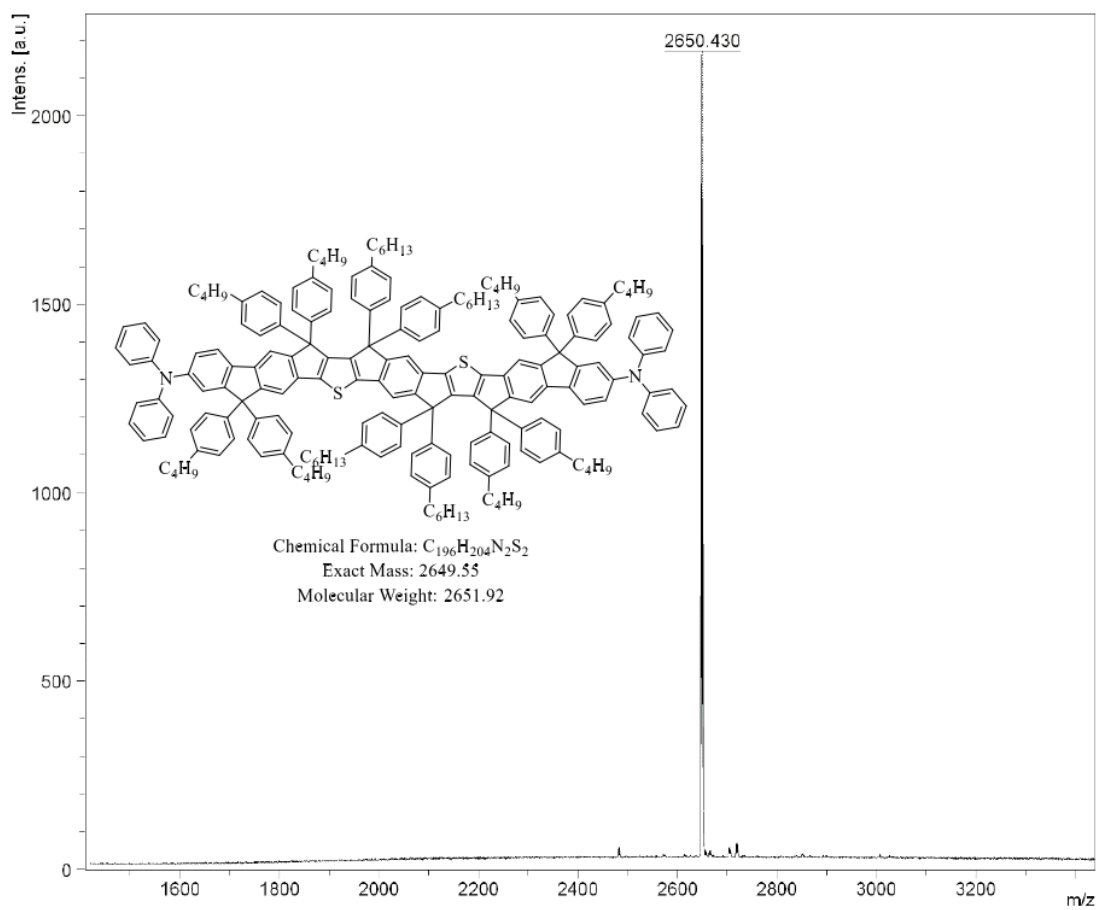


Figure S4. MALDI-TOF of LIDT.

