Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

FRET-mediated near infrared whispering gallery modes: studies on the relevance of intracavity energy transfer with *Q*-factors

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1. Materials and measurements

Unless otherwise noted, reagents and solvents were used as received from Aldrich Chemical Co. Ltd, Tokyo Chemical Industry Co. Ltd and Nakarai Tesque Co. An alternating copolymer, poly[(9,9-dioctylfluorene-2,7-diyl)-*alt*-(5-octylthieno[3,4-*c*]pyrrole-4,6-dione-1,3-diyl)] (**P1**, M_n = 24 kg mol^{-1}) and poly[(5-(2,4,6-triisopropylphenyl)thieno[3,4-*c*]phosphole-4,6-dione)-*alt*-(4,4-bis(2-ethylhexyl)-silolo-[3,2-*b*:4,5-*b*']dithiophene)] (**P2**, M_n = 6.5 kg mol^{-1}) were synthesized according to the reported procedures.[S1,S2] NMR spectra were recorded on a JEOL ECS-400 (400 MHz) spectrometer by using tetramethylsilane (0 ppm for ^{1}H NMR) as an internal standard. Gel permeation chromatography (GPC) was performed in THF solution using a TOSHO GPC system (HLC-8320GPC EcoSEC) equipped with two TSK gel Super-Multipore HZ-M columns and a UV detector (254 nm) or 5 μm-MIXED-D column (Polymer Laboratories), a PU-980 HPLC pump (JASCO), and an MD-915 multi-wavelength detector (JASCO). The molecular weight (M_n) and polydispersity index (PDI) of the polymer samples were calculated on the basis of a polystyrene calibration. Photoabsorption and PL spectra were recorded on a JASCO V-630 spectrophotometer and a JASCO FP-8500 spectrofluorometer, respectively. Thin films of polymers were prepared by drop casting from $CHCl_3$ solution. PL quantum yield (ϕ_{PL}) was recorded on a Hamamatsu model C9920-02 absolute PL quantum yield measurement system. SEM microscopy was performed on a Hitachi model SU-8000 FE-SEM operating at 10 kV. Silicon was used as a substrate and Au for coating. EDS measurements were performed on a Hitachi model S-3900N SEM equipped with an Oxford Instruments model X-Max50 silicon drift detector. Optical microscope observation was carried out using an Olympus model BX53 Upright Microscope. The HOMO and LUMO energy levels of **P1** were estimated by photoelectron yield spectroscopy (PYS) using a Riken Keiki model AC-3 spectrometer and photoabsorption spectroscopy, respectively. The HOMO and LUMO energy levels of **P2** were evaluated by electrochemistry and photoabsorption spectroscopy, respectively.

2. Simulations of WGMs

The simulations of the WGMs are conducted using Equations S1 and S2 for transverse electric (TE) and magnetic (TM) mode emissions, respectively,[S3]

$$\lambda_l^E = 2\pi r(\varepsilon\mu)^{\frac{1}{2}}\left[l+\frac{1}{2}+1.85576(l+\frac{1}{2})^{\frac{1}{3}}-\frac{1}{\varepsilon}\left(\frac{\varepsilon\mu}{\varepsilon\mu-1}\right)^{\frac{1}{2}}\right]^{-1} \quad \text{(S1)}$$

$$\lambda_l^H = 2\pi r(\varepsilon\mu)^{\frac{1}{2}}\left[l+\frac{1}{2}+1.85576(l+\frac{1}{2})^{\frac{1}{3}}-\frac{1}{\mu}\left(\frac{\varepsilon\mu}{\varepsilon\mu-1}\right)^{\frac{1}{2}}\right]^{-1} \quad \text{(S2)}$$

where λ_l^E and λ_l^H are the wavelengths of the l-th TM and TE mode photoemission, respectively, ε (= n^2) is the dielectric permittivity, μ (= 1) is the magnetic permeability, and r is the sphere's radius. Here, the much higher-order term was neglected. The average n values for **P1** and **P2** (~1.8) were obtained by spectroscopic ellipsometry measurements. For the simulation of the emission lines, TM and TE modes were calculated using the equations S1 and S2. Within the margin of error of the sphere's radius (given by optical microscopy), the simulation adapts the radius so that both TM and TE modes agree well for given orders l, effectively determining the radius with much higher precision. The spectra with WGM indices are shown in Figure S6.

