

Supporting Information

High gain, low loss, and low-threshold spherical organic laser based on highly miscible excited-state intramolecular proton transfer dyes

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Experimental

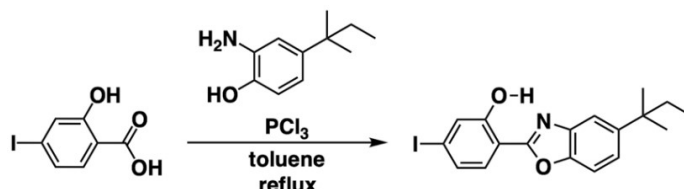
All the chemicals were purchased from Tokyo Chemical Industry, Fujifilm Wako Pure Chemical, or Merck (Sigma-Aldrich®), and used as received. Anhydrous tetrahydrofuran (THF) and toluene were purchased from Kanto Chemical, and passed through an AS ONE Glass Contour system equipped with two packed columns of neutral alumina and copper oxide under nitrogen before use. Triethylamine was distilled over calcium hydride. TLC analyses were performed on a glass coated with Silica gel 70 F₂₅₄ purchased from Fujifilm Wako Pure Chemical Co. Column chromatography was performed on PSQ60B silica gel (spherical) purchased from Fuji Silysia Chemical. ¹H and ¹³C NMR spectra were recorded in chloroform-*d* (CDCl₃) on a Varian Mercury 400 spectrometer, operating at 400 and 100 MHz, respectively, where chemical shifts were determined with respect to tetramethylsilane (TMS, δ 0.00) as an internal reference.

Dye-doped poly(methyl methacrylate) (PMMA) films were fabricated by the spin-coating method. PMMA (1.0 g) was dissolved in CHCl₃ (10 mL) and stirred at 65 °C for 16 h. An aliquot of this PMMA solution (100 mg mL⁻¹) was added to a vial containing ca. 1.0 mg of **1** or **2** weighed in advance. To this vial was added additional 0.1 mL of CHCl₃, allowing a homogeneous solution. 20 μ L of the solution was dropped on a quartz substrate and spin-coated at 1500 rpm for 30 seconds using a Mikasa MS-A-100 spin-coater, and the resulting film was air-dried before characterizations. Fluorescence spectra were measured on a JASCO FP-8500 fluorescence spectrophotometer. The excitation wavelengths are 365 and 340 nm for the PMMA films doped with **1** and **2**, respectively. Absolute photoluminescence quantum yields (PLQY) were evaluated on this spectrometer with a JASCO ILF-835 fluorescence integrate sphere unit. The optical textures were recorded by an Olympus model BX53-P polarizing optical microscope (POM) equipped with a Canon EOS kiss X7i digital camera.

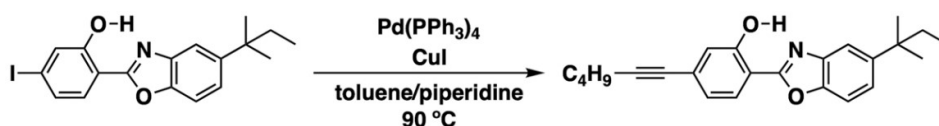
Optical microscopy (OM), fluorescent microscopy (FM), and POM images of **MS** were taken on Olympus model BX53 upright microscope. Scanning electron microscope (SEM) images were taken on a Hitachi model S-3700N SEM operating at 15 kV on a silicon substrate. μ -PL measurement with a ns-laser (CNI model MPL-F-355-10mW-10%, λ = 355 nm, pulse duration 7 ns, frequency 1 kHz, laser spot diameter 170 μ m) was conducted with an optical microscope (Nikon model Eclipse LD100D) equipped with an objective lens (Nikon, LU Plan Fluor, 100x, 0.90 NA) and a spectrometer (Lambda Vision model LV-MC3/T, grating: 1800 grooves mm⁻¹, optical resolution: 0.01 nm). μ -PL spectra with a fs laser were obtained through a spectrometer (MS7504, SOLAR TII) equipped with an optical microscope (ECLIPSE TE2000-U, Nikon). Optical pumping was performed with a femtosecond light source setup consisting of a high-energy ultrafast amplified laser (Solstice Ace, Spectra-Physics, Inc.) operated at a wavelength of 800 nm and a collinear optical parametric amplifier (TOPAS Prime, Spectra-Physics, Inc.).

1. Synthesis of 1 and 2

Compound **1** was synthesized according to our earlier report^{S1} and fully characterized by ¹H and ¹³C NMR spectra.



