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# Supporting Information

## Optical microresonator arrays of fluorescence-switchable diarylethenes with unreplicable spectral fingerprints

Daichi Okada, Zhan-Hong Lin, Jer-Shing Huang, Osamu Oki, Masakazu Morimoto, Xuying Liu, Takeo Minari, Satoshi Ishii, Tadaaki Nagao, Masahiro Irie, Yohei Yamamoto\*

\*e-mail: yamamoto@ims.tsukuba.ac.jp

#### Simulation of the WGM index.

Simulations of the WGMs were conducted using eq. 1 and eq. 2 for transverse electric (TE) and magnetic (TM) mode emissions, respectively,<sup>[S1]</sup>

$$\lambda_{l}^{E} = 2\pi r(\varepsilon\mu)^{\frac{1}{2}} \left[ l + \frac{1}{2} + 1.85576(l + \frac{1}{2})^{\frac{1}{3}} - \frac{1}{\varepsilon} \left( \frac{\varepsilon\mu}{\varepsilon\mu - 1} \right)^{\frac{1}{2}} \right]^{-1}$$
(eq. S1)  
$$\lambda_{l}^{H} = 2\pi r(\varepsilon\mu)^{\frac{1}{2}} \left[ l + \frac{1}{2} + 1.85576(l + \frac{1}{2})^{\frac{1}{3}} - \frac{1}{\mu} \left( \frac{\varepsilon\mu}{\varepsilon\mu - 1} \right)^{\frac{1}{2}} \right]^{-1}$$
(eq. S2)

where  $\lambda_l^E$  and  $\lambda_l^H$  are the wavelengths of the *l*-th TM and TE mode photoemission, respectively,  $\varepsilon (= n^2)$  is the dielectric permittivity,  $\mu (= 1)$  is the magnetic permeability, and r is the radius of the sphere. Here, higher-order terms were neglected. The average n values for  $\mathbf{1}_0$  (~1.56) and  $\mathbf{1}_C$  (~1.60) were obtained by spectroscopic ellipsometry measurements (Fig. S4A). For simulation of the PL lines, TE and TM modes were calculated using Equations S1 and S2. Within the margin of error of the radius of the sphere (obtained by optical microscopy), the simulation adapts a radius so that both TE and TM modes agree well for given orders l, effectively determining the radius with much higher precision. The spectra with WGM indices are shown in Fig. S2B.

#### Analytical model.

For the analytical model, we extend Equations S1 and S2 to higher-order terms to obtain higher accuracy of the spectral position of the WGMs. The extended formula for the peak positions of the TE ( $\lambda_{\ell}^{E}$ ) and TM modes ( $\lambda_{\ell}^{M}$ ) are shown by eq.S3 and eq.S4, respectively,<sup>[S2]</sup>

$$\lambda_{\ell}^{E} = 2\pi r(\varepsilon\mu)^{\frac{1}{2}} \left[ \left(\ell + \frac{1}{2}\right) + 1.85576 \left(\ell + \frac{1}{2}\right)^{\frac{1}{3}} - \frac{1}{\varepsilon} \left(\frac{\varepsilon\mu}{\varepsilon\mu - 1}\right)^{\frac{1}{2}} + \frac{3}{10\sqrt[3]{4}} * 1.8557^{2} \left(\ell + \frac{1}{2}\right)^{-\frac{1}{3}} - 1.8557 \left(\ell + \frac{1}{2}\right)^{-\frac{2}{3}} \frac{\frac{3}{\varepsilon^{\frac{3}{2}}}}{\sqrt[3]{2} * (\varepsilon-1)^{\frac{3}{2}}} \right]^{-1}$$
(eq. S3)

$$\lambda_{\ell}^{H} = 2\pi r (\varepsilon \mu)^{\frac{1}{2}} \left[ \left(\ell + \frac{1}{2}\right) + 1.85576 \left(\ell + \frac{1}{2}\right)^{\frac{1}{3}} - \frac{1}{\mu} \left(\frac{\varepsilon \mu}{\varepsilon \mu - 1}\right)^{\frac{1}{2}} + \frac{3}{10\sqrt[3]{4}} * 1.8557^{2} \left(\ell + \frac{1}{2}\right)^{-\frac{1}{3}} - 1.8557 \left(\ell + \frac{1}{2}\right)^{-\frac{2}{3}} \frac{3\varepsilon - 2}{3\sqrt[3]{2}\sqrt{\varepsilon}(\varepsilon - 1)^{\frac{3}{2}}} \right]^{-1} (\text{eq. S4})$$