3. Supporting Figures

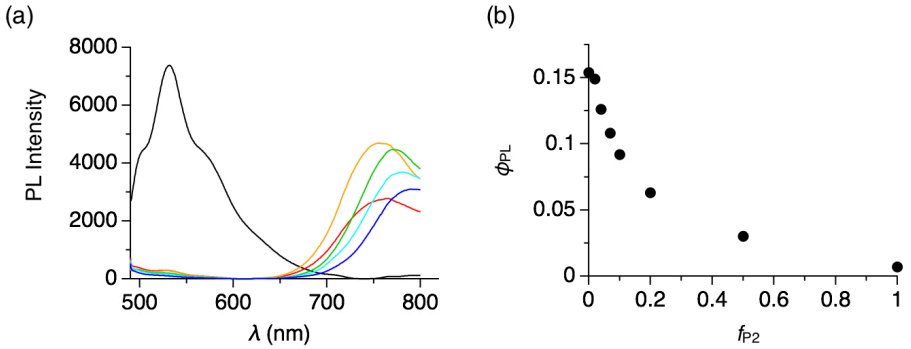

Figure S1. (a) PL spectra of cast films from $CHCl_3$ solutions containing **P1** and/or **P2**. f_{P2} = 0 (black), 0.02 (red), 0.04 (orange), 0.07 (green), 0.1 (light blue), and 0.2 (blue). (b) Plot of ϕ_{PL} versus f_{P2} of cast films from $CHCl_3$ solutions containing **P1** and/or **P2**.

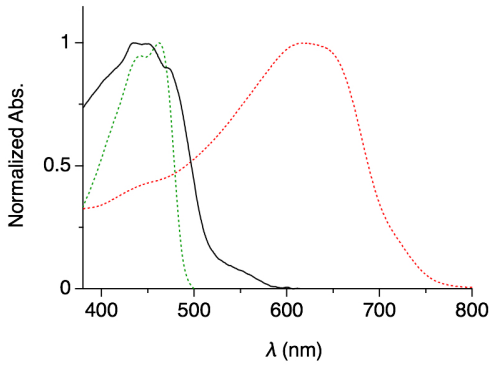

Figure S2. Excitation spectrum (black) of a cast film of the microspheres with f_{P2} = 0.05 with PL at 650 nm. Green and red curves show photoabsorption spectra of **P1** and **P2** in $CHCl_3$, respectively.

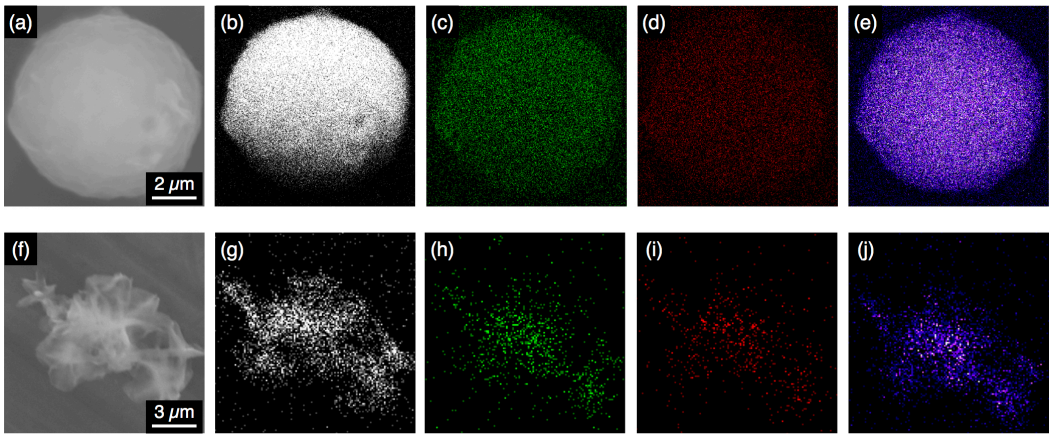

Figure S3. SEM micrographs (a, f) and EDX mapping images (b–e, g–j) of the microsphere with f_{P2} = 0.07 (a–e) and irregular aggregate with f_{P2} = 1 (f–j) on an aluminum stage. (b, g) C $K\alpha_1$ and $K\alpha_2$, (c, h) Si $K\alpha_1$, (d, i) P $K\alpha_1$, and (e, j) S $K\alpha_1$.

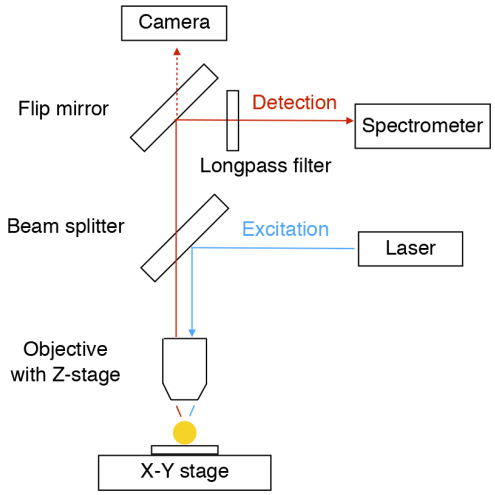

Figure S4. Schematic drawing of the experimental setup of μ-PL measurements.