2-((5-tert-pentyl)benzo[d]oxazol-2-yl)-5-iodophenol. To an anhydrous toluene solution (8.0 mL) of 2-hydroxy-4-iodobenzoic acid (793 mg, 3.00 mmol) and 2-amino-4-tert-pentylphenol (538 mg, 3.00 mmol) was added PCl_3 (0.262 mL, 3.00 mmol), and the mixture was refluxed for 18 h under Ar. After cooled down to r.t., the mixture was poured into water and extracted with CH_2Cl_2 . The organic extract was washed with water, dried over MgSO_4 , and evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using hexane/EtOAc (20/1 v/v) as an eluent, where the first fraction was collected and evaporated to dryness under reduced pressure, to allow isolation of 2-((5-tert-pentyl)benzo[d]oxazol-2-yl)-5-iodophenol as yellow solid (433 mg, 0.960 mmol, 32%). ¹H NMR (CDCl_3 , 400 MHz): δ 11.61 (s, 1H, OH), 7.69 (d, J = 8.0 Hz, 1H, Ar-H), 7.68 (d, J = 1.6 Hz, 1H, Ar-H), 7.54 (d, J = 1.6 Hz, 1H, Ar-H), 7.51 (d, J = 8.8 Hz, 1H, Ar-H), 7.39 (dd, J = 8.8, 1.6 Hz, 1H, Ar-H), 7.36 (dd, J = 8.4, 1.6 Hz, 1H, Ar-H), 1.71 (q, J = 7.6 Hz, 2H, CH_2), 1.37 (s, 6H, CH_3), 0.69 (t, J = 7.2 Hz, 3H, CH_3).



2-((5-tert-pentyl)benzo[d]oxazol-2-yl)-5-[hexyn-1-yl]phenol (2). To an anhydrous toluene/piperidine (1/1 v/v) solution (7.0 mL) of 2-((5-tert-pentyl)benzo[d]oxazol-2-yl)-5-iodophenol (242 mg, 0.537 mmol), $\text{Pd}(\text{PPh}_3)_4$ (93.6 mg, 0.0806 mmol), and CuI (30.4 mg, 0.159 mmol) was added 1-hexyne (52.9 mg, 0.644 mmol) under Ar, and the mixture was degassed by freeze-pump-thaw cycles for 3 times. The mixture was stirred at 90 °C for 17 h under Ar. After cooled down to r.t., the mixture was diluted with EtOAc, filtered through a pad of celite, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane/EtOAc (20/1 v/v) as an eluent, where the first fraction was collected and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on aminopropyl-modified silica gel using hexane/EtOAc (20/1 v/v) as an eluent, where the first fraction was collected and evaporated to dryness under reduced pressure, to allow isolation of **2** as pale yellow viscous liquid (125 mg, 0.346 mmol, 64%). ¹H NMR (CDCl_3 , 400 MHz): δ 11.52 (s, 1H, OH), 7.91 (d, J = 8.0 Hz, 1H, Ar-H), 7.67 (d, J = 1.6 Hz, 1H, Ar-H), 7.50 (d, J = 8.4 Hz, 1H), 7.37 (dd, J = 8.4, 1.6 Hz, 1H, Ar-H), 7.14 (d, J = 1.6 Hz, 1H, Ar-H), 7.02 (dd, J = 8.0, 1.6 Hz, 1H, Ar-H), 2.44 (t, J = 6.8 Hz, 2H, CH_2), 1.76–1.69 (m, 2H, CH_2), 1.65–1.58 (m, 2H, CH_2), 1.53–1.47 (m, 2H, CH_2), 1.37 (s, 6H, CH_3), 0.96 (t, J = 7.2 Hz, 3H, CH_3), 0.69 (t, J = 7.2 Hz, 3H, CH_3). ¹³C NMR (CDCl_3 , 100 MHz): δ 162.57, 158.21, 147.11, 146.97, 139.95, 129.07, 126.72, 123.73, 122.89, 120.14, 116.58, 110.01, 109.71, 93.48, 80.25, 38.25, 37.21, 30.67, 22.03, 19.24, 13.67, 9.14.

2. Variable Stripe Length (VSL) measurements

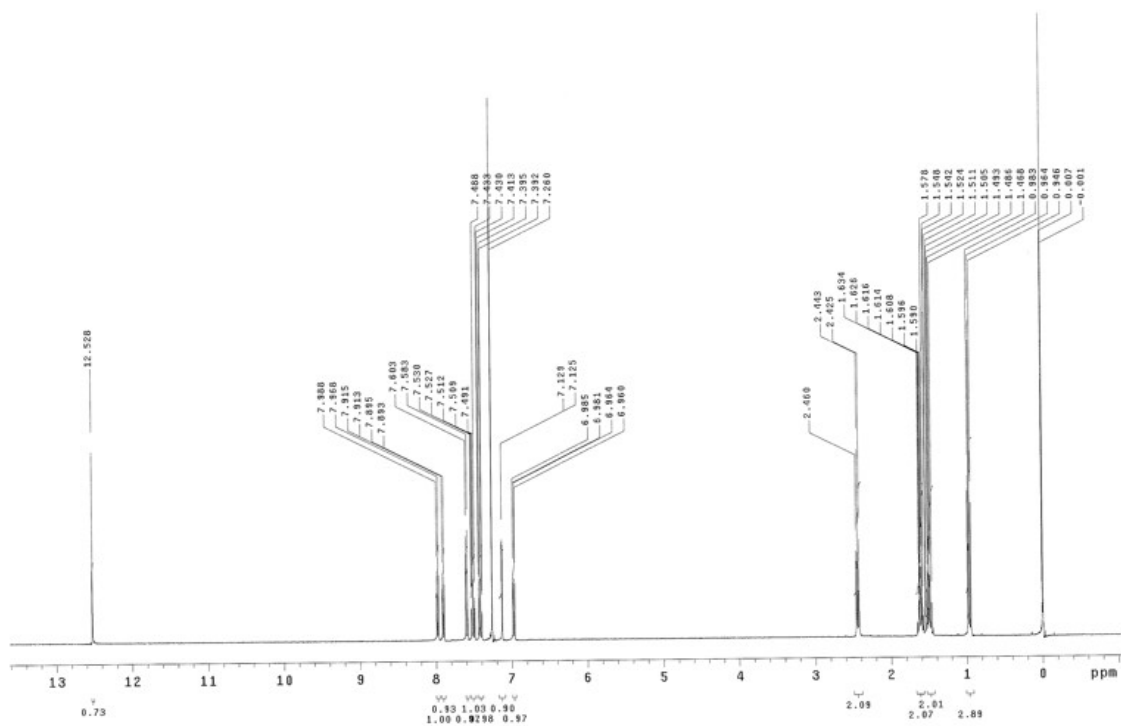
Variable stripe length (VSL) method is commonly employed to evaluate the modal gain in the polymer materials^{S2,S3}. The modal optical gain (g_{mod}) is estimated from the following equation

