Supporting Information

Controlled Outcoupling of Whispering-Gallery-Mode Lasers Based on Self-Assembled Organic Single-Crystalline Microrings

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Materials and experimental details

1. Materials:

The 3-[4-(dimethylamino)phenyl]-1-(2-hydroxy-4-fluorophenyl)-2-propen-1-one (HDFMAC) was synthesized through the classical Claisen–Schmidt condensation reaction.¹ 1-(4-fluoro-2-hydroxyphenyl)ethan-1-one and 4-(dimethylamino)benzaldehyde were purchased from Aldrich Chemical Co., and used without further purification.

2. Preparation of the organic crystalline microrings:

The ring-shaped structures aggregated from HDFMAC molecules were prepared via a liquid-phase self-assembly method. In a typical preparation, the HDFMAC solution was prepared by adding 1 mg HDFMAC into 1ml mixed solvent (ethanol/dichloromethane at volume ratio = 1:1), which was subsequently treated with sonication (40 KHz) for 30 s. 400 µL of the HDFMAC solution was drop-cast on the glass substrate. Then the self-assembly process was carried out in a weighing bottle (70*30 mm) with a glass cap at room temperature. As dichloromethane has a higher evaporation rate, the rest of the solution mainly consisted of ethanol with strong surface tension, leading to the formation of microdrops, which can serve as confined circular templates for the self-assembly of HDFMAC molecules. The HDFMAC nucleated preferentially at the edge of the microdrop. With the further evaporation of solvent, the assemblies grew into a curved belt that embraced the microdrop. As a result, self-assembled microrings without noticeable defects or joints were finally obtained after the complete evaporation of the solvent. The waveguide-coupled microring and double-ring coupled structures were respectively synthesised with different mixed solutions in ethanol/dichloromethane (volume ratio = 1:3, 3:1). The preparations were carried out at room temperature.

3. Simulation of electric-field intensity distributions:

The numerical studies on the field distributions in the self-assembled microrings was performed using commercial software COMSOL, which solves the Maxwell's equations with finite element method. For the numerical simulations of the TE and TM mode distributions at the cross-section of the microring resonator (Figures 2F in main text), the simulations were run using the Mode Analysis module. The cross-section of the ring was set as 250 nm wide and 2.5 μ m high. As for the 2D electric-field intensity distributions for the wire-ring coupled structure and double-ring coupled systems (Figures 3F and 4F), they were obtained using

Eigenfrequency module in the COMSOL program. In these simulations, the widths of both microrings and the coupled wire waveguide are set as 250 nm. The refractive indices of air, the self-assemble organic structures and the glass substrate used in the simulations were 1.00, 3.28 and 1.50, respectively. The zigzag patterns of the field intensity in Figure 3F and 4F come from the interference between multiple spatial modes at the same frequency.

4. Characterizations:

The morphology of the organic ring-shaped structues was examined with scanning electron microscopy (FEI Nova NanoSEM450) and transmission electron microscopy (TEM, JEOL JEM-2010). AFM images were taken on a Vecco Nanoscope IIIa atom force microscope. The cross-polarized optical images were measured on an optical microscope (Nikon ECLIPSE LV150). X-ray diffraction (XRD, Japan Rigaku D/max-2500) was measured with Cu Ka radiation. The absolute quantum yields were measured by using the Hamamatsu Absolute Quantum Yield Spectrometer C11347. The absorption and fluorescence spectra were measured on a UV-visible spectrometer (Perkin-Elmer Lambda 35) and a fluorescence microscopy images were taken from an inverted fluorescence microscope (Nikon Ti-U), by exciting the samples with a mercury lamp. The single organic ring-shaped structue was uniformly excited by a focused pulse laser beam (400 nm, 150 fs, 1000 Hz). The spatially resolved spectra were measured with a monochrometer (Princeton Instrument Acton SP 2300i) connected with an EMCCD (Princeton Instrument ProEM 1600B). Polarization profiles of the emission intensity were obtained by setting a polarizer in front of the detector.