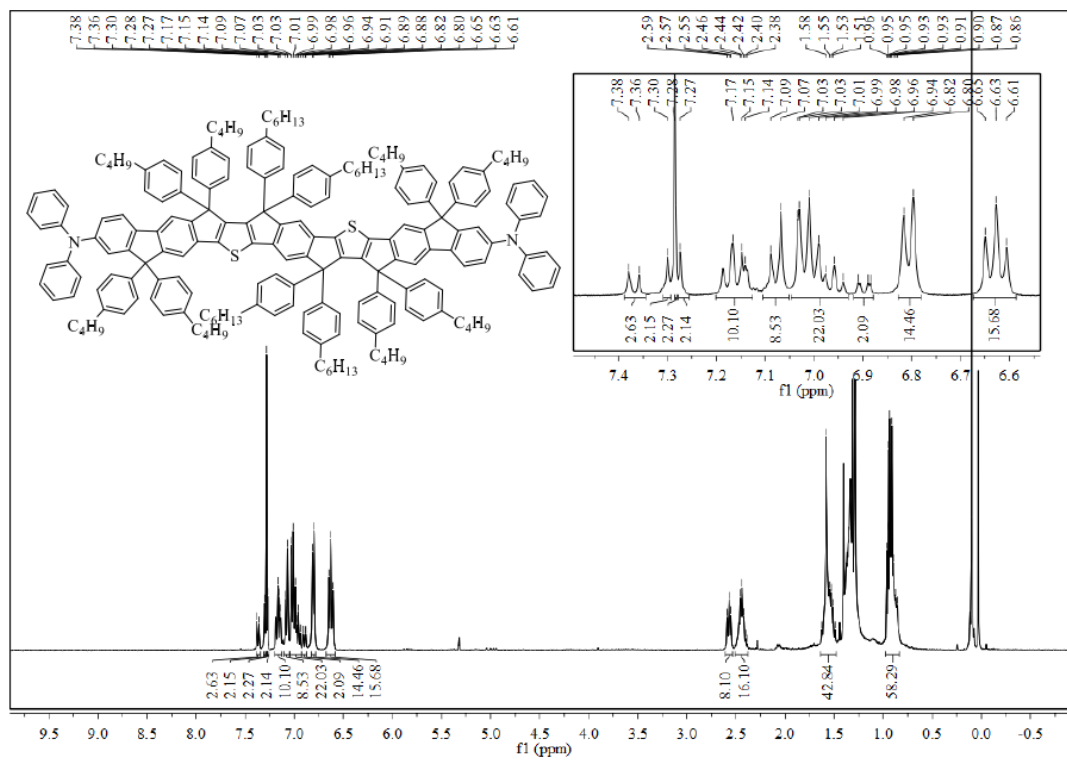


Figure S5. 1H NMR of LIDT.

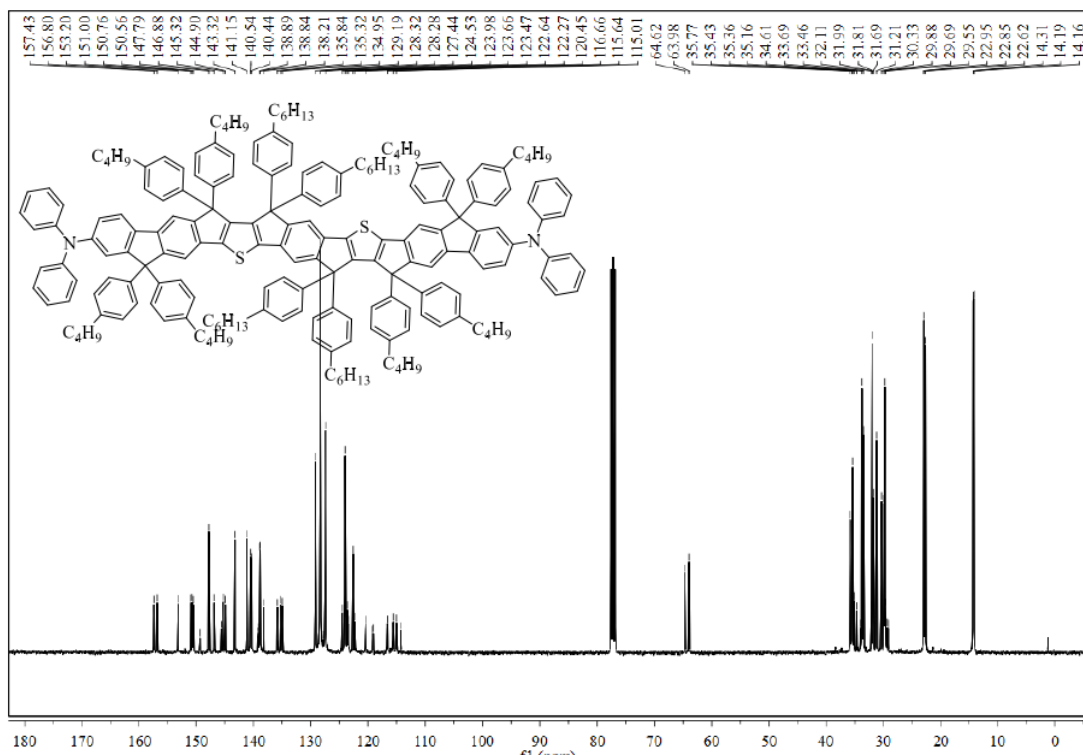


Figure S6. ^{13}C NMR of LIDT.