$$I_{\text{ASE}}(L) = \frac{A}{g_{\text{mod}}} (e^{g_{\text{mod}}L} - 1) \quad (2)$$

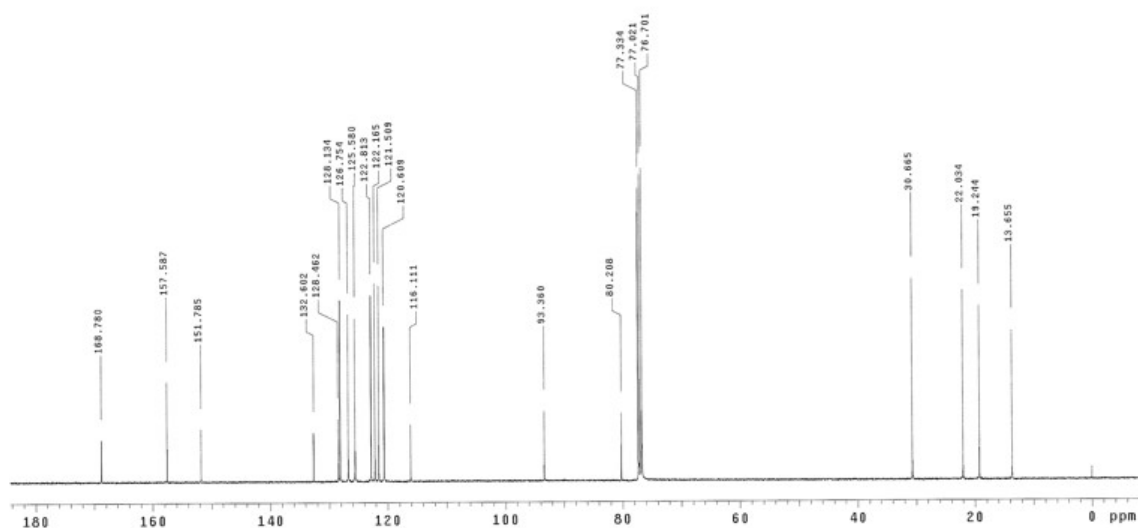
, where I_{ASE} is the PL intensity, L is stripe length, and A is the fitting parameter proportional to the density of excited particles. In our case, the concentration-dependent contribution of self-absorption in g_{mod} is excluded due to the large Stokes shift of the molecule, so the photogenerated exciton density can be discussed directly from the measured g_{mod} . **Fig. S13** shows the relationship between I_{ASE} and L in **1**-doped films. g_{mod} was estimated to be 5–10 cm⁻¹. The values did not change significantly depending on the concentration of the dye. This is presumably because all incident light is absorbed at the surface of the film in the present case, and the number of excitons generated in a unit length did not change even upon increasing the concentration of the dye. Note that the number of excitons per unit volume at the surface should increase at higher concentrations and provide a higher gain for the light that travels therein. The higher concentration at the surface does not result in the higher optical gain in the VSL measurements since the propagating light is distributed over the whole film. In contrast, light in a WGM resonator is localized at the circumference of the sphere and should be amplified significantly as increasing the excitons at the surface.