Name	HDFMAC
Empirical formula	C ₁₇ H ₁₆ F N O ₂
Formula weight	285.31
Temperature	173.1500 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Cell Lengths	a = 10.821(3) Å, b = 3.9030(10) Å, c = 32.750(9) Å
Cell Angles	$\alpha = 90^{\circ}, \beta = 97.778(3)^{\circ}, \gamma = 90^{\circ}$
Volume	1370.5(6) Å ³
Z	4
Density (calculated)	1.383 Mg/m^3
Absorption coefficient	0.100 mm^{-1}
F(000)	600
Crystal size	0.543 x 0.117 x 0.031 mm ³
Theta range for data collection	1.255 to 27.481°
Index ranges	-13<=h<=14, -5<=k<=5, -42<=l<=41
Reflections collected	8809
Independent reflections	3100 [R(int) = 0.0459]
Max. and min. transmission	1.00000 and 0.77532
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3100 / 0 / 193
Goodness-of-fit on F^2	1.133
Final R indices [I>2sigma(I)]	R1 = 0.0621, $wR2 = 0.1456$
R indices (all data)	R1 = 0.0705, wR2 = 0.1515
Largest diff. peak and hole	0.246 and -0.205 e.Å ⁻³

 Table S1. Crystal data and structure refinement for HDFMAC (CCDC No. 1854651).



Figure S1. Synthetic route of HDFMAC molecule.

Aqueous NaOH (1.0 g in 1 mL $H_2O)$ was added the mixture to of 1-(4-fluoro-2-hydroxyphenyl)ethan- 1-one (0.77 g) and 4-(dimethylamino)benzaldehyde (0.75 g) in ethanol (20 mL). The mixture was heated at 60 °C for 12 h. After cooling, the pH was adjusted to 1.0 with HCl (1 M). The mixture was then extracted with dichloromethane and water. After concentration of the mixture under reduced pressure, the resulting solids were purified by recrystallization from ethanol (10 mL) and dichloromethane (1 mL) to afford 1.41 g of HDFMAC.



Figure S2. The morphology of the HDFMAC microbelt. (A) Scanning electron microscope (SEM) image of the HDFMAC microbelt. Scale bar is 5 μ m. (B) Atomic force microscopy (AFM) image and corresponding cross section profile of a single HDFMAC microbelt.

The self-assembled HDFMAC microbelt with a high height to width (h/w) ratio of ~10 has a rectangular cross-section, defect-free surface and highly flat end facets, which is beneficial for the tight optical confinement and low-loss light waveguiding.



Figure S3. X-ray diffraction (XRD) patterns of HDFMAC powder (black) and microbelts (red).

The diffraction peaks of the nanowires can be indexed to a monoclinic single crystal (space group: *P* $2_1/c$, a=10.821 Å, b=3.903 Å, c=32.750 Å, $\alpha=\gamma=90^{\circ}$, $\beta=97.778^{\circ}$. CCDC No. 1854651).



Figure S4. The formation of microdroplets during the solvent evaporation. Optical microscopy image of solution microdroplets on glass substrate taken after the solvent was evaporated for 2 h. Scale bar is $20 \mu m$.

As dichloromethane has a higher vaporizing rate than ethanol,² the rest of the solution mainly consisted of ethanol with strong surface tension, leading to the formation of microdrops, which can serve as confined circular templates for the self-assembly of HDFMAC molecules.



Figure S5. SEM images of HDFMAC microrings with different sizes. When the concentration of HDFMAC units in the solution (1 mL) was adopted as 0.5, 1.5, and 2.5 mg/mL, the microrings with different diameters were finally obtained as ~13 μ m (A), 25 μ m (B) and 40 μ m (C), respectively. Scale bars are 10 μ m.