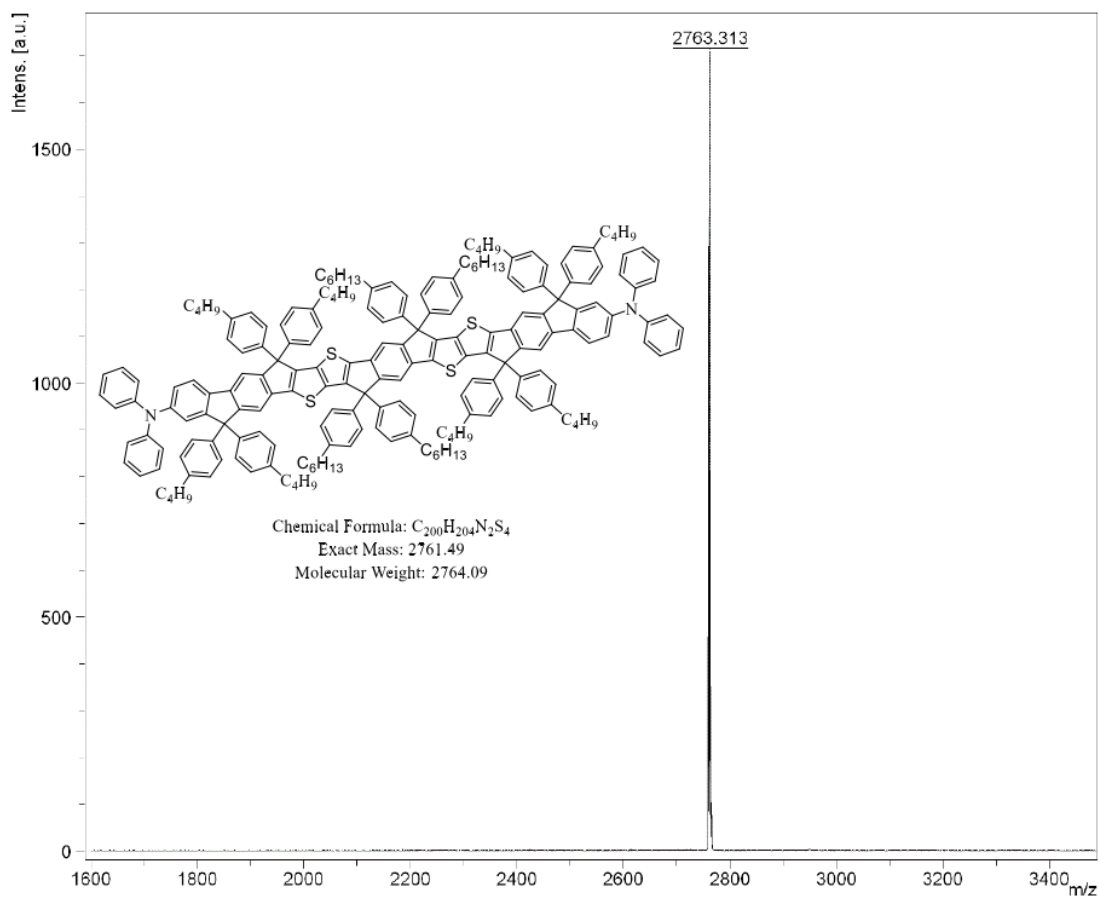


Figure S7. MALDI-TOF of LIDTT.