3. Transient absorption spectroscopy

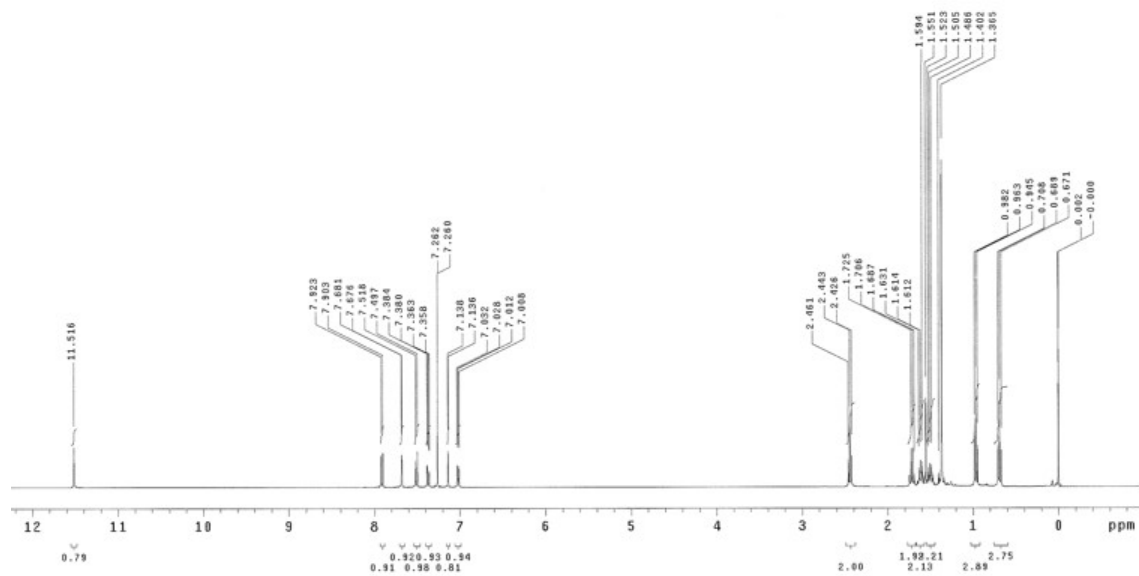
Transient absorption measurements on the femtosecond to nanosecond time scale were conducted by a homemade pump-probe system. An amplified femtosecond laser, Spirit One 1040-8 (Spectra-Physics, 1040 nm, the pulse width: ~270 fs), was split into two beams with a ratio of 1:9. For transient absorption measurement of **1** in CH₂Cl₂, the stronger beam was directed to a noncollinear optical parametric amplifier (NOPA), Spirit-NOPA-3H (Spectra-Physics) to generate the 360-nm femtosecond laser pulse for the pump beam. The pump beam was chopped prior to the sample at 500 Hz for signal differencing. For transient absorption measurements of PMMA films doped with **1**, the stronger beam was passed through a BBO crystal (type I, $\theta = 23.2^\circ$, 5x5x6 mm³, Optronscience, Inc., Japan) to generate a second harmonic (520 nm). Then, the fundamental (1040 nm) and the second harmonic beams were separated by a beam splitter. A fundamental beam was passed through a half-wave plate to match the polarization to the second harmonic. Each beam passes through different optical pathways and was directed to another BBO crystal (type I, $\theta = 32.1^\circ$, 5x5x1 mm³, Optronscience, Inc., Japan) to generate a third harmonic (347 nm) for the pump beam. The other weaker beam was focused to a deuterated water placed in a 10-mm quartz cuvette to generate the white light continuum for the probe beam. Both pump and probe beams were focused to the sample solution placed in the 2-mm quartz cuvette. The polarization between the pump and probe pulses was set at magic angle. The transmitted probe beam was detected with multichannel detection system, PK120-C-RK (UNISOKU), composed of a CMOS linear image sensor and a polychromator. The obtained spectra were calibrated for group velocity dispersion using the data obtained by the optical Kerr signal of CH₂Cl₂ between the pump pulse and the white-light continuum. The instrumental response function was shorter than approximately 100 fs. The sample solutions were stirred with a stirrer during the experiments. The measurements were performed at room temperature.



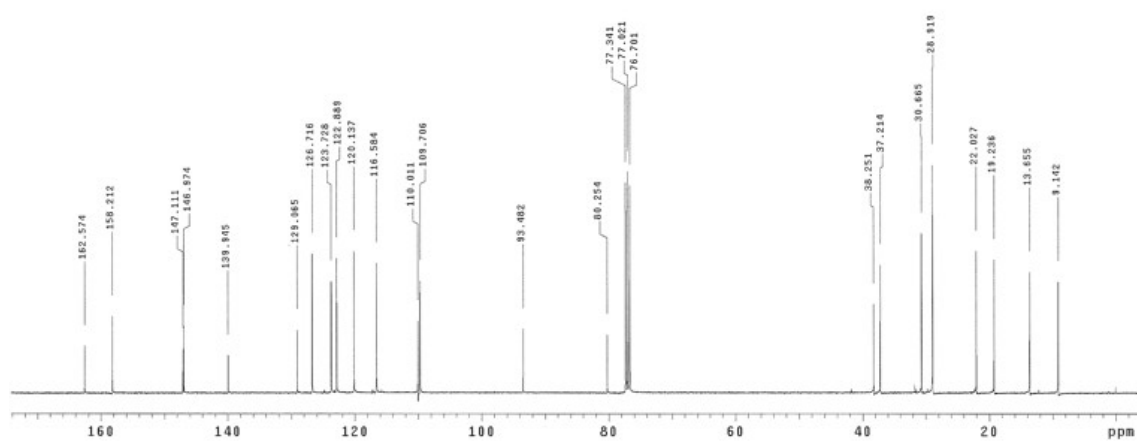
Supporting Figure 1. ¹H NMR spectrum of **1** in CDCl₃ at r.t.