The diameter of the HDFMAC microring was tuned from ~ 13 to 40 μ m by changing the concentration of HDFMAC units from 1 to 5 mg/mL, which could be utilized to modulate the WGM lasing modes in the microrings.



Figure S6. The absorption and fluorescence spectra of HFDMAC crystals (solid) and in PS (dashed).

The aggregation-induced red shift and narrowing of the fluorescent spectra reduced the overlap with its absorption spectra, resulting in a large Stokes shift (\sim 212 nm), which can effectively diminish the reabsorption of light during propagation along the boundary of the microrings.³



Figure S7. Absolute fluorescence quantum yields (Φ) of HFDMAC microbelts and HFDMAC monomers. A_{em} is the integrated area of the emission spectra of the sample. A_{ex, no} sample and A_{ex, with sample} are the integrated area of the excitation light at 400 nm without and with sample, respectively.

The single-crystal microbelts are highly emissive with $\Phi_{\text{MBs}} \approx 0.23$, which is much greater than that of the monomers with $\Phi_{\text{M}} \approx 0.01$. The strongly enhanced emission could be attributed to the synergetic effect of intramolecular planarization and J-type aggregated π - π stacking (limited the excimer formation), suggesting the occurrence of a more effective emission,⁴ which is highly favorable for the optical gain and amplification.



Figure S8. Schematic demonstration of the experimental setup for the optical characterization.

A homemade micro-photoluminescence system was used to exam the optical properties of the ring-shaped structures. A focused pulse laser beam (400 nm, 150 fs, 1000 Hz) was used to pump the ring-shaped structure through a neutral density filter. The microring resonators were dispersed on a glass substrate (refractive index about 1.5). An objective lens ($50\times$, numerical aperture 0.8) was used to focus the pump beam to a 1-µm-diameter spot on the ring vertically. The PL signal was collected by the same microscope objective, passed through the dichroic mirror (DM 400 nm), then a longpass emission filter (420 nm) to eliminate the exciter light, focused by a group of lenses onto a confocal iris. The output signal can be spatially selected by the iris and recorded using a spectrometer. By rotating the polarizer in front of the detector, the polarization of the light signal can be obtained.



Figure S9. Pump fluence-dependent PL peak intensity (black line) and FWHM (red line) of the microbelt-coupled microring.

As illustrated in Figure S9, with the increase of pump fluence, the PL peak intensity in the gain region was dramatically amplified. The plot of the corresponding PL peak intensities vs pump fluence reveals a clear knee behavior at the threshold of ~15.9 µJ cm⁻². These results confirm the lasing action in the microbelt-coupled microring.



Figure S10. The waveguide loss of the microbelt. (A) Bright-field and PL images obtained from a single HFDMAC microbelt by exciting the wire at different positions, respectively. The right tip is adopted as the emitting tip. Scale bar is 10 μ m. (B) Spatially resolved PL spectra from the right tip of the microbelt for different separation distances between the excitation spot and the right tip shown in (A). (C) The logarithmic plot of relative intensity I_{tip}/I_{body} against the guiding distance X between the excited spot and the emitting tip.

The line in Figure S10C was fitted by a function $\log(I_{tip}/I_{body}) = -\alpha X$, where α is the fitting parameter and represents the waveguide loss (dB/µm). The optical propagation loss coefficient of the HFDMAC microbelt is 0.0067 dB/µm, which would help to realize the output of the WGM lasing modes from the microbelt.



Figure S11. PL spectra collected from the inner (A) and outer (B) rings at pump fluence of $21.3 \ \mu J \ cm^{-2}$.

In Figure S11, both the spectra collected from the inner and the outer rings show the development of the second mode (652.8 nm) at pump fluence of 21.3 μ J cm⁻², and the mode spacing ($\Delta\lambda$) between the first (641.1 nm) and second modes is determined to be 11.7 nm. The experimental data is consistent with theoretical prediction data (11.4 nm), which revealed that the Vernier effect existed in the double ring-coupled cavity and was the key factor on the single mode operation.

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