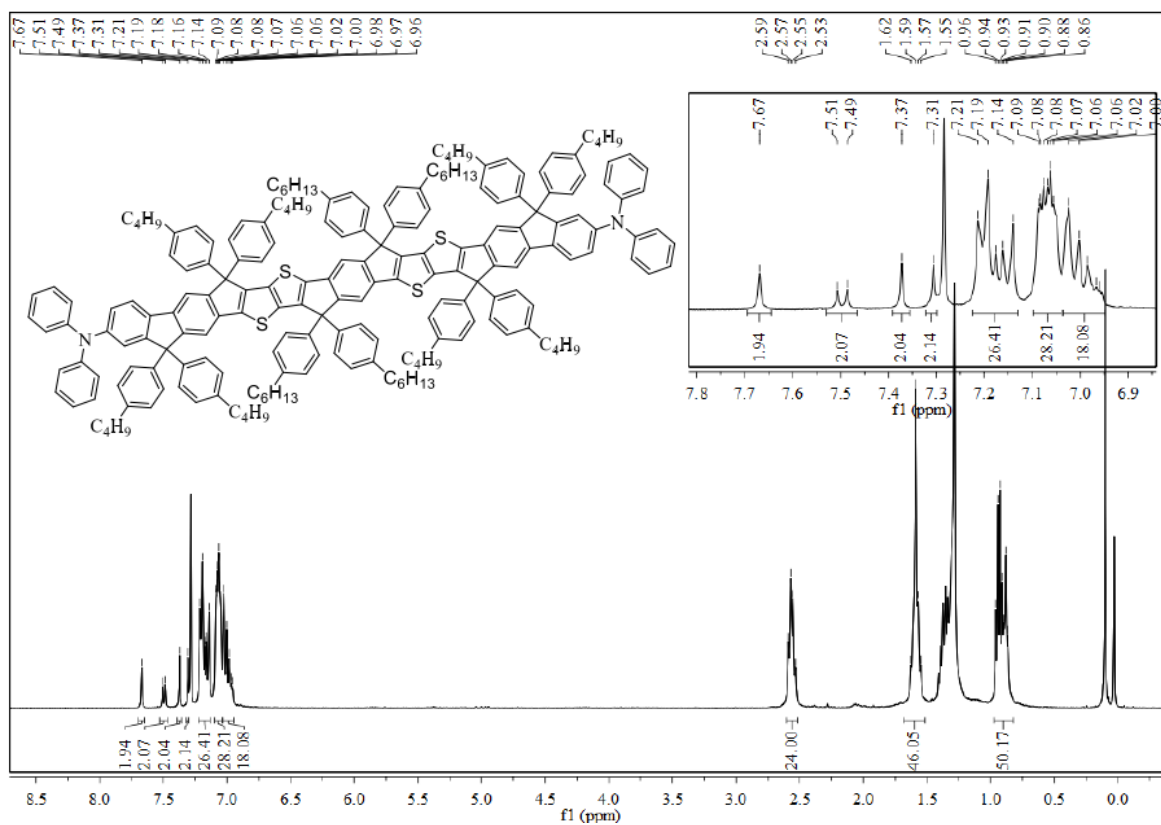


Figure S8. ¹H NMR of LIDTT.