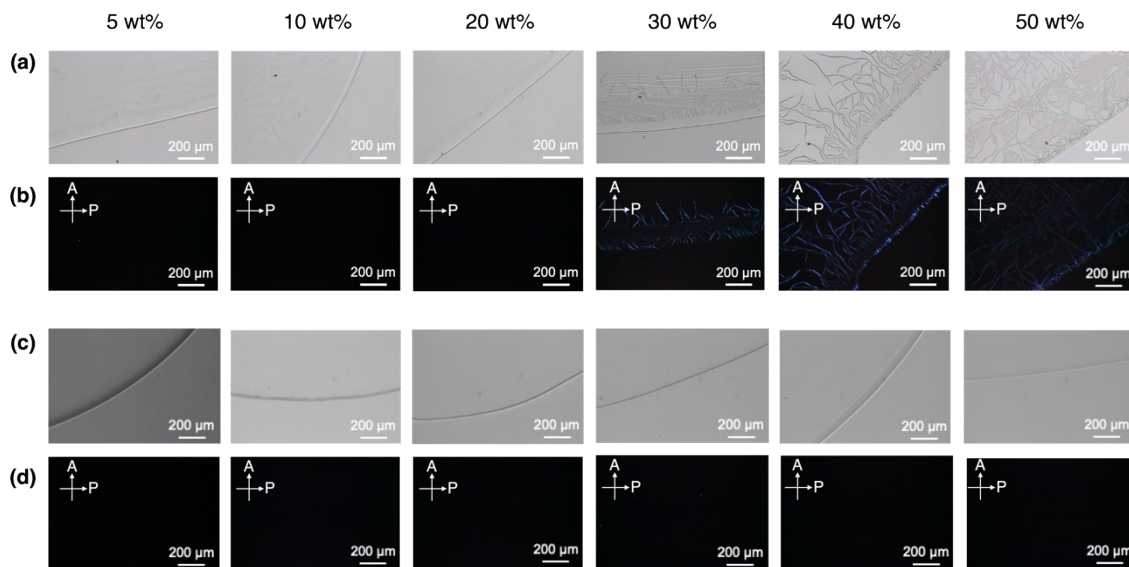
Supporting Figure 2. ¹³C NMR spectrum of **1** in CDCl₃ at r.t.



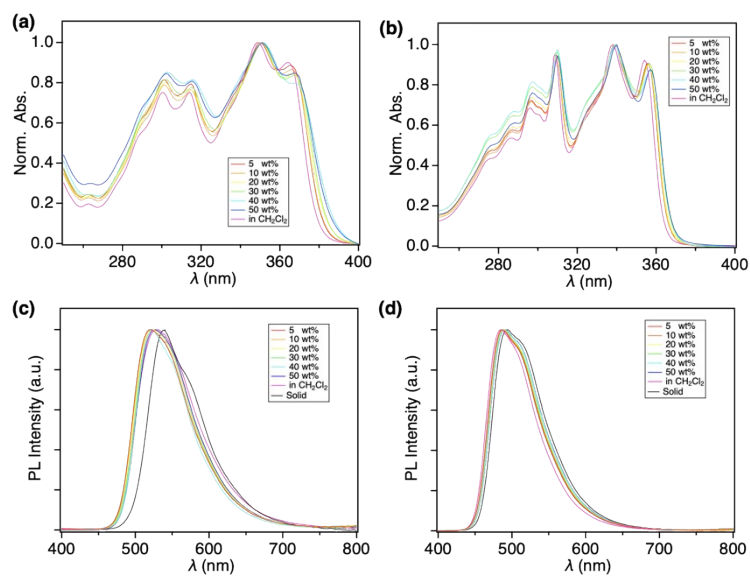
Supporting Figure 3. ¹H NMR spectrum of **2** in CDCl₃ at r.t.



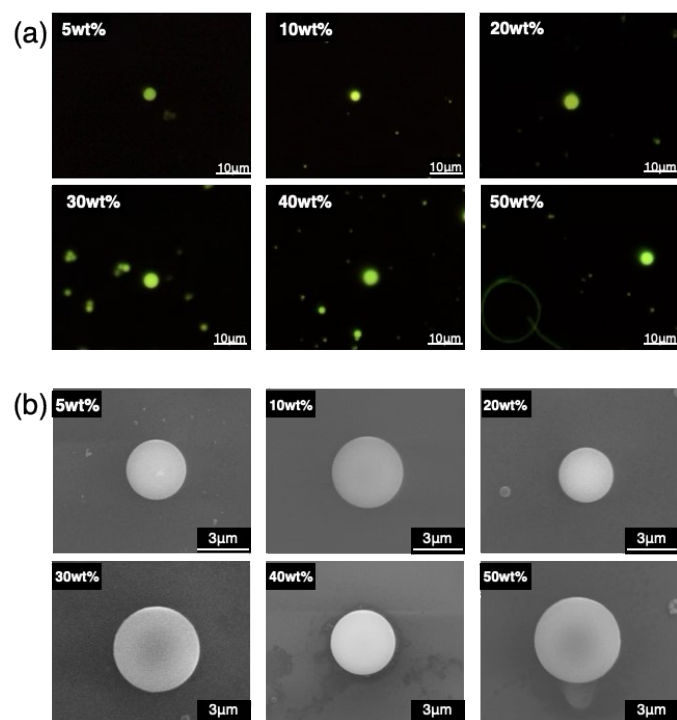
Supporting Figure 4. ¹³C NMR spectrum of **2** in CDCl₃ at r.t.