Here,  $\ell$  is the angular momentum number, *m* is the azimuthal mode number,  $\varepsilon = n^2$  is the dielectric permittivity,  $\mu$  is the magnetic permeability, and *r* is the radius of the sphere. For a perfectly spherical resonator, all modes with m ranging from  $-\ell$  to  $+\ell$  degenerate into a single peak, as shown in Fig. 1C in the main text. However, for oblate microspheres, the spherical symmetry is destroyed. This leads to two observable changes in the PL spectrum. First, the compression of  $R_z$  leads to a reduction of the effective size of the spherical cavity. Therefore, a pronounced blueshift is observed compared to the perfect sphere. As seen in Fig. S4A, all modes show a spectral blueshift as  $R_z$  is reduced. Second, degenerate modes with different  $\ell$  but same *m* have different sensitivities are observed from the different slopes as  $R_z$  is reduced from 1,675 to 1,425 nm. This modal profile-dependent sensitivity leads to the splitting of degenerate WGMs in the oblate spheres prepared directly on the substrate.

The spectral shift as a function of the asymmetry factor measured by the ellipticity  $\beta$  can be expressed as

$$\lambda(m) = \lambda_0 \left[ 1 - \frac{\beta}{6} \left( 1 - \frac{3m^2}{\ell(\ell+1)} \right) \right]$$
(eq. S5)

Here, the ellipticity  $\beta$  is defined as  $(r_{pol} - r_{equ})/r_{eff}$ , with  $r_{pol}$  being the radius along the polar direction ( $R_z$  in this work),  $r_{equ}$  being the radius in the equatorial plane ( $R_x$  and  $R_y$  in this work), and  $r_{eff}$  defined as  $(r_{equ}^2 \cdot r_{pol})^{1/3}$ . S1,S2 Here, we use experimentally measured dimensions by referencing the SEM images. The refractive index and permeability are set to n = 1.6 and  $\mu$ = 1. We start from  $r_{pol} = r_{equ} = 1,675$  nm, i.e., a perfect sphere with  $R_x = R_y = R_z = 1,675$  nm, and gradually reduce to  $r_{pol} = 1,415$  nm, i.e., an oblate sphere with  $R_x = R_y = 1,675$  nm and  $R_z$ = 1,415 nm. Here, we illustrate the WGM splitting using the  $TE^{21}$  peak of a perfect sphere as an example. Figure S4 shows the splitting of  $TE^{21}$  as a function of  $R_z$ . The blue lines trace the peak positions obtained from the analytical model, and the spectra are obtained from FDTD simulations. To illustrate the spatial distribution of the electric fields of the degenerate WGMs, we plot modal profiles of the spherical harmonics and denote the modes with  $(\ell, m, x)$ , where  $x = \ell - |m|$ . To better visualize the field distribution of the Eigen modes of the spherical harmonics, the amplitude of each mode was squared, and then, taken the square-root was taken for direct plotting in polar coordinates. As examples, the modal profiles of four degenerate WGMs of TE<sup>21</sup> with  $(\ell, m, x) = (21, 21, 0), (21, 20, 1), (21, 16, 5)$  and (21, 5, 16)are plotted on top of the spectra in Fig. S4A. When  $m = \ell$ , i.e.,  $(\ell, m, x) = (21, 21, 0)$ , the modal profile shows the simplest TE-WGM along the equator. As the *m* value decreases, the modal profile gradually transforms the field distribution towards the poles. Therefore, the degenerate WGMs with smaller *m* values show larger spectral blueshift, i.e., larger slopes of the blue lines in Fig. S5. This difference in the modal distribution leads to different sensitivities of the degenerate WGMs to the compression of  $R_z$ , i.e., different slopes for each blue line in Fig. S4.

#### FDTD numerical simulations.

For numerical simulations, we performed finite-difference time-domain simulations (FDTD Solution, Lumerical Solution Inc., Canada) to obtain the optical response of the microspheres. Three orthogonally orientated dipole sources are placed at the same position on the equator of the microsphere to mimic the emission from randomly orientated chromophores at the focal spot on the surface of the microsphere (Fig. S4B). Auto nonuniform mesh with a mesh accuracy of 2 was used. In the FDTD simulations, we used the experimentally obtained permittivity of  $\mathbf{1}_{\rm C}$  (Fig. S2D). The imaginary part of the permittivity was reduced 100 times to clearly see the WGMs. This means that the spectral positions of the WGMs are correct, but the relative intensity of the peak is amplified. The substrate was set to SiO<sub>2</sub>, and the material properties of SiO<sub>2</sub> were obtained from the Handbook of Optical Constants of Solids by Palik. Two-dimensional frequency-domain field and power monitors were placed on top of the microsphere to record the emission spectrum (Fig. S4B). Twelve perfectly matched layers were used for all boundaries of the FDTD simulation box. The apodization function was applied to the 2D monitor to remove the signals from transient modes emerging in the first 150 fs. This apodization is critical to obtain the modal profile of the long-lived WGMs. The tabular summary in Figs. 3E and S4C was obtained by the FDTD simulations with the abovementioned settings. The  $R_z$  of the sphere was reduced from 1,675 nm (perfect sphere) to 1,415 nm (oblate sphere).