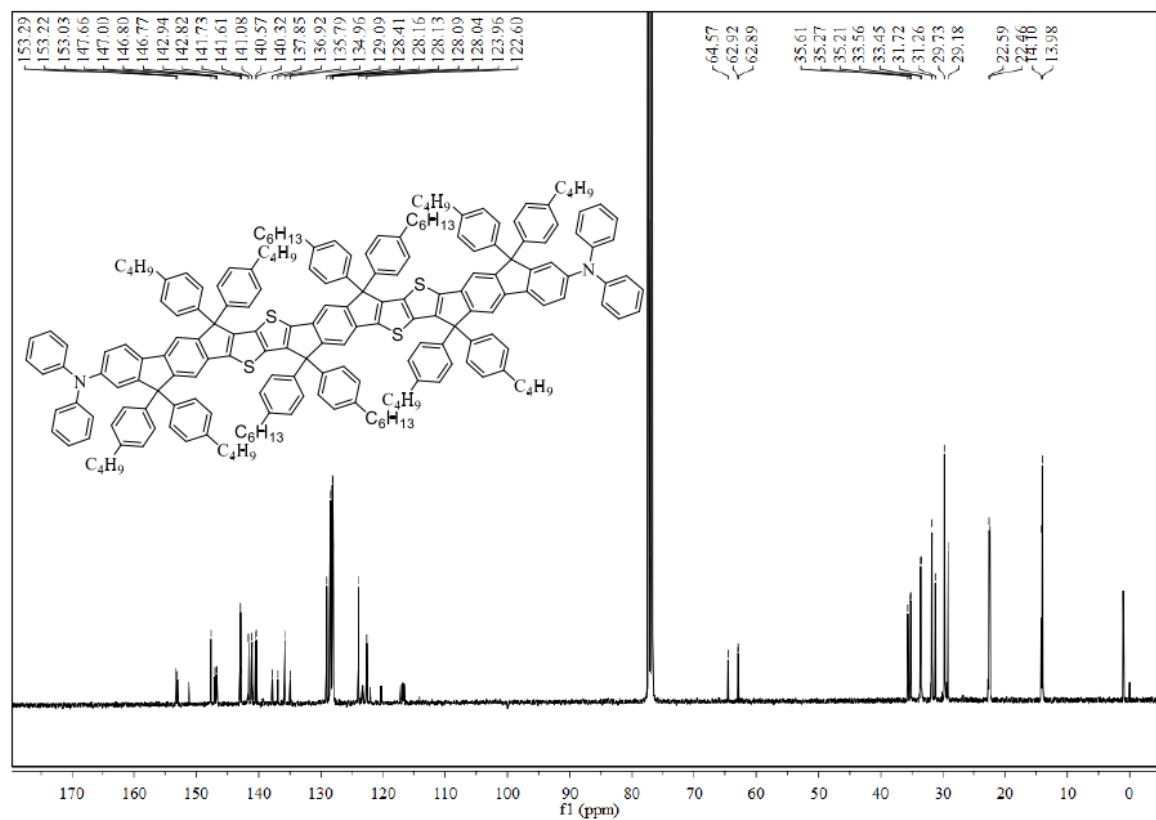


Figure S9. ¹³C NMR of LIDTT.

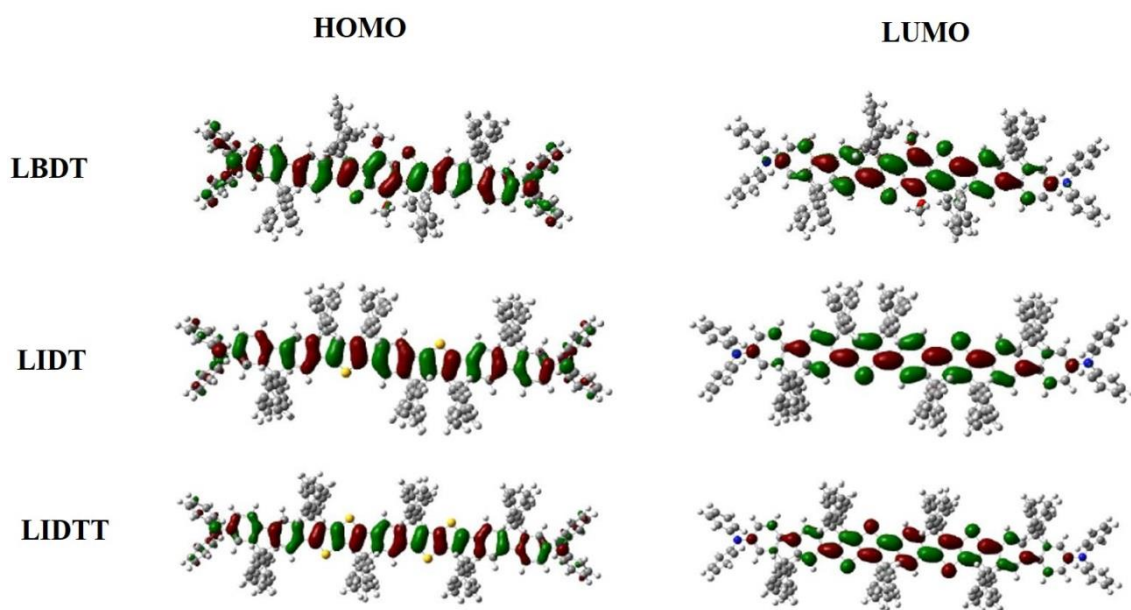


Figure S10. HOMO and LUMO distributions of LBDT, LIDT and LIDTT.