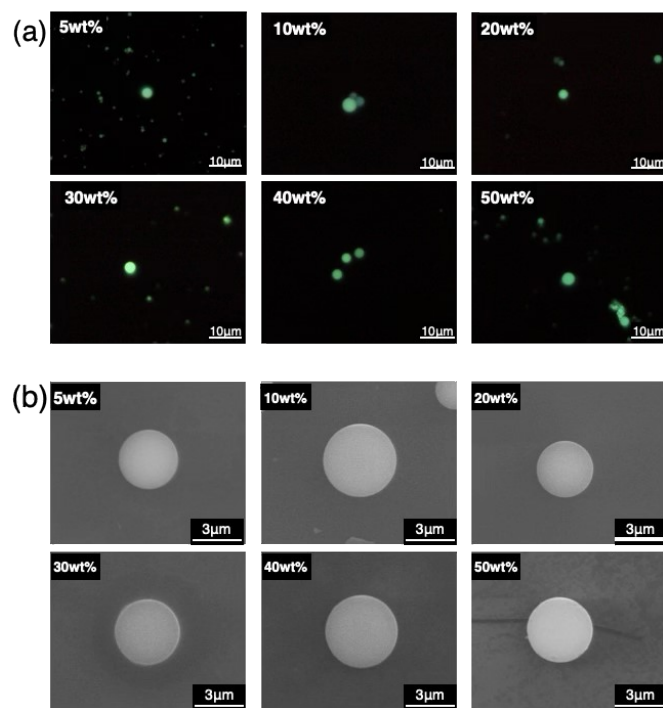
Supporting Figure 5. OM and POM images at the edge of PMMA films with different doping concentrations of **1** (a, b) and **2** (c, d).



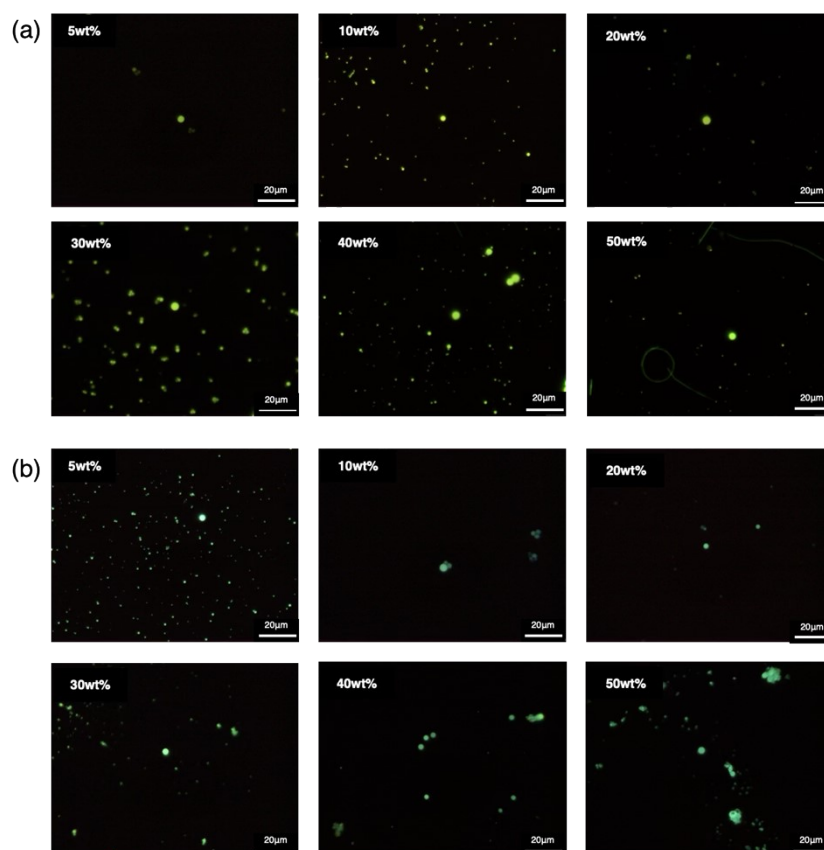
Supporting Figure 6. (a, b) Normalized absorption spectra of CH_2Cl_2 solution (5.0×10^{-5} M) and PMMA films of **1** (a) and **2** (b) with varied doping concentration ($r = 5, 10, 20, 30, 40$, and 50 wt%). (c, d) PL spectra of **1** (c) and **2** (d) in the crystalline state, solution state (CH_2Cl_2 , 5.0×10^{-5} M), and film states ($r = 5, 10, 20, 30, 40$, and 50 wt%).