To visualize the field distribution of WGMs in the FDTD simulation, we recorded the near-field intensity in the xz and xy planes by two 2D field profile monitors in the FDTD simulations (Fig. S4B). The total electric field distribution has been recorded at all wavelengths. The near-field intensity distribution helps us to assign the modes and track their spectral shift as the sphere is compressed. For clear presentation of the WGM splitting due to compression, we present the spectral shift of only the eight most pronounced degenerate WGMs of TE<sup>21</sup> from three spheres with  $R_z = 1,675, 1,575$  and 1,415 nm. Fig. S4C shows the mode splitting as  $R_z$  is reduced. For the perfect sphere ( $R_z = 1,675$  nm), all eight WGMs are degenerate, and the TE<sup>21</sup> mode shows a single spectral peak, as shown by the black trace in

Fig. S4C. As  $R_z$  is reduced to 1,575 nm, the eight modes are clearly separated. Further reducing  $R_z$  to 1,415 nm, the spectrum best matches the experimental one, and the splitting of the eight modes further increases. In fact, for oblate spheres with  $R_z$  smaller than 1,575 nm, the splitting of degenerate WGMs is so large that WGMs of  $\ell$  start to overlap with WGMs of  $\ell$ -1. Therefore, for the oblate sphere with  $R_z = 1,415$  nm, the modal profile of some modes becomes blurrier and more complex. Nevertheless, the eight modes can still be clearly identified and tracked.

In general, the results from full-wave FDTD simulations and analytical models both agree well with the experimental results. The analytical model shows a small deviation from the experimental and FDTD results. The deviation is because the analytical model neglects the contribution of higher-order terms and the dispersion of the refractive index. Additionally, the analytical model does not include the substrate, which indeed has a significant influence on the WGM spectra. For example, WGMs with small m values can be predicted by the analytical model but cannot be observed in the FDTD simulations or experiments because these modes leak at the contact point to the substrate.<sup>S2</sup>

### **Supporting References**

S1. A. N. Oraevsky, (2002) Whispering-gallery waves. *Quant. Elect.* 32: 377–400.
S2. D. Braam, *et al.* (2016) Optically induced mode splitting in self-assembled, high quality-factor conjugated polymer microcavities. *Sci. Rep.* 6: 19635.



**Figure S1.** (A) Normalized photoabsorption (broken curves) and PL spectra (solid curve) of dioxane solutions of  $\mathbf{1}_{O}$  (black) and  $\mathbf{1}_{C}$  (green). (B) Schematic representation of the interface precipitation method. (C) SEM micrograph of the resultant microspheres. Inset: SEM with side view (tilt angle: 75°). (D) Histogram of *d* of the resultant microspheres. (E) X-ray diffraction pattern of a powder sample of the microspheres of **1**. (F–H) Fluorescent micrographs of microspheres of  $\mathbf{1}_{C}$  (F), which was irradiated at 450–490 nm light for 60 min (G) and then irradiated at 350–390 nm light for 1 min (H).  $\lambda_{ex} = 450-490$  nm.



**Figure S2.** (A) Schematic representation of the  $\mu$ -PL setup with ps laser pumping. (B) PL spectra of a single microsphere of  $\mathbf{1}_{C}$  with *d* of 2.0, 3.0, 3.8, and 4.3  $\mu$ m. Blue and red numeric indicates WGM indices with TE and TM modes, respectively. (C) Variation of PL spectra of a single microsphere of  $\mathbf{1}_{O}$ , upon 90 s irradiation with UV-LED at  $\lambda = 375$  nm (from the top to the middle) and then 120 min irradiation with laser at  $\lambda = 470$  nm (from the middle to the bottom).  $\lambda_{ex} = 470$  nm. (D) Real (solid curves) and imaginary (broken curves) parts of the refractive indices of  $\mathbf{1}_{C}$  (black) and  $\mathbf{1}_{O}$  (red), measured by spectroscopic ellipsometry of thin film of 1. (*E*) PL spectra of a single microsphere of  $\mathbf{1}_{O}$  (I) and its change upon UV irradiation for 1 min (II), Vis irradiation for 150 min (III) and UV irradiation for 1 min (IV). (*B*) Plot of the maximum PL intensity for (I)–(IV) in (*F*).