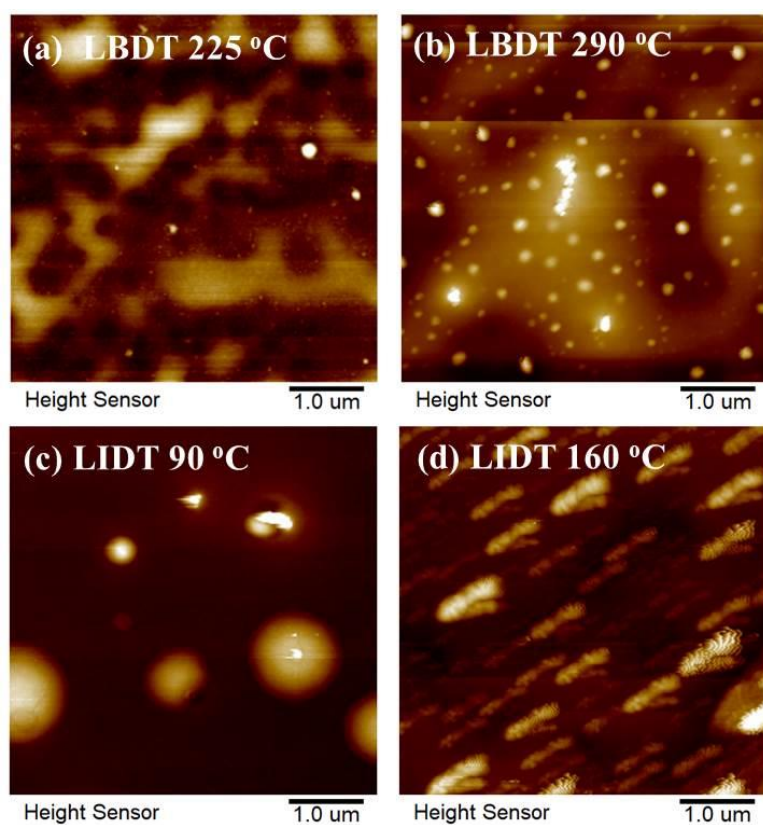


Figure S11. AFM images of LBDT and LIDT with various annealing temperatures.

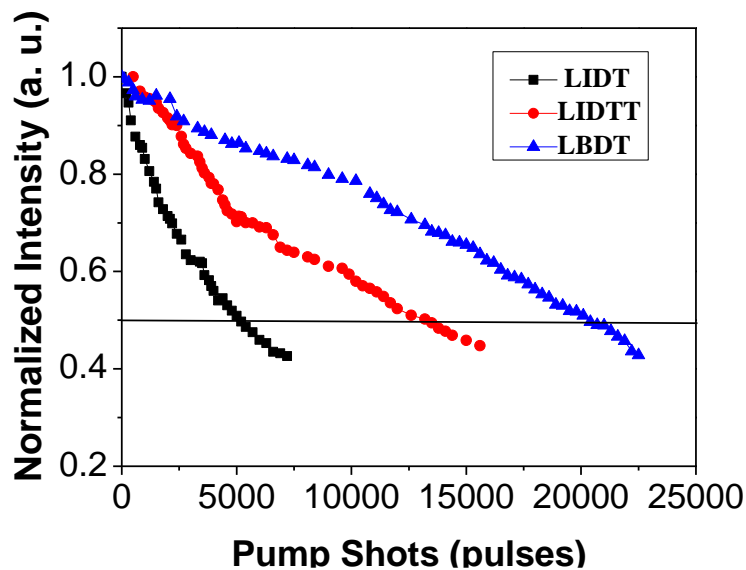


Figure S12. The ASE photostability of LIDT, LIDTT and LBDT films pumped in open ambient atmosphere.

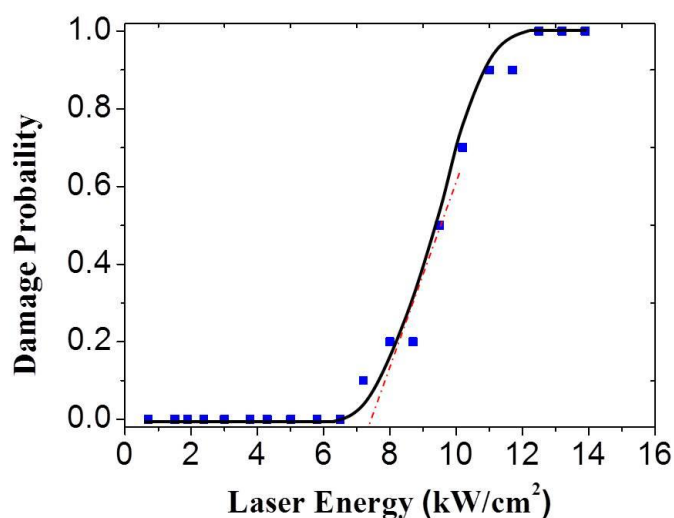


Figure S13. The plot of laser energy versus damage probability, indicating the laser damaging threshold.

Methods of preparation of organic lasers

The films were optically pumped with a Q-switched, neodymium ion doped yttrium aluminium garnate [Nd³⁺:YAG] laser focused with a cylindrical lens to form a stripe-shaped excitation zone on the sample, with an optical parametric oscillator that delivered 5 ns pulses at a repetition rate of 10 Hz.