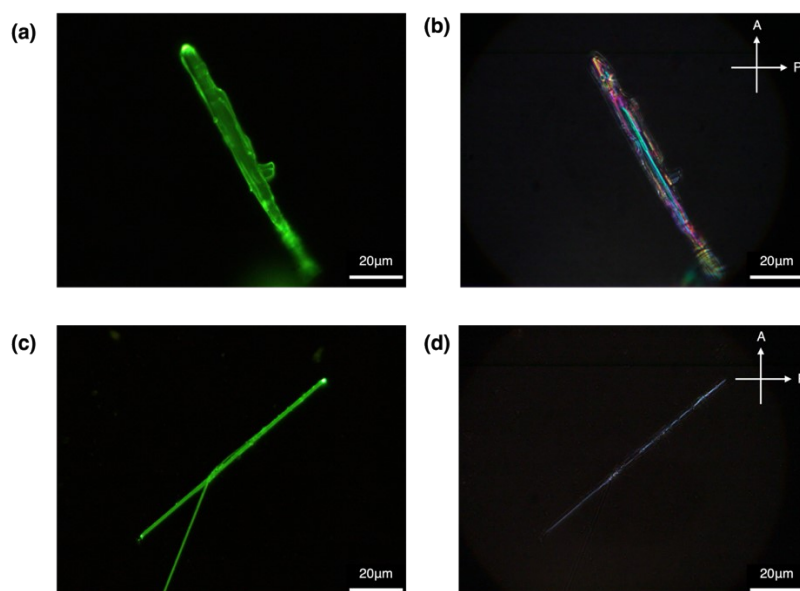
Supporting Figure 7. FM (a) and SEM (b) images of MS^1 with different r .



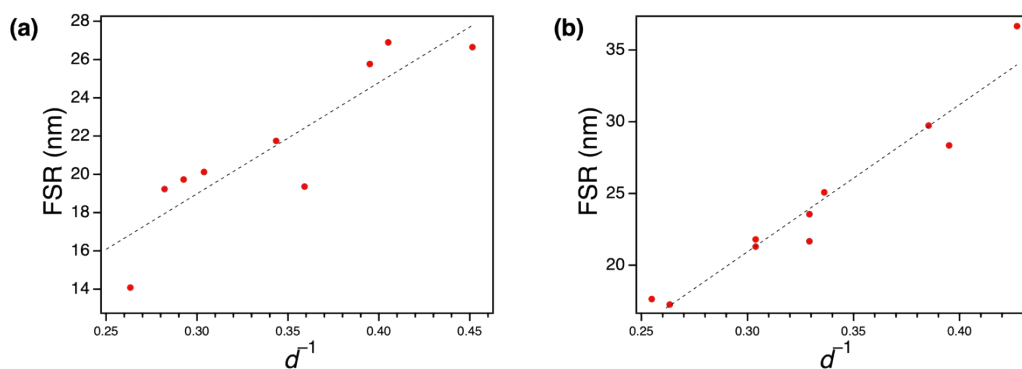
Supporting Figure 8. FM (a) and SEM (b) images of MS^2 with different r .



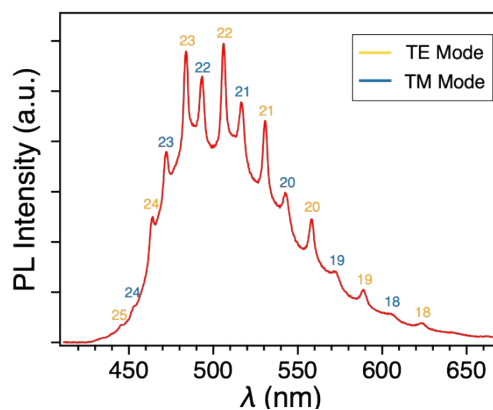
Supporting Figure 9. Un-magnified FM images of MS^1 (a) and MS^2 (b) with different r .



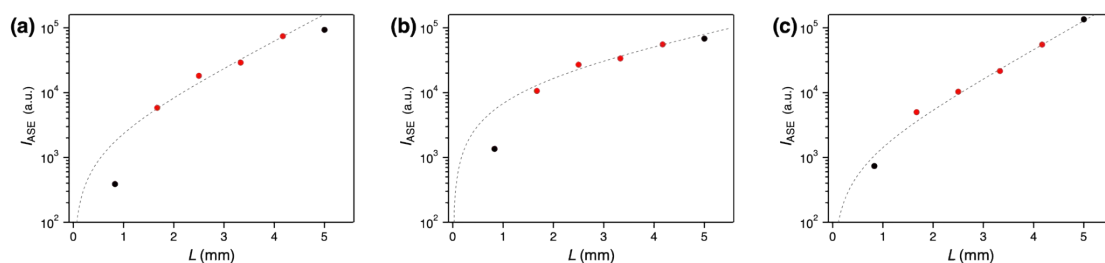
Supporting Figure 10. FM (a, c) and POM (b, d) images of non-spherical precipitates obtained at $r = 100$ (a, b) and 50 wt% (c, d).