**Figure S3.** (A, B) SEM micrographs of microspheres, prepared by drop casting ethanol solution of **1** on a SiO<sub>2</sub>/Si substrate (A, side view with tilt angle: 75°; B, top view). (C) Plot of  $R_z/R_x$  versus  $d (= 2R_x)$  of the microspheres, prepared by drop casting ethanol solution of **1** on a SiO<sub>2</sub>/Si substrate. (D) Plots of Q<sub>av</sub> for isotropic microspheres (black) and oblate microspheres (red) versus  $d (= 2R_x)$ .



Figure S4. (A) Overlay of FDTD simulated WGM spectra and analytically predicted wavelength shift (blue lines) of the degenerate WGMs of an oblate microsphere with shape transition from  $(R_x, R_y, R_z) = (1675, 1675, 1675)$  to  $(R_x, R_y, R_z) = (1675, 1675, 1415)$ . The  $R_z$ is reduced with a step of 10 nm. The blue lines show the corresponding WGM wavelengths at various  $R_z$  calculated using the analytical model described by Equation S5. Four examples of 3D modal profiles of the degenerate WGMs are shown on top of the spectra. (B) Set up of dipole sources to excite WGMs and monitors for recording far-field PL spectrum and nearfield field intensity distribution. (C) Left: simulated emission spectra showing peaks of WGMs in a perfect microsphere with  $R_x = R_z = R_y = 1675$  nm (black trace) and two oblate spheres with  $R_x = R_z = 1675$  nm but  $R_z = 1575$  nm (red trace) and  $R_z = 1415$  nm (blue trace). Right: 2D modal field intensity profiles simulated by FDTD. The profiles are recorded with 2D field profile monitor in xy and xz planes at the peak wavelengths of spectra of the two oblate spheres, i.e. red and blue spectra in the left panel. The 3D modal profiles of spherical harmonics with same l quantum number are inserted on top for reference. The colored symbols are assigned to track specific modes and are marked out in the spectra shown in the left panel.



Figure S5. Photograph (A) and optical micrographs (B–E) of the microdisk arrays. Objective lens: x10 (B), x20 (C), x50 (D), x100 (E). Insets in (B–E) show fluorescent micrographs of each array.  $\lambda_{ex} = 450-490$  nm. (F)  $\mu$ -PL spectrum of a microdisk. Inset shows optical microscopy image of microdisk array. The microdisk at the center (circled) was used for the  $\mu$ -PL measurement.



**Figure S6.** (A) Plot of height/diameter versus diameter of the resultant hemispheres. (B–E) Fluorescence micrographs of character (B) and painting (C–E) drawn on the microarray upon irradiation at  $\lambda = 350-390$  nm for 3 min to the microarray of  $\mathbf{1}_0$  through a patterned photomask. (D) and (E) are the magnified micrographs of the box parts in (C) and (D), respectively.  $\lambda_{ex} = 450-490$  nm.



**Figure S7.** (A, C) Fluorescence micrographs of a painting drawn on the microarray upon irradiation at  $\lambda = 350-390$  nm for 3 min to the microarray of 1<sub>0</sub> through a patterned photomask. (ii) and (iii) are the magnified micrographs of the box parts in (i) and (ii), respectively.  $\lambda_{ex} = 450-490$  nm. (B, D)  $\mu$ -PL spectra of each hemisphere. The numbers correspond to those denoted in the micrographs (iii).



Shape	Perfect sphere	Oblate ellipsoid	Hemisphere	Disk
Method	Interface precipitation	Drop-cast & dry	Immersion	Solvent vapour annealing
Image	2	2µm	2 <i>µ</i> m	
Height/Diameter	1.0	0.80-1.0	0.70–0.90	0.25–0.40

Figure S8. Molecular structures of 2,6-dimethylphenyl-substituted DAE  $2_{\rm C}$  (A) and 2methylthiophenyl-substituted DAE  $3_{\rm C}$  (B), and fluorescence microscopy images of microarrays of 2 (A) and 3 (B). (C) Optical micrograph of the resultant micro-hemisphere array of 3 with a 5 x 5 matrix. (D) PL spectra of the arrayed micro-hemispheres of 3. The labels correspond with the matrix in (C). (E) Tabular summary of the shape, preparation method, SEM images and height/diameter ratio of the resultant micro-objects of DAE 1.