Supporting Information

Pick and Place Distributed Feedback Lasers from Organic Single Crystals

Suqian Ma, Mengjie Wei, Sai Kiran Rajendran, Markus Karl, Bin Xu, Malte C. Gather, Wenjing Tian*, Graham A. Turnbull*, and Ifor D. W. Samuel*

Materials:

Scheme S1 Synthesis route of BDPV2T, DSB-Me, and P2T-CF₃.

BDPV2T: Compound **BDPV2T** was synthesized through two steps with a yield of 70% according to our previous work.^[1] 2,2'-Bithiophene (**1**) was reacted with *n*-butyllithium and dimethyl formamide to give 5,5'-diformyl-2,2'-bithiophene (**2**), and then, **2** was reacted with diphenylmethane (**3**) to afford **BDPV2T**. ¹H NMR (500 MHz, DMSO-*d*₆, δ): 7.59-7.54 (m, 6H), 7.45 (s, 2H), 7.33-7.30 (m, 10H), 7.19 (d, *J*=6.5 Hz, 4H), 7.03 (d, *J*=4 Hz, 2H), 6.92 (d, *J*=4 Hz, 2H). MS (EI): *m/z*: calcd for C₃₆H₂₆S₂: 522.15, found: 522.24.

DSB-Me: Compound **DSB-Me** was synthesized through two steps with a yield of 90%. 1,4-Bis(chloromethyl)benzene (**4**) was reacted with triethyl phosphite to give tetraethyl 1,4-phenylenebis(methylene)diphosphonate (**5**) according to our previous work.^[2] Then Compound **5** (0.5 g, 1 mmol) was stirred with *t*-BuOK (1.184 g, 11 mmol) in THF (30 mL) under N₂

atmosphere. Compound 4-methylbenzaldehyde (**6**, 0.6 g, 5 mmol) in THF (20 mL) was added dropwise to the solution, and the mixture was heated to 50 °C and stirred for 12 h under nitrogen atmosphere. After removing the solvent (THF), the resultant precipitate was washed successively with methanol and filtered off to give 0.28 g of compound **DSB-Me** as light yellow powder. ^1H NMR (500 MHz, CDCl_3) δ 7.49 (s, 4H, Ph), 7.42 (d, $J=8$ Hz, 4H, Ph), 7.17 (d, $J=8$ Hz, 4H, Ph), 7.08 (d, $J=8$ Hz, 4H, CH=CH), 2.36 (s, 6H, CH_3). MS (EI): m/z : calcd for $\text{C}_{24}\text{H}_{22}$: 310.43, found: 310.09.

P2T-CF₃: Compound **P2T-CF₃** was synthesized according to the previous reported method.^[3] ^1H NMR (500 MHz, DMSO) δ 7.92 (d, $J=8$ Hz, 4H, Ph), 7.79 (d, $J=8$ Hz, 4H, Ph), 7.74 (d, $J=4$ Hz, 2H, Th), 7.50 (d, $J=4$ Hz, 2H, Th). MS (EI): m/z : calcd for $\text{C}_{22}\text{H}_{12}\text{F}_6\text{S}_2$: 454.45, found: 454.10.

Figure S1 Absorption, PL and ASE spectra of DSB-Me, BDPV2T, and P2T-CF₃ single crystals.

Figure S2 Time-resolved fluorescence spectra of DSB-Me, BDPV2T, and P2T-CF₃ crystals measured on an Edinburgh FLS980 spectrometer using time-correlated single-photon counting (TCSPC) method.

Table S1 Summary of photophysical properties of DSB-Me, BDPV2T, and P2T-CF₃ crystals.

Name	λ_{em} (nm)	PLQY	τ (ns)	k_r (ns ⁻¹)	k_{nr} (ns ⁻¹)
BDPV2T	533	30%	0.96	0.31	0.73
DSB-Me	485	59%	4.23	0.14	0.10
P2T-CF ₃	550	36%	1.37	0.26	0.47

Figure S3 Emission spectra on a logarithmic scale for the data of Figure 2a.

Table S2 Summary of lasing threshold of different organic single crystals

Name	Type	Threshold ($\mu\text{J cm}^{-2}$)	Reference
BDVP2T	DFB	122 (1 ns)	this work
BP2T	DFB	25 (120 fs)	[4]
BSB-Me	DFB	10 (120 fs)	[5]
<i>o</i> -MSB	Self-cavity	0.54 (150 fs)	[6]
β DBDCS	Self-cavity	0.4 (300 ps)	[7]
P6T	Self-cavity	750 (500 ps)	[8]

Figure S4 Angle-resolved PL of TM modes. The sample was excited by a 442 nm CW laser, and the excitation energy is below the threshold.

Refractive Index

The refractive index of BDPV2T crystal is measured on the basis of thin-film interference and the reflectance spectra.^[9] Provided that the light is propagating perpendicular to the crystal surface, the group refractive index n_g is expressed as $n_g = \Delta m / 2d\Delta\nu$, where Δm is the variation of mode, d is the crystal thickness, $\Delta\nu$ is the variation of wavenumber. Using the adjacent peaks or valleys in Figure S6, the n_g at specific wavelengths can be calculated as shown in Figure S7, where black squares and red circles represent the n_g of c axis and b axis, respectively.