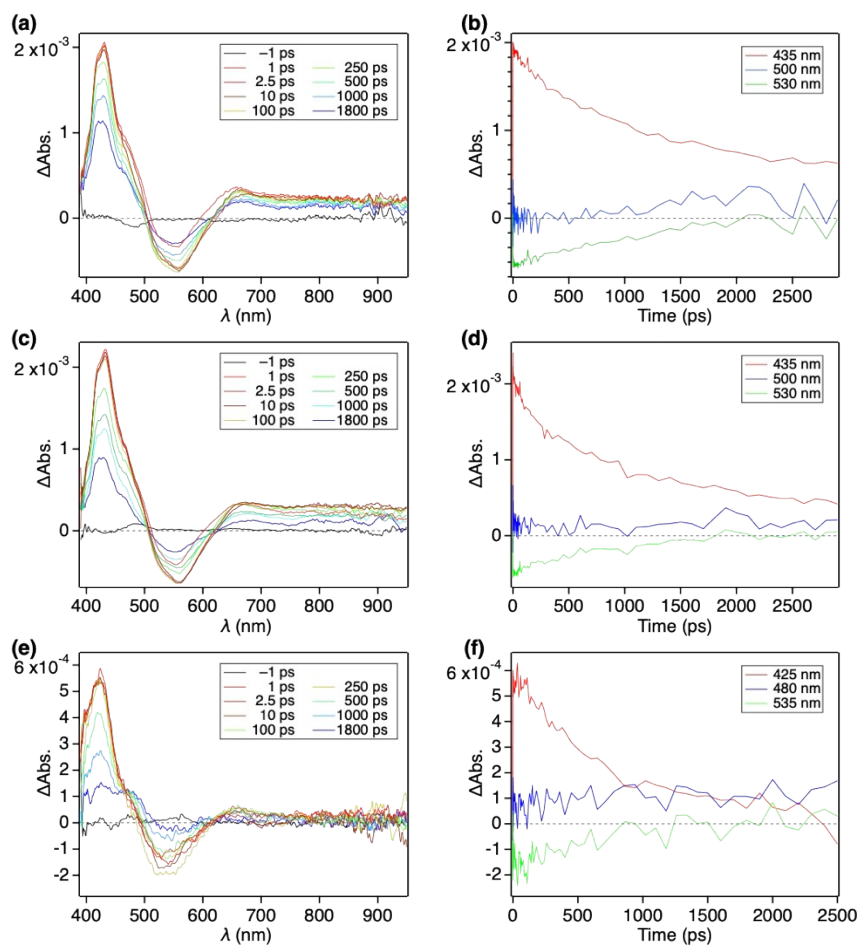
Supporting Figure 11. Plots of free spectral range (FSR) versus inverse of diameter (d^{-1}) of MS^1 (a) and MS^2 (b). The grey dashed lines represent the regression lines.



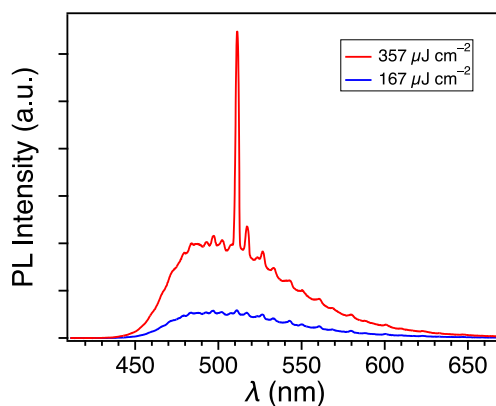
Supporting Figure 12. μ -PL spectrum of $\text{MS}^2_{5\%}$. The TE and TM modes of the WGM are indicated in orange and blue numbers, respectively.



Supporting Figure 13. Plots of PL intensities from films doped with **1** with r of 10 (a), 20 (b), and 30 wt% (c) against the length of the stripe in the VSL measurements. The black dashed curves represent the fitting curves obtained from the data points shown as red circles.



Supporting Figure 14. (a, c) Transient absorption spectra of a PMMA films doped with **1** photoexcited at 347 nm (100 nJ pulse⁻¹). (a) $r = 10$ wt% and (c) $r = 20$ wt%. (b, d) Time-dependent changes of differential absorbance ($\Delta\text{Abs.}$) at wavelengths of 435, 500 and 530 nm. (b) $r = 10$ wt% and (d) $r = 20$ wt%. (e) Transient absorption spectra of a CH₂Cl₂ solution of **1** photoexcited at 360 nm (20 nJ pulse⁻¹). (f) Time-dependent changes in differential absorbance ($\Delta\text{Abs.}$) of a CH₂Cl₂ solution of **1** at wavelengths of 425, 480 and 535 nm.



Supporting Figure 15. μ -PL spectra of MS₂_{30%} upon optical pumping by a nanosecond pulse laser with a power density of 167 (blue curve) and 357 (red curve) $\mu\text{J cm}^{-2}$.

Supporting Table 1. Photoluminescence quantum yield (PLQY) of **1** and **2** in PMMA films, CH₂Cl₂ (5.0 × 10⁻⁵ M) and solid states.

	5 wt%	10 wt%	20 wt%	30 wt%	40 wt%	50 wt%	in CH ₂ Cl ₂	Solid
1	0.34	0.34	0.33	0.35	0.38	0.35	0.10	0.53
2	0.48	0.46	0.46	0.45	0.44	0.43	0.39	0.47

Supporting References

- [S1] W. Zhang, S. Suzuki, S. Cho, G. Watanabe, H. Yoshida, T. Sakurai, M. Aotani, Y. Tsutsui, M. Ozaki and S. Seki, *Langmuir*, 2019, **35**, 14031.
- [S2] S. Yuyama, T. Nakajima, K. Yamashita and K. Oe, *Appl. Phys. Lett.* 2008, **93**, 023306.
- [S3] F. Vogelbacher, X. Zhou, J. Huang, M. Li, K.-J. Jiang, Y. Song, K. Unterrainer and R. Hainberger, *Opt. Mater. Express* 2019, **9**, 1208.