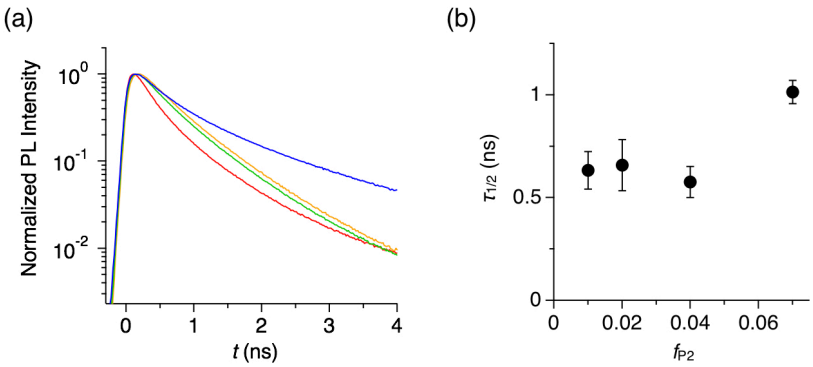

Figure S5. (a) PL decay profiles at λ_{PL} = 675–730 nm of a single microsphere with f_{P2} = 0.01 (red), 0.02 (orange), 0.04 (green), and 0.07 (blue). λ_{ex} = 470 nm. (b) Plots of $\tau_{1/2}$ versus f_{P2} at λ_{PL} = 675–730 nm. The plots are the average value with the measurements of 5–7 isolate microspheres.

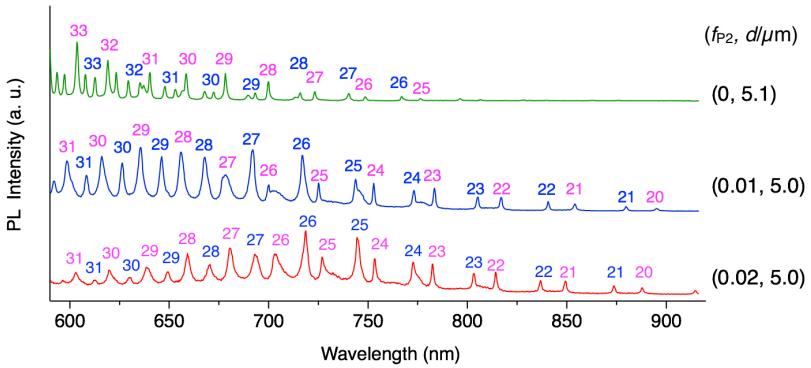

Figure S6. PL spectra and WGM indices of single microspheres with f_{P2} = 0 (green), 0.01 (blue), and 0.02 (red). The numeric with blue and pink colors denotes TE and TM modes, respectively.

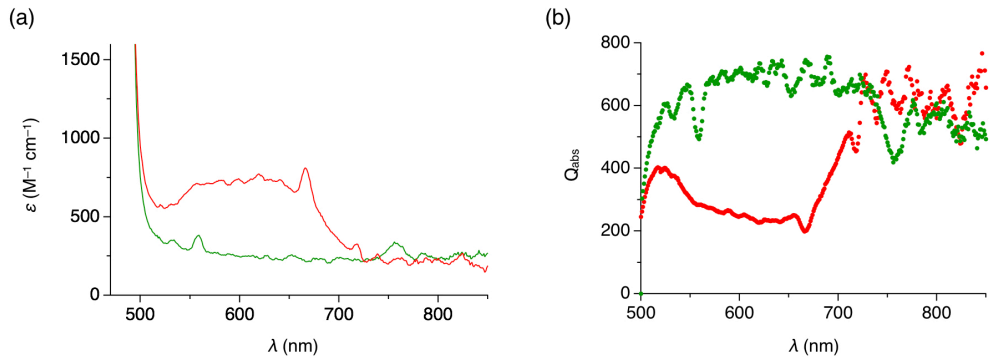

Figure S7. Wavelength dependency of molar absorption coefficient ε (a) and Q_{abs} (b) for **P1** (green) and **P1**/**P2** with f_{P2} = 0.02 (red). The reported data on the wavelength dependency of refractive index of **P1** is used.[S4]

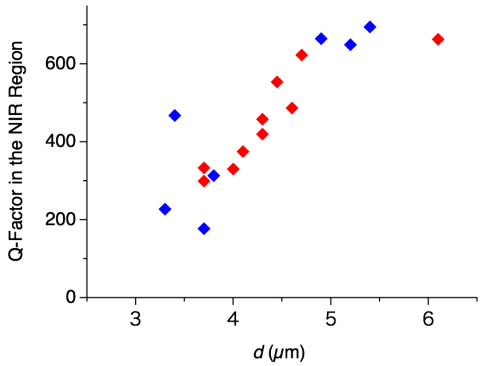

Figure S8. Plots of Q-factor in the NIR region versus diameter of the microspheres with f_{P2} = 0.02 (blue) and 0.04 (red).

4. Supporting References

S1. H. Saito, J. Kuwabara, T. Kanbara, *J. Polym. Sci., Part A: Polym. Chem*. 2015, **53**, 2198.

S2. Y. Takeda, K. Hatanaka, T. Nishida, S. Minakata, *Chem. Eur. J*. 2016, **22**, 10360.

S3. A. N. Oraevsky, *Quant. Elect*. 2002, **32**, 377.

S4. S. Kushida, D. Braam, T. D. Dao, H. Saito, K. Shibasaki, S. Ishii, T. Nagao, A. Saeki, J. Kuwabara, T. Kanbara, M. Kijima, A. Lorke, Y. Yamamoto, *ACS Nano* 2016, **10**, 5543.