Assuming the phase refractive index n can be described by the Sellmeier equation:

$$n = \sqrt{A + B/[1 - (C/\lambda)^2]} \quad (\text{S1})$$

n_g is expressed as follows:

$$n_g = \frac{A[1 - (\frac{C}{\lambda})^2]^2 + B}{\sqrt{[1 - (\frac{C}{\lambda})^2]^3} \sqrt{A[1 - (\frac{C}{\lambda})^2] + B}} \quad (\text{S2})$$

where λ is the wavelength, A and B are dimensionless fitting parameters, C is a parameter with the dimension of length (wavelength). After fitting the data in Figure S7 using Equation S2 (solid lines), appropriate values of A , B , and C can be obtained. Once the parameters A , B , and C have been determined, the phase refractive index as a function of wavelength can be calculated using the Sellmeier equation (Equation S1) as shown in Figure 3c.

Figure S5 Thickness of the crystal shown in Figure 3b. The thickness of this crystal is 2480 nm.

Figure S6 Polarized reflectance spectra of BDPV2T crystal shown in Figure 3b along (a) *c*-axis and (b) *b*-axis.

Figure S7 Group index fitting along *c*-axis and *b*-axis.

Figure S8 (a) Simulated growth morphology of BDPV2T crystal by Materials Studio, viewing perpendicular to the *bc*-plane. (b) Molecular packing in the *bc*-plane.

Figure S9 Angle dependent emission from an individual BDPV2T crystal on a substrate without grating. The linear polarizer is inserted between crystal surface and the optical fiber, where the angle of 0° refers to the polarizer being parallel to the crystal c -axis.

Figure S10 Anisotropy of laser polarisation from an individual BDPV2T crystal on a 1D linear grating, with pump energy density well above the lasing threshold. The crystal c -axis is aligned parallel to the grating grooves.

Single crystal lasers were fabricated with different crystal axis alignment relative to the direction of the 1D linear grating to consider the influence of the anisotropy of the single crystal on the lasing properties. As shown in Figure S11, the crystal c-axis (red arrow) is aligned at 90°, 45°, and 0° to the grating grooves (blue arrow) in samples (a) to (c). Figure S11(d) and (e) show the corresponding lasing properties as a function of the angle θ .

Figure S11 Lasing properties of different rotation angles (θ) between the crystal c-axis and the direction of grating grooves. Bright field images of the samples with $\theta =$ (a) 90°, (b) 45°, and (c) 0°, where the blue arrow is the direction along the grating grooves, the red arrow is the direction of crystal c-axis. The grating period is 350 nm, and scale bar is 200 μm . (d) Normalized lasing spectra of these samples with pump energy density well above the lasing threshold. (e) Input-output characteristics of these single-crystal lasers.

Table S3 Effective indices calculated and simulated by COMSOL software at different TE modes.

TE mode	λ^a	n at λ^b	n_{eff}^c (calculated)	n_{eff} (simulated)
TE0	713 nm	2.04	2.037	1.984
TE1	634 nm	2.08	1.811	1.813
TE2	558 nm	2.16	1.594	1.596

^a The wavelength of different TE modes are determined from the intersections in Figure 3a.

^b The refractive indices at different wavelength are determined from Figure 3c.

^c The effective indices at different wavelength are calculated from $\lambda = n_{\text{eff}}\Lambda$.

Figure S12 AFM image of 350 nm 1D linear grating.

Figure S13 Lasing spectra of selectively pumping different areas on the same sample.

Figure S14 Lasing spectra of the single crystal laser samples using different grating periods.

Figure S15 Lasing threshold as a function of crystal thickness.

References

- [1] S. Ma, K. Zhou, M. Hu, Q. Li, Y. Liu, H. Zhang, J. Jing, H. Dong, B. Xu, W. Hu, W. Tian, *Adv. Funct. Mater.* **2018**, *28*, 1802454.
- [2] S. Ma, J. Zhang, J. Qian, J. Chen, B. Xu, W. Tian, *Adv. Opt. Mater.* **2015**, *3*, 763–768.
- [3] S. Ando, J. Nishida, H. Tada, Y. Inoue, S. Tokito, Y. Yamashita, *J. Am. Chem. Soc.* **2005**, *127*, 5336-5337.
- [4] H.-H. Fang, R. Ding, S.-Y. Lu, J. Yang, X.-L. Zhang, R. Yang, J. Feng, Q.-D. Chen, J.-F. Song, H.-B. Sun, *Adv. Funct. Mater.* **2012**, *22*, 33.
- [5] H.-H. Fang, R. Ding, S.-Y. Lu, X.-L. Zhang, J. Feng, Q.-D. Chena, H.-B. Sun, *J. Mater. Chem.* **2012**, *22*, 24139.
- [6] X. Wang, H. Li, Y. Wu, Z. Xu, H. Fu, *J. Am. Chem. Soc.* **2014**, *136*, 16602.
- [7] S. Varghese, S.-J. Yoon, S. Casado, R. Fischer, R. Wannemacher, S. Y. Park, J. Gierschner, *Adv. Opt. Mater.* **2014**, *2*, 542.
- [8] M. Ichikawa, R. Hibino, M. Inoue, T. Haritani, S. Hotta, K. Araki, T. Koyama, Y. Taniguchi, *Adv. Mater.* **2005**, *17*, 2073.
- [9] T. Yamao, N. Sakamoto, S. Hotta, H. Mizuno, H. Yanagi, *Jpn. J. Appl. Phys.* **2012**, *51*, 11PD03.